THE ANALYSIS AND INTERPRETATION OF HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA

by

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ABSTRACT

The high resolution nuclear magnetic resonance spectra of three compounds containing three nonequivalent spin 1/2 nuclei (H^1) have been observed at several magnetic field strengths. The compounds studied were styrene, 2,4-dichloroaniline and 2,5-dichloroaniline. The spectra, which depart considerably from first order behavior, have been analyzed and it was found that the same set of parameters describe the spectra at all the magnetic fields used. Using these compounds, combination lines have been observed for the first time and it was demonstrated that these lines are not always of small intensity, as had been commonly supposed. It was shown that in styrene the spin-spin coupling constants have the same sign.

Methods were developed which aid greatly in the analysis of spectra of systems of three spins, when these spectra show the results of intermediate coupling between the nuclei. Using these methods it is possible, in favorable cases, to determine the relative signs of the coupling constants without a complete analysis.

Two substituted ethanes, $CHClBrCBrF_2$ and $CHCl_2CClF_2$, were studied; the spectra were found to exhibit the effects of internal rotation. The temperature dependences of certain chemical shifts and spin-spin couplings were measured, and an attempt made to interpret them in terms of the simple theory of rotational averaging which has appeared in the literature.

Thesis Supervisor: John S. Waugh

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Chemistry

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I. INTRODUCTION: SPECTRA OF THREE-SPIN SYSTEMS

The Hamiltonian used to describe the fine structure in the nuclear magnetic resonance spectra of liquid and gaseous samples was proposed by Hahn and Maxwell (17) and by Gutowsky et al. (16), and has been justified by Ramsey (32, 33) and Ramsey and Purcell (34). There are two kinds of effects involved: shielding of the nucleus from the external magnetic field by induced electron currents and orientation-independent coupling of pairs of magnetic nuclei by the electrons. The Hamiltonian describing these two effects can be written

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}$$

where $\mathcal{H}^{(0)} = -\hbar\sum_i \gamma_i H_i I_{zi}$ (1)

and $\mathcal{H}^{(1)} = -\hbar\sum_{i<j} 2\pi A_{ij} \underline{I}_i \cdot \underline{I}_j$

Here $\hbar$ has the usual significance, γ_i is the magnetogyric ratio of nucleus i, H_i the magnetic field at nucleus i, I_{zi} the z component of the spin angular momentum, A_{ij} a coupling constant, and $\underline{I}_i$ and $\underline{I}_j$ the spin angular momenta. $\mathcal{H}^{(0)}$ is dependent upon magnetic field while $\mathcal{H}^{(1)}$ is not, because A_{ij} is assumed to be independent of magnetic field, as predicted by Ramsey and Purcell (34). There is good experimental and theoretical justification (32) for assuming H_i to be of the form $H_o(1-\sigma_i)$, that is, linear in the external field. The A_{ij} for some selected compounds have been shown to be independent of magnetic field between the values 200--6000 gauss, to within the experimental error of approximately 1°/o (31, 16). Over the temperature range studied by Gutowsky et al. (16), no change in the values A_{ij} were detected. The dependence of H_i on magnetic field and the independence of A_{ij} can be assumed until refuted by some more sensitive method of measuring the effects by which H_i (σ_i) and A_{ij} are manifest. The work described herein deals with this question only indirectly.

The ability of the Hamiltonian to describe the positions of lines and their intensities -- the observable features of a magnetic resonance spectrum -- has been tested in many cases. If

$$\lambda_{ij} \equiv \frac{2\pi A_{ij}}{\gamma |H_i - H_j|} \ll 1$$

for all pairs of nuclei, then the interpretation is simple: a first order perturbation treatment is sufficient, and it has always been possible to determine a set of parameters, the σ_i and A_{ij}, which adequately describes the experimental spectra.

Some simple cases where first order theory is not adequate have been investigated. Following the notation used by Bernstein, Pople, and Schneider (7), nuclei i and j for which $\lambda_{ij} \cong 1$ will be denoted by the first letters of the alphabet A,B,C---; nuclei i, for which $\lambda_{ij} \ll 1$ with all others j, will be called by other letters, such as P, X, or Y. In this notation, three nuclei with only $\lambda_{12} \cong 1$ would be called ABX. Systems AB (17), AB_n with n = 2,3,4 (6), and A_2X_2 (24) have been treated exactly. Some other systems have been discussed (7, 15, 20, 30), but the results are not easily presented in closed form. One of these systems is ABX, which has been treated by Bernstein, Pople, and Schneider (7) and Gutowsky _et al._ (15). This is a special case of the general system of three nuclei which will be treated in detail in section II. A perturbation treatment has also been presented (2) for cases in which the λ_{ij} are appreciable but still less than unity. Here the perturbation is expanded in terms of the λ's, and in one case (4) it has been carried out to third order. In all cases it has been possible to get satisfactory agreement between theory and experiment, and the parameters σ_i and A_{ij} have been obtained.

The case of three non-equivalent nuclei, ABC, is more complicated than those previously mentioned, and it is quite worthwhile to determine for this case whether satisfactory agreement with experiment exists when the values of λ_{ij} approach unity or even exceed it. Here the perturbation treatment may not be valid because there is a possibility that the series in the λ's will not converge. In fact, the three-spin system is the simplest one in which it is possible that neither a series in λ nor one in $1/\lambda$ will converge.

For one to be able to interpret the spectra of three-spin systems conveniently, the spectra cannot depart greatly from those in which a first order theory is appropriate. If this is true, the three λ_{ij} are significant but not large, and the case does not present a difficult enough test to the theory. It is possible, however, to analyze a spectrum taken at a higher magnetic field (in which some $\lambda \cong 1/2$) and then to take a spectrum at a lower magnetic field, where the λ's are larger. If the same set of parameters is assumed to hold at the lower field and the spectrum calculated on that basis agrees with experiment, then the theory has been put to a significant test ($\lambda \cong 2$) and has withstood that test.

The spectra at several magnetic fields can be used at the same time to verify that the same set of parameters, σ_i and A_{ij}, describes the spectrum at different magnetic fields. This relates to the dependence of H_i and A_{ij} on magnetic field, but the proper dependence has been shown previously only for cases in which all $\lambda_{ij} \ll 1$.

Systems containing three or more spins are of particular interest because of some additional properties of their spectra. As Anderson (2) has mentioned, in this case it is possible to determine the relative signs of the three or more A_{ij}, although the absolute signs can never be determined (Appendix A). Several theories (16, 21, 33) indicate that for protons all the coupling constants should be positive; however, one paper has appeared in the literature (1) in which the author claims to have found an instance in which all the proton couplings are not of the same sign. Since it has been possible to find the signs of the A's in very few cases, it is important to do so in more cases in order to verify or reject theories of their origin.

II. THEORY OF THE CASE ABC

The case ABC is, as explained earlier, the general case of three spin 1/2 nuclei in which one or more $\lambda_{ij} \cong 1$. In this case the coupling of nuclei i and j cannot be treated as a perturbation on $\frac{\gamma}{2\pi} H_o(\sigma_j - \sigma_i)$ and the problem must be solved exactly. The Hamiltonian for this case is

$$h^{-1}\mathcal{H} = -\Big\{\nu_o(1-\sigma_1)I_{z_1} + \nu_o(1-\sigma_2)I_{z_2} + \nu_o(1-\sigma_3)I_{z_3} + A_{12}\underline{I}_1 \cdot \underline{I}_2 + A_{13}\, \underline{I}_1 \cdot \underline{I}_3 + A_{23}\underline{I}_2 \cdot \underline{I}_3\Big\}$$

where $\nu_o = \frac{\gamma}{2\pi} H_o$, H_o being the external applied magnetic field and γ the magnetogyric ratio for the unshielded nuclei. σ_i is the fractional shielding of nucleus i, and $\underline{I}_i$ I_{zi}, etc., are the spin angular momenta and their components. z is taken along the direction of the magnetic field.

As has been noted above, ν_o is the frequency of precession of a bare nucleus in the external field. Although the value of $\nu_o\sigma$ is important in some theories, experimentally only differences between frequencies, such as $\nu_o(1-\sigma_i)-\nu_o(1-\sigma_j)$, can be measured easily because there is no good way in nuclear resonance techniques to introduce a standard with frequency ν_o. For this reason it is convenient to modify the Hamiltonian, letting

$$\nu_o(1-\sigma_i) = \nu_i = \nu_o{}' - \nu_i{}' = \nu_o{}'(1-\delta_i)$$

where $\nu_o{}'$ is any convenient reference such that the $\nu_i{}'$ are of the same order of magnitude as $\nu_o(1-\sigma_i)-\nu_o(1-\sigma_j)$. Because ν_o and $\nu_o{}'$ differ by less than 0.01 %,

$$\frac{\nu_i-\nu_j}{\nu_i} = \frac{\nu_i-\nu_j}{\nu_j} = \frac{\nu_i-\nu_j}{\nu_o} = -(\sigma_i-\sigma_j) = -(\delta_i-\delta_j)$$

The values $\sigma_i-\sigma_j$ will be given in parts per million; however, values of $\nu_i-\nu_j$ will be given in cycles per second when the value of ν_o is given (40 Mc., for instance). It is apparent that

$$\frac{\nu_i{}'}{\nu_o{}'} = \delta_i, \qquad \nu_i{}' = \nu_o{}'\,\delta_i = \frac{\gamma}{2\pi} H_o\delta_i$$

Henceforth the prime on ν_o will be dropped, and it will be understood that ν_o is some convenient reference, rather than the Larmor frequency for free nuclei. This lengthy discussion of a minor problem in notation is necessary since there is no standard notation used in the literature, and often the meaning of the symbols used is not explicitly given; fortunately, it is usually fairly clear to those working in the field.

The zero order wave functions to be used are simple product functions of α and β, the two spin states for spin 1/2 nuclei. One such wave function is $\alpha(1)\beta(2)\alpha(3)$, by which is meant nuclei 1 and 3 in the α state, and 2 in the β state. This will be abbreviated $\alpha\beta\alpha$. In the present case with three nuclei there will be $2^3 = 8$ wave functions. Each of these wave functions is characterized by an eigenvalue of the operator $F_z = \sum_i I_{zi}$, which represents the total spin of the system and is a good quantum number. There will be one wave function for each of the values $F_z = \pm 3/2$, and three each for the values $\pm 1/2$.

The rules for finding the matrix elements of the Hamiltonian in this representation are easily derived by considering the effects of the spin operators appearing in the Hamiltonian upon the wave functions (13). These rules have been presented in a simple form by Bernstein, Pople, and Schneider (7), and their notation, modified somewhat, will be used.

With the Hamiltonian in the form

$$\mathcal{H} = \mathcal{H}^{(o)} + \mathcal{H}^{(1)}$$

$$\mathcal{H}^{(o)} = -h \sum_i \nu_o(1-\sigma_i)I_{zi}$$

$$\mathcal{H}^{(1)} = -h \sum_{i<j} A_{ij}\underline{I}_i \cdot \underline{I}_j$$

their rules give

$$(\psi_m|\mathcal{H}^{(o)}|\psi_m) = -\tfrac{1}{2}h \sum_i \nu_o(1-\sigma_i)\ S_i$$

$$(\psi_m|\mathcal{H}^{(1)}|\psi_m) = -\tfrac{1}{4}\ h \sum_{i<j}A_{ij}T_{ij}$$

m≠n,

$$(\psi_m|\mathcal{H}^{(o)}|\psi_n) = 0$$

$$(\psi_m|\mathcal{H}^{(1)}|\psi_n) = -\tfrac{1}{2}\ hA_{ij}U_{ij}$$

where $S_i = \pm 1$ as nucleus i is in the α or β state

$T_{ij} = \pm 1$ as nuclei i and j are parallel or antiparallel

$U_{ij} = 1$ if ψ_m and ψ_n differ by the interchange of spins i and j only, and is zero otherwise.

With these rules the matrix elements given in Table I can be found. The values actually given are $h^{-1}H_{mn}$ and from here on all energies will be in cycles per second. The wave functions are grouped according to the values of the total spin F_z. Because F_z is a good quantum number,

TABLE I

MATRIX ELEMENTS OF $\mathcal{H}$

No.	Function	F_z	H_{nn}
1	βββ	$-\frac{3}{2}$	$\frac{3}{2}\nu_o - \frac{1}{2}(+\nu_1'+\nu_2'+\nu_3') - \frac{1}{4}(+A_{12}+A_{13}+A_{23})$
2	αββ	$-\frac{1}{2}$	$\frac{1}{2}\nu_o - \frac{1}{2}(-\nu_1'+\nu_2'+\nu_3') - \frac{1}{4}(-A_{12}-A_{13}+A_{23})$
3	βαβ	$-\frac{1}{2}$	$\frac{1}{2}\nu_o - \frac{1}{2}(+\nu_1'-\nu_2'+\nu_3') - \frac{1}{4}(-A_{12}+A_{13}-A_{23})$
4	ββα	$-\frac{1}{2}$	$\frac{1}{2}\nu_o - \frac{1}{2}(+\nu_1'+\nu_2'-\nu_3') - \frac{1}{4}(+A_{12}-A_{13}-A_{23})$
5	ααβ	$\frac{1}{2}$	$-\frac{1}{2}\nu_o + \frac{1}{2}(+\nu_1'+\nu_2'-\nu_3') - \frac{1}{4}(+A_{12}-A_{13}-A_{23})$
6	αβα	$\frac{1}{2}$	$-\frac{1}{2}\nu_o + \frac{1}{2}(+\nu_1'-\nu_2'+\nu_3') - \frac{1}{4}(-A_{12}+A_{13}-A_{23})$
7	βαα	$\frac{1}{2}$	$-\frac{1}{2}\nu_o + \frac{1}{2}(-\nu_1'+\nu_2'+\nu_3') - \frac{1}{4}(-A_{12}-A_{13}+A_{23})$
8	ααα	$\frac{3}{2}$	$-\frac{3}{2}\nu_o + \frac{1}{2}(+\nu_1'+\nu_2'+\nu_3') - \frac{1}{4}(+A_{12}+A_{13}+A_{23})$

$$H_{23} = H_{67} = -\frac{1}{2}A_{12}$$

$$H_{24} = H_{57} = -\frac{1}{2}A_{13}$$

$$H_{34} = H_{56} = -\frac{1}{2}A_{23}$$

All matrix elements are real, so the matrix is symmetric about the main diagonal.

there are no elements connecting wave functions 1 or 8 and any others, and none connecting 2, 3, and 4 with 5, 6, and 7. Functions 1 and 8 are then eigenfunctions, and the corresponding diagonal matrix elements are the energies for these states.

There will be some discussion later of a "first order" spectrum, and it is helpful to define the term at this point. The situation considered is one in which $\mathcal{H}^{(1)}$ is considered to be a perturbation upon $\mathcal{H}^{(o)}$. The first order correction to the energy is just the expectation value of the perturbation; for state m, for instance, this is just $(\psi_m|\mathcal{H}^{(1)}|\psi_m)$. This is equivalent to using an approximate Hamiltonian in which $-h\sum_{i<j}A_{ij}I_{zi}I_{zj}$ is substituted for the $\mathcal{H}^{(1)}$ given above. This approximate Hamiltonian gives the correct diagonal terms but gives no off-diagonal ones such as are being included here. To solve the problem exactly, two cubic equations will have to be solved to get the energies corresponding to the diagonal elements 2, 3, and 4, and 5, 6, and 7.

Because all the diagonal matrix elements include $(1/2)\nu_o$ or $(3/2)\nu_o$ in addition to terms in ν_1', ν_2', A_{12}, etc., it is advantageous to subtract the term involving ν_o, which is some 10^5 times the other terms. The diagonal terms will always have the form $(H_{nn} - E)$ and the ν_o term can be considered to be included in E. For the energies 2--4, let $E' = E - \frac{1}{2}\nu_o$, and for the energies 5--7, let $E' = E + \frac{1}{2}\nu_o$, etc. An energy difference taken to find a transition frequency will be, for instance,

$$+ (E_2 - E_5) = + (E_2' + \tfrac{1}{2}\nu_o) - (E_5' - \tfrac{1}{2}\nu_o)$$

$$= E_2' - E_5' + \nu_o$$

With this convention, E_i' will henceforth be called just E_i, and it will be understood that the value of ν_0 should be included.

The eigenfunctions can be found by standard techniques (10). There is a set of equations

$$(H_{22} - E_2)a_{22} + H_{23}a_{23} + H_{24}a_{24} = 0$$

$$H_{23}a_{22} + (H_{33} - E_2)a_{23} + H_{34}a_{24} = 0$$

$$H_{24}a_{22} + H_{34}a_{23} + (H_{44} - E_2)a_{24} = 0$$

which give the coefficients for the proper wave function corresponding to E_2 and there are two more sets for E_3 and E_4. Energy levels E_5, E_6, and E_7 are treated similarly. To get a unique set of numbers a_{22}, a_{23}, and a_{24} the additional condition of normalization is imposed:

$$a_{22}^2 + a_{23}^2 + a_{24}^2 = 1.$$

The eigenfunction for level 2 is then

$$\phi_2 = a_{22}\psi_2 + a_{23}\psi_3 + a_{24}\psi_4$$

The intensity of the transition $\phi_i \rightarrow \phi_j$ is proportional to

$$(\phi_j | I_x | \phi_i)^2 = I_{ji}$$

with $$I_x = \sum_i I_{xi}$$

The value for I_{ji} can be found if ϕ_i and ϕ_j are expanded in terms of the product wave functions ψ.

$$\phi_i = \sum_k a_{ik}\psi_k , \qquad \phi_j = \sum_\ell a_{j\ell}\psi_\ell$$

so that $I_{ji} = \left[\sum_{\ell} \sum_{k} a_{j\ell} a_{ik} (\psi_{\ell} | I_x | \psi_k) \right]^2$

$(\psi_{\ell} | I_x | \psi_k)$ is zero unless ψ_{ℓ} and ψ_k differ in the spin of one nucleus only, in which case it has a constant value for nuclei of the same species (7), experimental conditions remaining constant. This value will be taken as unity.

Up to this point the calculation of a spectrum, given the values ν_i' and A_{ij}, has been considered. In practice, the inverse is necessary: the determination of the parameters from an experimental spectrum. Because of the cubic equations involved, it is not feasible to do this by explicit solution of the general secular equation. The method of assuming a set of parameters, calculating a spectrum, and adjusting the parameters for the best fit can be used, and in the cases discussed here it is not impractical to do so.

The correspondence between the system with $\lambda_{ij} \cong 1$ and that at an imagined high magnetic field where $\lambda_{ij} \ll 1$ can be used to aid in the initial choice of parameters. Under the latter condition, the off-diagonal terms can be neglected, and the energies will be just the diagonal elements; the transitions will all have the same intensity. The transitions allowed by the selection rule, $\Delta F_z = -1$, and their frequencies are given in Table II.

Experimentally the spectrum is observed by changing the external field H_o. Increasing H_o is taken toward the right so that the nucleus with the largest σ (all $\sigma > 0$) will give the signal farthest to the right. This signal would appear at the lowest frequency for a given H_o. The inverse relation can be seen from the Bohr condition which must be satisfied for the transition to occur

$$\nu = \frac{\gamma}{2\pi} H_o(1-\sigma)$$

or

$$H_o = \frac{2\pi\nu}{\gamma} \frac{1}{1-\sigma} = \frac{2\pi\nu}{\gamma} (1 + \sigma + \sigma^2 + ---)$$

TABLE II

FIRST ORDER TRANSITIONS $\Psi_i \longrightarrow \Psi_j$

Transition ν_{ji}	Origin	Energy $-(H_j - H_i)$
78	1	$\nu_1' - \frac{1}{2}(+A_{12} + A_{13})$
46	1	$\nu_1' - \frac{1}{2}(-A_{12} + A_{13})$
35	1	$\nu_1' + \frac{1}{2}(-A_{12} + A_{13})$
12	1	$\nu_1' + \frac{1}{2}(+A_{12} + A_{13})$
68	2	$\nu_2' - \frac{1}{2}(+A_{12} + A_{23})$
47	2	$\nu_2' - \frac{1}{2}(-A_{12} + A_{23})$
25	2	$\nu_2' + \frac{1}{2}(-A_{12} + A_{23})$
13	2	$\nu_2' + \frac{1}{2}(+A_{12} + A_{23})$
58	3	$\nu_3' - \frac{1}{2}(+A_{13} + A_{23})$
37	3	$\nu_3' - \frac{1}{2}(-A_{13} + A_{23})$
26	3	$\nu_3' + \frac{1}{2}(-A_{13} + A_{23})$
14	3	$\nu_3' + \frac{1}{2}(+A_{13} + A_{23})$

Here ν is the transmitter frequency and H_o the magnetic field. If H_o is fixed, a smaller ν is needed for a larger σ; if ν is fixed, a larger H_o is needed for a larger σ. It is for this reason that the negatives of the energy differences are given in Table II. ν' and δ have been chosen to have the same sign, and this sign is such that if the transition occurs at a higher magnetic field than that of the reference (to the right of the reference in a standard spectrum), then ν' or δ will be positive. The correspondence of σ and δ is then complete.

The spectrum corresponding to the energy differences in Table II can be represented by plotting $-(E_j-E_i)$, the frequency of the line, across the page with a vertical line for each transition; the height of the line represents the intensity of the transition. (The zero on the abscissa is understood to be at ν_o, the reference frequency.) With all $A_{ij} > 0$ and $A_{23} > A_{13} > A_{12}$, the twelve lines are as shown in Figure 1. There are three more spectral lines which are forbidden in first order because they are those for transitions such as $\alpha\alpha\beta \longrightarrow \beta\beta\alpha$, in which all three spins flip. These transitions are called combination lines.

The lines can be divided into three groups of four lines, each group corresponding to the transitions of a particular nucleus as influenced by the four possible orientations of the other two. These relations are shown in Table III. The two values for A_{12} given in Table III are the same because

$$H_1 = - H_5 - H_6 - H_7$$

$$H_8 = - H_2 - H_3 - H_4$$

and $$H_1 - H_2 - H_3 + H_5 = - H_2 - H_3 - H_6 - H_7$$

FIGURE 1

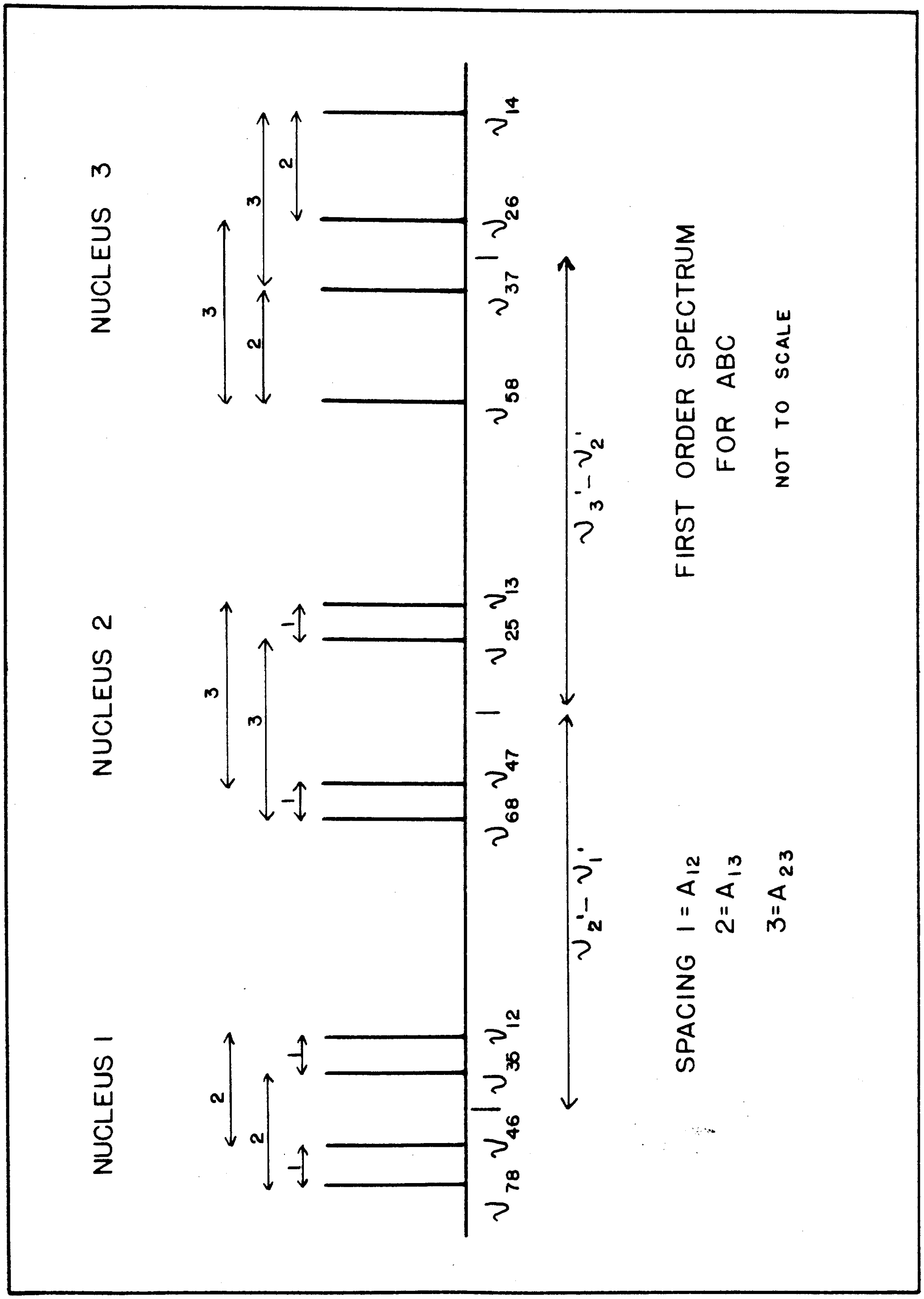

NUCLEUS 1
NUCLEUS 2
NUCLEUS 3
ν78 ν46 ν35 ν12
ν68 ν47 ν25 ν13
ν58 ν37 ν26 ν14
1
2
3
ν2' − ν1'
ν3' − ν2'
SPACING 1 = A12
2 = A13
3 = A23
FIRST ORDER SPECTRUM
FOR ABC
NOT TO SCALE

TABLE III

THE A_{ij} AS THEY APPEAR IN A FIRST ORDER SPECTRUM

$$A_{12} = \left.\begin{array}{l} \nu_{46} - \nu_{78} \\ \nu_{47} - \nu_{68} \end{array}\right\} = H_4 - H_6 - H_7 + H_8$$

$$\left.\begin{array}{l} \nu_{12} - \nu_{35} \\ \nu_{13} - \nu_{25} \end{array}\right\} = H_1 - H_2 - H_3 + H_5$$

$$A_{13} = \left.\begin{array}{l} \nu_{35} - \nu_{78} \\ \nu_{37} - \nu_{58} \end{array}\right\} = H_1 - H_2 - H_4 + H_6$$

$$\left.\begin{array}{l} \nu_{12} - \nu_{46} \\ \nu_{14} - \nu_{26} \end{array}\right\} = H_3 - H_5 - H_7 + H_8$$

$$A_{23} = \left.\begin{array}{l} \nu_{13} - \nu_{47} \\ \nu_{14} - \nu_{37} \end{array}\right\} = H_1 - H_3 - H_4 + H_7$$

$$\left.\begin{array}{l} \nu_{25} - \nu_{68} \\ \nu_{26} - \nu_{58} \end{array}\right\} = H_2 - H_5 - H_6 + H_8$$

Here $H_1 \equiv H_{11}$

and $$H_4 - H_6 - H_7 + H_8 = - H_2 - H_3 - H_6 - H_7$$

therefore $H_1 - H_2 - H_3 + H_5 = H_4 - H_6 - H_7 + H_8$

Similar relations hold for A_{13} and A_{23}. The spacing between the centers of two groups of lines will be the value of $\nu_j' - \nu_i'$.

It is now possible to show that *any* spectrum of a system of three spin 1/2 nuclei is of the same form as a first order spectrum as far as line *positions* are concerned; that is, it is possible to find an assignment of lines into three groups of four lines each, which has the same property of repeated spacings, although the spacings are not now just the A_{ij}, but are more complicated functions. Some other properties of the spectrum will also be investigated which will make possible some statements regarding the uniqueness of the assignment. To do these things, the correspondence between the spectrum for all values of λ and a first order spectrum must be demonstrated.

First it is useful to demonstrate that in the calculation of the energies from a set of parameters, each energy can be identified with a particular diagonal element of $\mathcal{H}$, in the sense that if the diagonal element and the energy are observed as functions of magnetic field, in the limit of infinite magnetic field the two must approach a common value. In proceeding from parameters to energies, the identification of the energies with the diagonal elements can be considered in each of the 3x3 determinants separately.

One factor of the secular determinant is

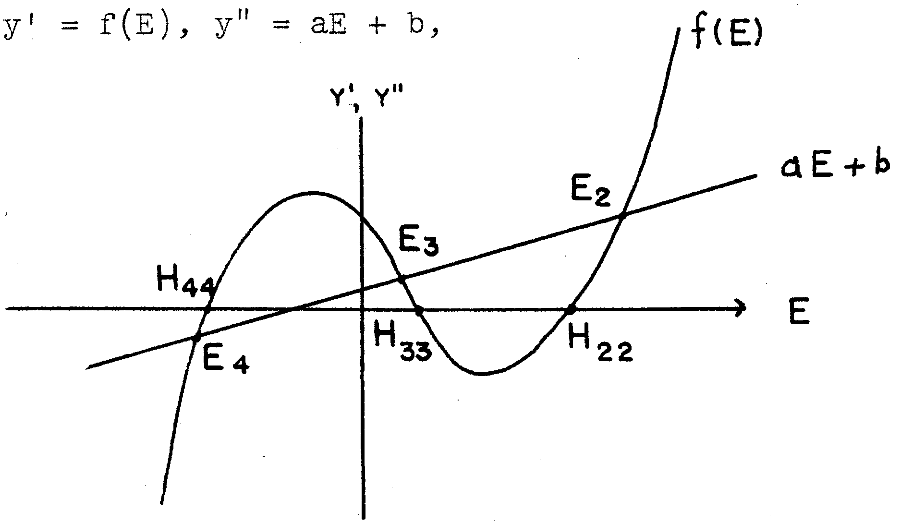
$$\begin{vmatrix} H_{22}-E & \delta H_{22} & \delta H_{24} \\ \delta H_{23} & H_{33}-E & \delta H_{34} \\ \delta H_{24} & \delta H_{34} & H_{44}-E \end{vmatrix} = 0$$

where δ is a variable inserted to introduce continuity into the argument only, and is unity for proper solution of the problem. This equation becomes

$$(E-H_{22})(E-H_{33})(E-H_{44}) = \delta(H_{23}^{2}+H_{24}^{2}+H_{34}^{2})E$$
$$+\delta^{3}H_{23}H_{24}H_{34}$$
$$-\delta^{2}(H_{22}H_{34}^{2}+H_{33}H_{24}^{2}+H_{44}H_{23}^{2})$$

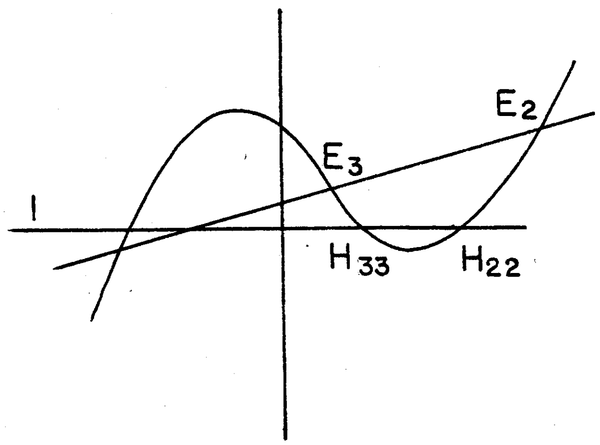
or $f(E) = aE + b$

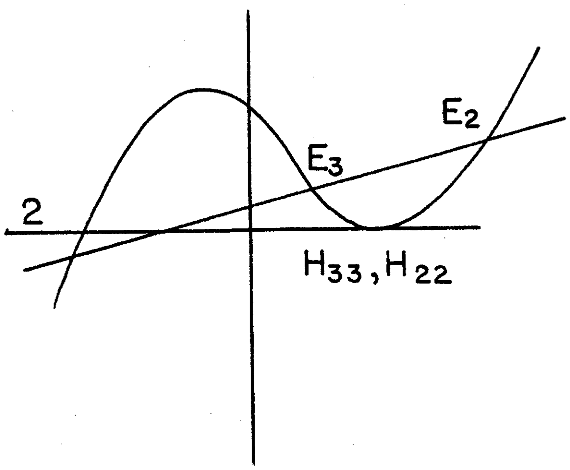
Plotting $y' = f(E)$, $y'' = aE + b$,

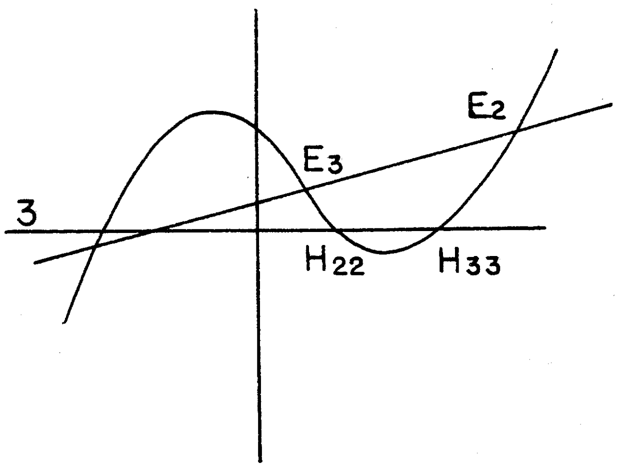


If $\delta = 0$, then $aE + b = 0$, the E axis, and the roots of $f(E) = aE + b$ are just the diagonal values. Now if δ is changed continuously from 0 to 1, the line $aE + b$ will move until it arrives at the final position shown and the values of E at the intersection of $f(E)$ and $aE + b$ will be the proper solution for this part of the problem. It is obvious in the construction shown that the largest root E_2 corresponds to the largest diagonal value H_{22}. A similar correspondence holds for the other two values.

If the convention $(\nu_A' < \nu_B' < \nu_C')$ is established, then at high magnetic fields where the chemical shifts are much larger than the spin-spin couplings, the diagonal values will be in the order $H_{22} > H_{33} > H_{44}$. Now if the magnetic field is reduced, the values of the H_{nn} and E_n change, and it is possible that at some field two diagonal values, for instance H_{22} and H_{33}, can become equal. This situation is illustrated below by three plots of the cubic equation for successively smaller magnetic fields.







In the second diagram it seems meaningless to ask: to which diagonal value does E_2 correspond? However, as the magnetic field is changed, the energy levels must change continuously, therefore, the labeling of the roots is correct as shown in the second and third diagrams. Even though at the field considered above there is a change from $H_{22} > H_{33}$ to $H_{22} < H_{33}$, E_2 remains larger than E_3. The only possibility of a change in the order of the energies is in the case considered above. Because no change occurred there, the levels must remain in the order $E_2 > E_3 > E_4$ for all magnetic fields.

At all magnetic fields of interest there can be no crossing of energy levels of differing F_z because the ν_i' and A_{ij} constitute very small additions to the Zeeman energy ν_o. There exists, then, a non-crossing rule for the energies, similar to that used in other forms of spectroscopy. Here the variable is magnetic field, and the energies do not cross as it is changed. Presumably some modification of this rule is necessary when two or more nuclei become equivalent.

If, in the sums given in Table III, the diagonal values of $\mathcal{H}$ are replaced by the corresponding energy values, the four spacings which were equal to some A_{ij} will remain equal to one another, but will no longer equal that A_{ij}. This relation can be proved by using $H_1 = E_1 = - E_5 - E_6 - E_7$ (and $H_8 = E_8 = -E_2 - E_3 - E_4$) which is true because the expanded determinant for $F_z = -(1/2)$ given above has the same coefficient of E^2 as $(E-H_2)(E-H_3)(E-H_4)$. This coefficient is minus the sum of the roots of the cubic equation in either case; therefore, $H_2+H_3+H_4 = E_2+E_3+E_4$. This relation is also demonstrated by noting that under the unitary transformation from the ψ's to the proper wave functions ϕ, the trace of the sub-matrix representing the $F_z = -(1/2)$ state is preserved.

If the spacings which correspond to the A_{ij} are added, there results one very useful bit of information. Remembering that Table II lists $-(H_j-H_i)$,

$$-(E_1-E_2-E_3+E_5) - (E_1-E_2-E_4+E_6) - (E_1-E_7-E_3-E_4) =$$

$$-3E_1+2E_2+2E_3+2E_4-E_5-E_6-E_7 =$$

$$2(E_2+E_3+E_4+E_5+E_6+E_7) =$$

$$-2(E_1+E_8) = A_{12} + A_{13} + A_{23}$$

Therefore, although complete information is lacking, the sum of the coupling constants is known. Any set of trial parameters should take advantage of the sum of the A_{ij} in order to reduce the number of parameters which need to be determined.

In finding the sum of the A's, care must be used to take the differences $\nu_{12} - \nu_{35}$, etc., in the proper direction. If, as has been assumed, the A_{ij} are all positive, the absolute values of the spacings can be used. There is another procedure which may be simpler. If a change is made from $A_{12} < A_{13}$ to $A_{12} > A_{13}$, it is obvious from Table II that the inner lines in the group of four corresponding to nucleus 1 interchange assignment, while the outer ones remain the same. Because of the correspondence between the diagonal matrix elements and the energies, this change in assignment holds whether a first order spectrum or one in which some $\lambda_{ij} \cong 1$ is being considered. Therefore, in all cases the sum of the frequencies of the lowest field line in each group is

$$\begin{aligned} S_1 &= \nu_{78} + \nu_{68} + \nu_{58} = -(E_7 + E_6 + E_5 - 3E_8) \\ &= E_1 + 3E_8 \end{aligned}$$

The sum of the highest line in each group is

$$\begin{aligned} S_2 &= \nu_{12} + \nu_{13} + \nu_{14} = -3E_1 + E_2 + E_3 + E_4 \\ &= -3E_1 - E_8 \end{aligned}$$

Now,

$$\begin{aligned} S_2 - S_1 &= -4E_1 - 4E_8 \\ &= 2(A_{12} + A_{13} + A_{23}) \end{aligned}$$

which also yeilds the sum of the coupling constants. In addition, taking $S_2 + S_1 = -2E_1 + 2E_8 = \nu_1' + \nu_2' + \nu_3'$ gives the sum of the chemical shifts. This sum is based on the reference ν_o so that no information is found about the two values $\nu_3' - \nu_1'$ and $\nu_2' - \nu_1'$, which are actually the parameters which are important in determining the spectrum of the group of three spins. The sum $1/3\ (\nu_1' + \nu_2' + \nu_3')$ tells only where the center of the transitions for the group occurs, relative to the reference.

The centers of the multiplet groups may be in the same order as the ν_i', but a more detailed treatment of the energy levels is necessary to show this (if it is indeed true), and it has not as yet been possible to perform such a treatment.

It is useful to sum up what has been found so far. Any spectrum of three spins can be broken down into three groups of four lines, each group corresponding to transitions of a particular nucleus (the word "corresponding" has been used in the same sense as above, exact identification being possible only in the limit of infinite magnetic field). These three groups of first order lines have the same property of repeated spacings as in a first order spectrum. There are, in general, three more lines which are the combination lines forbidden in first order, but which become observable in a strongly perturbed case because of mixing of the wave functions. Not all of these are usually observable, although one or two often are. The intensities of the first order lines can very greatly from unity, and some may not be observable if the λ_{ij} are large. These facts should be remembered in trying to assign lines in a spectrum.

Some information about the line intensities can be obtained by considering only the form of the solution for them. The allowed transitions $\Delta F_z = -1$ occur in three groups: transitions from state 8 to the three 5, 6, and 7, from 2,3, and 4 to 1, and from 5, 6, and 7 to 2, 3, and 4. There are obviously fifteen altogether. The forms of the proper wave functions are as follows:

$$\phi_i = \sum_j a_{ij} \psi_j$$

where i, j = 1--8. The matrix of the a_{ij} must be unitary, because one orthonormal set of wave functions is being carried into another. The form of the total matrix of the a_{ij} is:

$$\begin{bmatrix} 1 & & & 0 \\ & (3x3) & & \\ & & (3x3) & \\ 0 & & & 1 \end{bmatrix}$$

If the matrix is unitary, the individual 3x3 ones must of course be unitary also. Using this property and

$$\phi_i = \sum_j a_{ij}\,\psi_j \qquad i,\ j = 2,\ 3,\ 4$$

$$\phi_i = \sum_j a_{ij}\,\psi_j \qquad i,\ j = 5,\ 6,\ 7$$

it follows that:

$$\sum_i a_{ij}\,a_{ik} = \delta_{jk}$$

and

$$\sum_i a_{ji}\,a_{ki} = \delta_{jk} \qquad \text{for } i,\ j,\ k = 2,\ 3,\ 4 \text{ or } 5,\ 6,\ 7$$

If it is noted that $(\psi_i|I_x|\psi_j)$ is one if $i=8$, $j=5,6,7$
or $i=2,3,4$ $j=1$

and for a given $i=5$, 6, or 7 there are two values for the matrix element of one, and one value zero when j takes on 2, 3, and 4, some relations among the line intensities can mow be demonstrated. Considering the first group of transitions 8 ⟶ 5, 6, 7:

$$\begin{aligned}
\sum_{\text{Group I}} I_{ij} &= \sum_i (\phi_i|I_x|\phi_8)^2 \qquad i = 5,6,7 \\
&= \sum_i \Big[\sum_j a_{ij}\,(\psi_j|I_x|\psi_8)\Big]^2 \qquad j = 5,6,7 \\
&= \sum_{i,j,k} (\psi_j|I_x|\psi_8)(\psi_k|I_x|\psi_8)\,a_{ij}\,a_{ik} \\
&\qquad\qquad k = 5,6,7 \\
&= \sum_{j,k} (\psi_j|I_x|\psi_8)(\psi_k|I_x|\psi_8) \sum_i a_{ij}\,a_{ik} \\
&= \sum_{j,k} (\psi_j|I_x|\psi_8)(\psi_k|I_x|\psi_8)\,\delta_{jk}
\end{aligned}$$

$$= \sum_j (\psi_j|I_x|\psi_8)^2 = 3$$

with the previous convention that $(\psi_j|I_x|\psi_8) = 1$ when $j = 5$, 6, or 7. The proof for the lines in Group II, levels 2, 3, and 4 ⟶ 1 is identical.

In Group III:

$$\sum_{\text{Group III}} I_{ij} = \sum_i \sum_j (\phi_i|I_x|\phi_j)^2 \qquad \begin{matrix} i = 2,3,4 \\ j = 5,6,7 \end{matrix}$$

$$= \sum_i \sum_j \left[\left(\sum_k a_{ik}\psi_k|I_x|\sum_\ell a_{j\ell}\psi_\ell\right)\right]^2$$

$$\begin{matrix} k = 2,3,4 \\ \ell = 5,6,7 \end{matrix}$$

$$= \sum_i \sum_j \left[\sum_k \sum_\ell a_{ik}a_{j\ell}(\psi_k|I_x|\psi_\ell)\right]^2$$

$$= \sum_{i,k,m} \sum_{j,\ell,n} \left[a_{ik}a_{j\ell}a_{im}a_{jn}(\psi_k|I_x|\psi_\ell) \times (\psi_m|I_x|\psi_n)\right] \qquad \begin{matrix} m = 2,3,4 \\ n = 5,6,7 \end{matrix}$$

$$= \sum_{k,m} \sum_{\ell,n} \left[(\psi_k|I_x|\psi_\ell)(\psi_m|I_x|\psi_n) \times \sum_i a_{ik}a_{im} \sum_j a_{j\ell}a_{jn}\right]$$

$$= \sum_{k,m} \sum_{\ell,n} (\psi_k|I_x|\psi_\ell)(\psi_m|I_x|\psi_n)\delta_{km}\delta_{\ell n}$$

$$= \sum_k \sum_\ell (\psi_k|I_x|\psi_\ell)^2 = 6$$

Obviously $\displaystyle\sum_{\text{all lines}} I_{ij} = 12$

The fact that the sums of the intensities of two sets of lines must be one-fourth of the total intensity helps greatly in assigning transitions to lines in a spectrum.

Up to this point it has been possible to assign the lines into three multiplets. The assignment may be somewhat tentative if less than the theoretical number of first order lines is observable because of degeneracy, if some lines are very weak, or if there appear to be more than four repeats of some line spacing.. The change from $A_{12} < A_{13}$ to $A_{12} > A_{13}$ does not change the assignment of the outer lines in the four line "multiplet", so that if all the A_{ij} are assumed to be positive (the case in which this is not true will be considered later) the line at the lowest magnetic field in each four line group belongs to Group I. The highest field ones are those in Group II. Any assignment must meet the additional test that the sums of the intensities of the lines in groups I and II must have the proper values.

Because of the possibility of negative values of A_{ij}, the effect on the spectra of such changes in sign should be investigated. With three A_{ij} which can each be either positive or negative, there are eight possibilities, but four of these are related to the other four by the reversal of <u>all</u> the signs. As is shown in Appendix A, there is no way to distinguish between systems related by reversal of the signs of all A_{ij}; therefore, only four possibilities need to be considered: one with all A_{ij} positive, and three with one negative.

In the first order spectrum of Figure 1, reversal of the sign of an A_{ij} interchanges the assignment of the pairs of lines separated by that A_{ij}. In the figure, changing to $-|A_{12}|$ will interchange assignments of lines 1 and 2, 3 and 4, etc. In <u>any</u> spectrum for three spins, the corresponding change occurs, and there will be four possible ways to assign lines to transitions. These alternate assignments should be considered to see what effects they have upon the rules set up to test the grouping of lines into four line multiplets.

The sum of the chemical shifts can still be determined because only the sum of the center positions of each multiplet is needed. To use the intensity sums, the assignment which corresponds to some A_{ij} negative can be set up (assuming the assignment into groups of four which is for all A's positive has been found) by interchanging the assignments of all pairs of lines whose separation corresponds to the A_{ij} which is to be negative. The new values for the appropriate transitions are then used in the sums. In some cases which depart considerably from first order, the intensity sums over groups I and II will be three for only one or two of the four possible assignments, allowing some to be eliminated. In a first order spectrum, there exists no difference among the four possible arrangements of the signs of the A_{ij}.

In finding the sum of the A_{ij}, the correct assignment must also be used. If $(\nu_{12} - \nu_{35} + \nu_{12} - \nu_{46} + \nu_{13} - \nu_{47})$ is chosen as the sum of the splittings in the assignment corresponding to positive A's, then the same sum with new values for the ν's should be used in other assignments. The algebraic sum of the A's results.

For there to be more than one assignment, other than the four possibilities discussed so far, there must exist a fortuitous relation among the parameters such that some line spacings repeat more than four times. In this case it is probable that the λ_{ij} are large, in which case the intensities can probably determine the correct assignments. If this fails, the only recourse is taking the spectrum at another value of the magnetic field, H_o. If a set of parameters can be found that predicts the spectrum at two magnetic fields, it is extremely likely that it is the correct one, neglecting the possible existence of other assignments differing only in the signs of the A's. It should be added here that in the specific cases discussed later, trying to use a set of parameters with a negative A_{ij} causes some small change in all parameters; however, by far the major change is that the A has a different sign.

After using the methods just described to determine a correct assignment, there remains the problem of finding the six parameters A_{12}, A_{13}, A_{23}, ν_1', ν_2', and ν_3'. The method used here is that of assuming a set of parameters, calculating a spectrum on that basis, and adjusting the parameters for the best fit, defined as the point at which the differences between experimental and calculated spectra are equal to or less than the estimated error in the experimental spectrum. There remains a small range for each of the parameters in which there is agreement between calculated and experimental spectra. One comment on this method is helpful: it is found that if in first order a change in A_{12}, for instance, is indicated by comparison of the experimental and calculated spectra, then making a change in this direction improves the fit between them. The choice of parameters is restricted by the fact that the sums of chemical shifts and coupling constants are known.

III. EXPERIMENTAL

Three systems of three spins, each of which has three nonequivalent protons coupled to each other, were selected for study. 2,4- and 2,5-dichloroaniline were studied in solution, the three protons on the benzene ring being of interest in both cases. The protons studied are completely independent of the amine protons, which have a transition in a different region of the spectrum. The 2,5-dichloroaniline (Eastman Kodak, White Label) was studied as a saturated solution in carbon tetrachloride (reagent grade). This solution was in the neighborhood of three molar, but the exact concentration is not important because any changes in the spectra with concentration are very small, and because the same sample was used for all spectra. To increase solubility, the 2,4-dichloroaniline (Eastman Kodak, White Label) was dissolved in 80 % carbon tetrachloride with 20 % acetone by volume. The total length of the spectrum was about 3 cps. less (at 40 Mc.) than when pure carbon tetrachloride was used, probably because of a change in the chemical shifts. No explanation is offered for this effect, although it could be a basis for further work. The dependence of this effect upon the concentration of the dichloroaniline is small, since several samples made up at different times gave the same spectra.

The third sample was styrene (Eastman Kodak, White Label), the three vinyl protons being those of interest. There is probably very little interaction between ring protons and those on adjacent carbon atoms in side chains, since no splitting of spectral lines attributable to a coupling between these protons has been observed.

All samples were outgassed on a vacuum line by freezing, pumping and melting several times, and sealed into 5 mm. Pyrex tubes. This procedure is necessary for best resolution since the dissolved oxygen is paramagnetic and, at concentrations resulting from equilibration with the atmosphere, widens the lines noticeably by shortening the spin-lattice relaxation times. The styrene was subjected to a crude distillation while under vacuum, reducing the concentration of the inhibitor to a level such that the samples had to be used within several days to prevent polymerization products and increased viscosity from affecting the spectra.

All spectra were taken on a conventional Varian V4300B High Resolution NMR spectrometer, operating at 10 and 40 megacycles. For the 22.55 Mc. work, a transmitter-receiver following the Varian design was used. The standard 40 Mc. Varian crossed coil probe was used in this case, but with a different receiver coil, constructed so that it resonated at the proper frequency with the capacity included in the probe. It was not necessary to change the tuning of the transmitter coil in the probe when working at 22.55 Mc.

The spectra were recorded on the attached Sanborn recorder, using only the center portion of the chart to reduce nonlinearity to an acceptable level. At present it is possible to measure line intensities more accurately than when these data were taken, and the use of a more linear recorder is advisable. Also, it is recognized now that in some cases accurate intensities are very important. The error introduced by the recorder used here is not considered to affect any of the results in an important way, however.

The spectra were recorded as functions of time, as is usual. Fortunately the method of changing magnetic field is such that the deviation from a linear change of field with time is so small as to be negligible. There are some other factors which influence the magnetic field, such as power line voltage and temperature of themagnet.

However, the changes in field introduced by these factors do not preclude the assumption that the magnetic field changes linearly with time.

The samples were in 5 mm. O.D. Pyrex tubes, so that it was possible to spin them for best resolution (3, 8).

The procedure used to measure the line positions is standard, but several precautions are necessary to reduce error to a minimum. The spectra were taken at a sweep rate (magnetic field sweep) chosen to reduce the effects of the several experimental errors. For rapid sweeps, the line positions become uncertain and resolution decreases because of transient effects. One particular transient effect, "wiggles" (9), is especially disturbing where several lines occur close together. Too large a sweep rate, then, causes deterioration of the spectrum. If the sweep rate is too slow the change of magnetic field with time may not remain linear, since the changes in magnetic field caused by other factors (such as temperature changes) become relatively more important. Furthermore, changes in magnetic field caused by variation in the power line voltage occur mainly in small "steps" and the longer the time spent in scanning a spectrum, the more likely that one or more of these "steps" is to occur. For measurement of positions it appears best to err (if at all) toward the faster sweeps, since the uncertainty in line positions increases more slowly there than in the opposite case. For intensity measurement and for observation of small lines near larger ones, it is decidedly better to reduce the transient distortion as much as possible by employing a slow sweep.

Twelve or more spectra were taken at the chosen sweep rate and the best of these spectra -- those showing no obvious effects of change in magnetic field -- were selected and the relative positions measured. Two prominent lines at each end of the spectrum were used to establish the 0 and 100% points of a relative scale, and all the other positions were measured relative to these points by interpolation and extrapolation. The individual line positions were averaged; this procedure is possible since the positions are on a common basis. This average spectrum can be used for calculation of parameters; however, the parameters will differ from the true ones by a scale factor.

To determine this scale factor it is necessary to measure the length of the selected interval (100%) in the spectrum. This calibration is done by the standard method of modulating the magnetic field H_o and observing the side bands produced (38). For each line in the spectrum there will be two or more side bands symmetrically disposed around the line. For suitable adjustment of the modulation level and frequency, it is possible to observe three essentially identical spectra with the spacing between equivalent points just $\Delta H = \frac{2\pi\nu_m}{\gamma}$ where ΔH is the difference in magnetic field of the two points, and ν_m the frequency of the audio modulation. If one prefers, the spacing of the spectra can be left in frequency units. From a recording of the three spectra with a known audio modulation frequency, the spacing between the lines selected as 0 and 100% can be determined. Several such calibrations are averaged.

The frequency of the audio oscillator used for producing the modulation was calibrated against a tuning fork, the frequency of which had been measured to better than 0.1% by a frequency counter. The 60 cycle power frequency was also used as a secondary standard. At present it is known that this frequency is within 0.1 cps. of 60.0 cps., by direct measurement with a Hewlett-Packard frequency counter.

The intensities can be measured from either the peak height or the integrated area under the curve. Both methods seem to give similar reproducibility. If, as in the spectra taken here, there is no indication of differing line widths, the peak height method is probably better. This statement is true because field instability is the most important source of error and a change in magnetic field during the time a line is being traversed will affect the width of the line, and hence the area, but will not appreciably change the height. If the radio frequency power level is too high for a given sweep rate, there occurs the phenomenon known as saturation (9). The main result is that the lines become broader, reducing the resolution and modifying the intensities observed. The complications introduced by this effect are avoided by keeping the power level low, but still large enough to maintain a proper signal-to-noise ratio. Finally, both methods of intensity measurement are subjected to error because of uncertainty in the positioning of the base line. This uncertainty occurs most commonly when the lines are not all completely resolved.

The intensities from each spectrum are normalized so that the total intensity is twelve. This number is used because it is that which appears in a calculated spectrum if the definitions given in Section II are used. The intensities of a set of spectra may now be averaged, since they are on a common basis.

IV. RESULTS AND DISCUSSION

In Figures 2, 4, 5, 7, and 8 are shown typical spectra of the three compounds studied. These of course are individual spectra, and their line positions and intensities are not in all cases identical to the average of these quantities used in the analysis. Shown with the spectra are ones calculated using parameters which result in the best fit between the calculated and average experimental spectra at 40 Mc. This determination is discussed in more detail later. The results for the three compounds will be given individually.

Styrene

The upper trace in Figure 2 shows the spectrum of styrene at 40 Mc. Eleven of the first order lines of the vinyl protons are obvious toward the right. The large line on the left and several small satellites on each side are from the five ring protons. The twelfth line of the vinyl group is somewhat obscured by the satellites on the large line. In addition, there is a small combination line which is observable at a larger amplification. Its position is at about 37 cps. on the scale and agrees with that given in the calculated spectra. Below the experimental trace are two calculated spectra based upon two possible assignments of transitions to line frequencies. The two given here match the average experimental one to within experimental error. (In Figure 3 are given two other assignments which do not fit the experimental intensities, but do fit the line positions.) The chemical shifts are designated by the solid triangles; these are the positions where the resonances for the three protons would occur if there were no spin-spin coupling. It is seen that these positions are not exactly in the centers

FIGURE 2

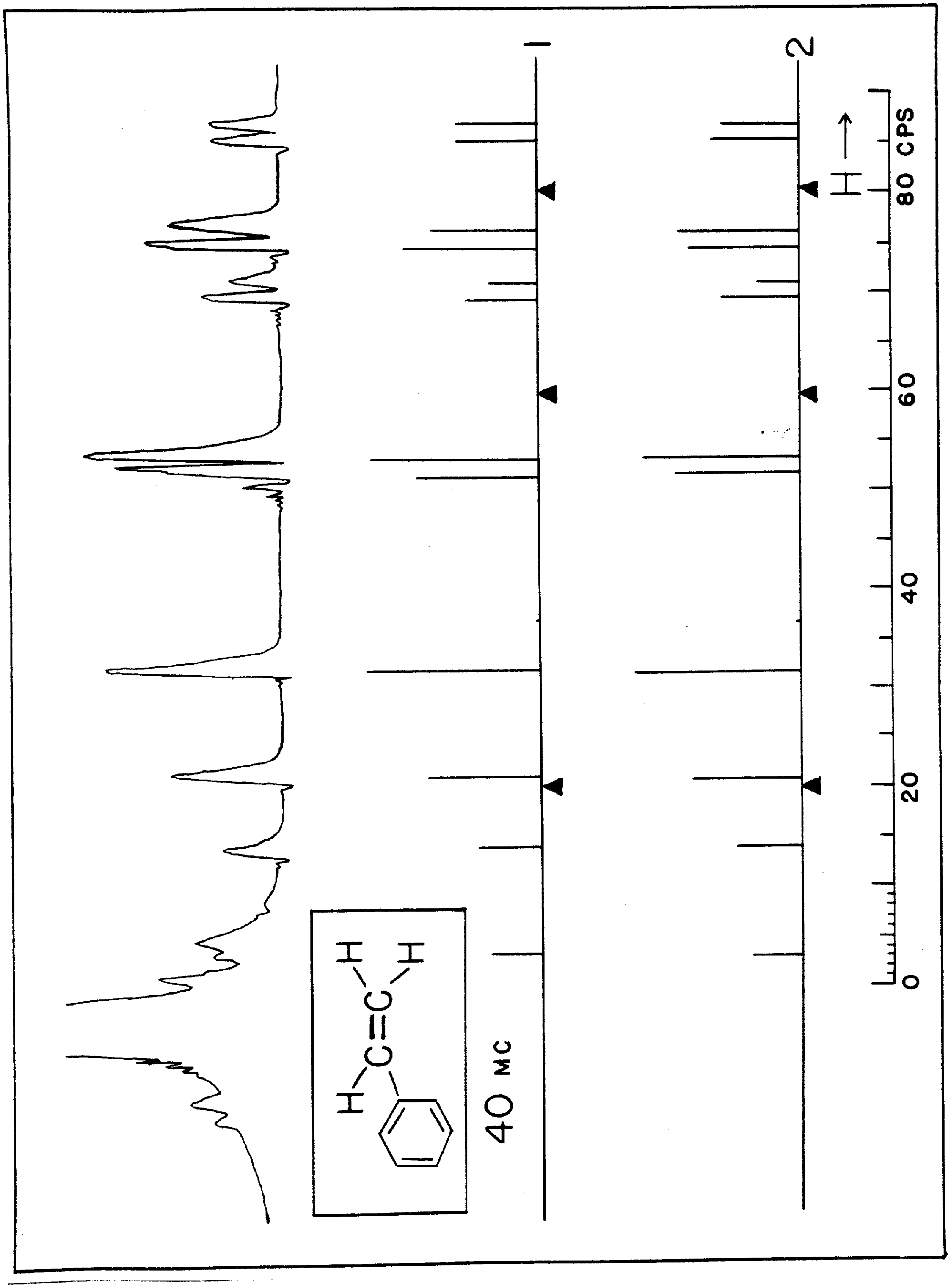
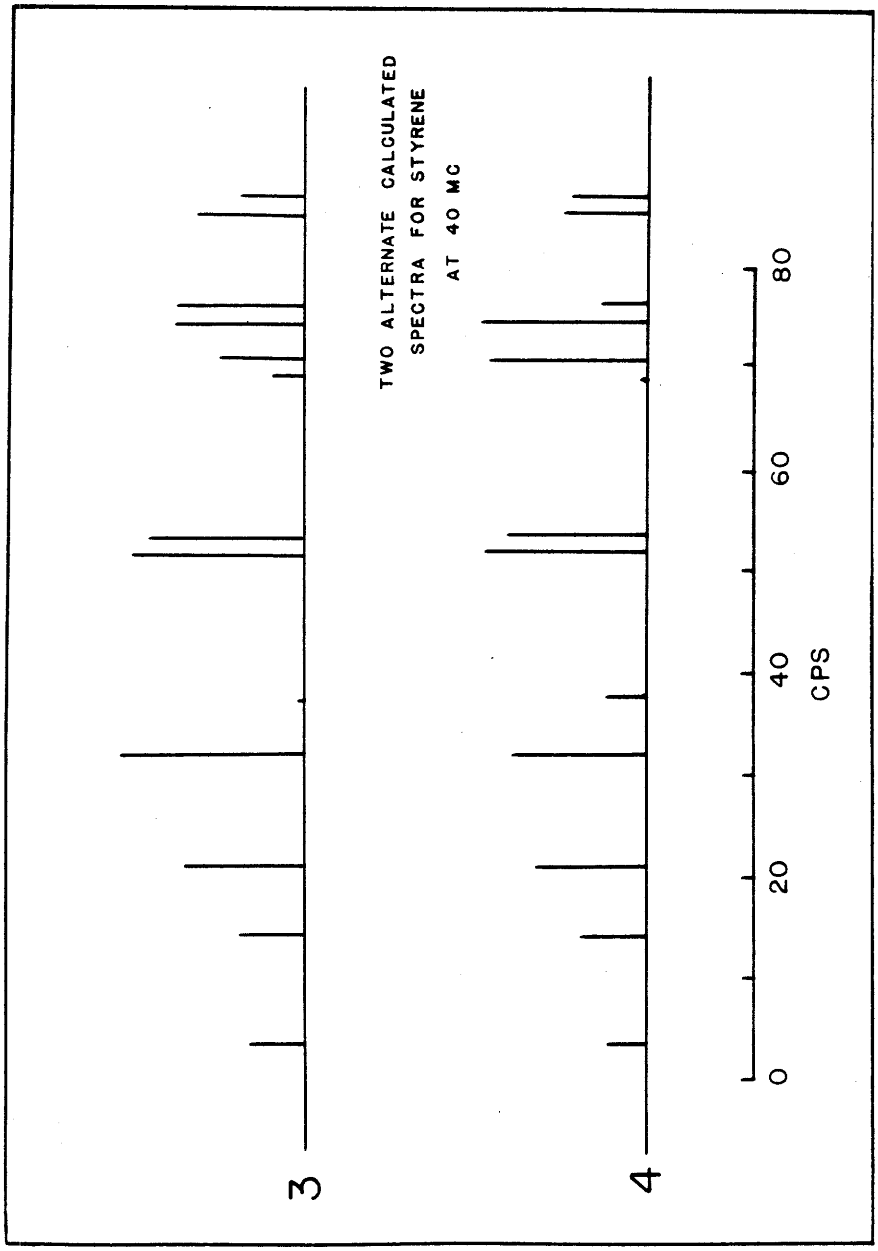


FIGURE 3


TWO ALTERNATE CALCULATED
SPECTRA FOR STYRENE
AT 40 MC
3
4
0
20
40
60
80
CPS

of the groups of four lines; this fact indicates departure from a first order spectrum.

Table IV lists the thirteen observed and calculated line positions and intensities at 40 Mc. The calculated ones are for assignment #1. For styrene at 40 Mc. the probable error in a line position, based upon deviations from the mean, is about 0.15 cps., varying somewhat for different lines. There is some additional error introduced when the scale factor is measured, so the absolute line positions have a probable error of about 0.20 cps. Measurement of the frequency of the audio oscillator probably does not increase this error. The probable error in the intensity of a line is 5% or 0.05 units (based on a total of 12 for all lines), whichever is larger; the error in the intensity of the small combination line is about 25%.

The quality of the analysis of the spectrum is indicated by the average of the deviations $|\nu_{exp} - \nu_{calc}|$. The average for styrene is 0.22 cps., approximately the probable error in a line position. The average deviation in intensity is about 0.1, somewhat larger than the probable error in the experimental line intensity. There are some systematic errors in measuring intensities, such as recorder nonlinearity and saturation of the lines, which cannot easily be taken into account, so the agreement here is considered to be good also. The errors in line positions are comparable with those in the latest work involved with measurements on this scale (2, 7, 15, 30). The line intensities are somewhat better than those given by Bernstein, Pople, and Schneider (7).

The parameters used to calculate the spectrum #1 are:

$$\delta_2 - \delta_1 = 0.98 \pm 0.01 \text{ ppm.}$$

$$\delta_3 - \delta_1 = 1.50 \pm 0.01$$

TABLE IV

STYRENE - 40 Mc.

Transition		Origin	Position*		Intensity	
1	2		Observed	Calculated	Observed	Calculated
78	46	1	2.60	3.00	0.28	0.51
35	12	1	13.50	13.74	0.53	0.64
46	78	1	20.78	20.74	0.94	1.12
12	35	1	31.78	31.47	1.60	1.70
36	36	comb. or x	36.87	36.67	0.018	0.025
68	47	2	51.23	51.07	1.51	1.19
25	13	2	53.05	52.87	1.86	1.65
47	68	2	68.68	68.81	0.75	0.70
13	25	2	70.60	70.60	0.48	0.48
58	58	3	74.15	74.00	1.28	1.30
26	26	3	75.96	75.80	1.10	1.05
37	37	3	84.41	84.74	0.78	0.81
14	14	3	86.05	86.52	0.86	0.82

*Because positions were not measured relative to any standard, a constant was added to these positions to have them agree with the scale in the figures. The position of the observed lines has been adjusted in a similar way to get the best fit. Lines of intensity less than 0.01 have been omitted.

$A_{12} = 17.8 \pm 0.5$ cps.
$A_{13} = 11.3 \pm 0.5$
$A_{23} = 1.2 \pm 0.5$

The numbering of the nuclei corresponds to the order of their chemical shifts across the spectrum toward the right in Figure 2. The errors quoted here are larger than those in line positions. If the spectrum were first order, the error should be $\sqrt{2}$ times the error in one line position, since A_{12}, for instance, is just a difference in two line positions. Here there is not a first order case, so the values of the parameters are coupled somewhat. A crude analysis of the error introduced into the sum, $\sum |\nu_{exp} - \nu_{calc}|$, by changing one parameter was made, and the errors stated are based upon this. For purposes of discussion, the values λ_{ij} are listed at the three frequencies used.

Frequency	λ_{12}	λ_{13}	λ_{23}
40 Mc.	0.45	0.19	0.06
22.55	0.80	0.34	0.11
10	1.80	0.75	0.25

The spectra calculated at 22.55 Mc. and 10 Mc., using the same parameters as for spectrum #1, are shown in Figures 4 and 5. The experimental ones are shown in the same figures. The assignments and detailed positions and intensities are shown in Table V. Here the probable error in line position is 0.10 cps.; the mean deviation $|\nu_{exp} - \nu_{calc}|$ has about the same value. The intensities for the 22.55 Mc. spectrum agree about as well as at 40 Mc., but the deviations and experimental errors increase to about 0.2 units at 10 Mc. because the lines are no longer completely resolved. The agreement is considered excellent nevertheless. The assignment #2 which agrees at 40 Mc. does not agree at all at 10 Mc., showing that it is incorrect,

FIGURE 4

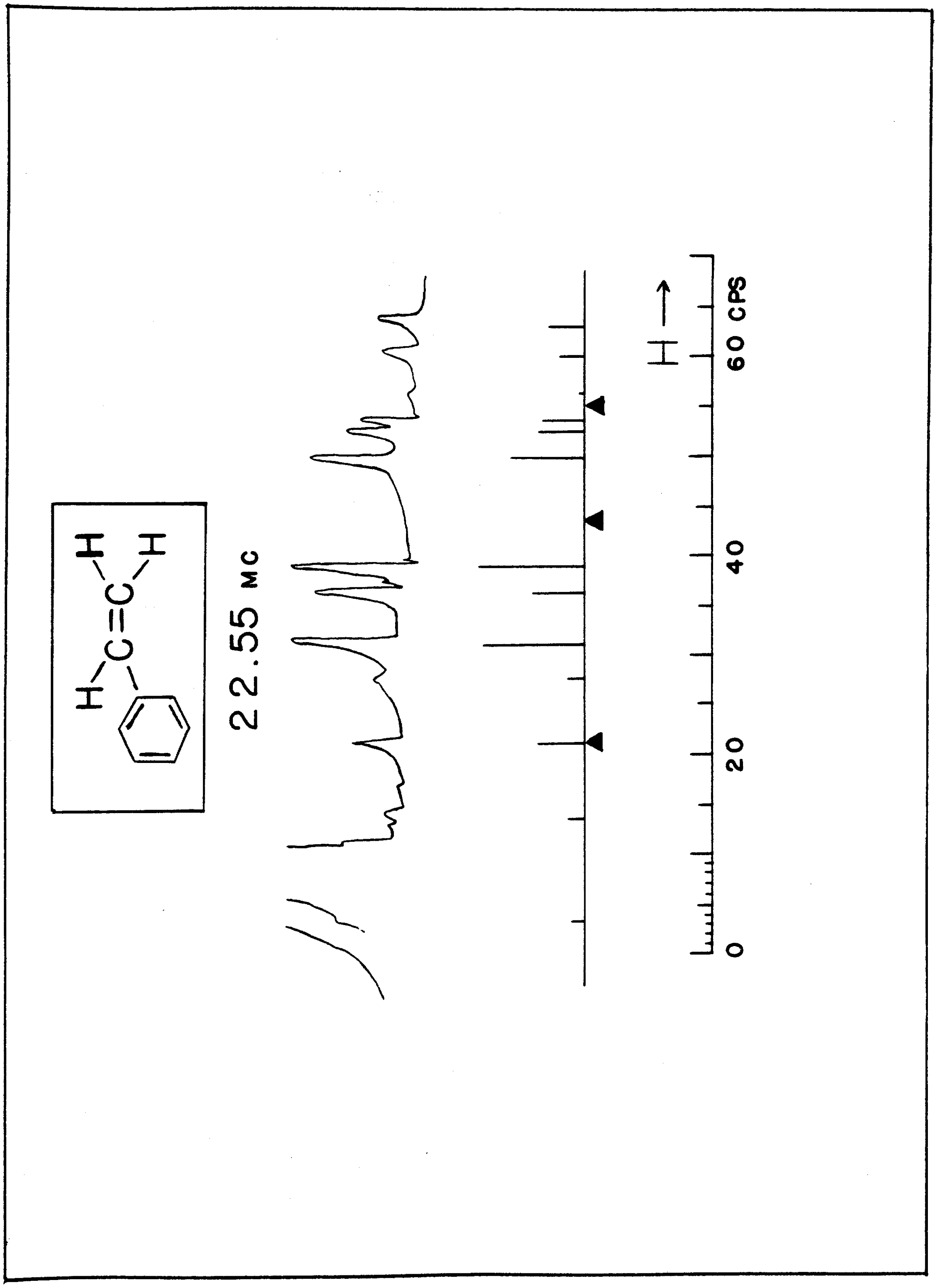


FIGURE 5

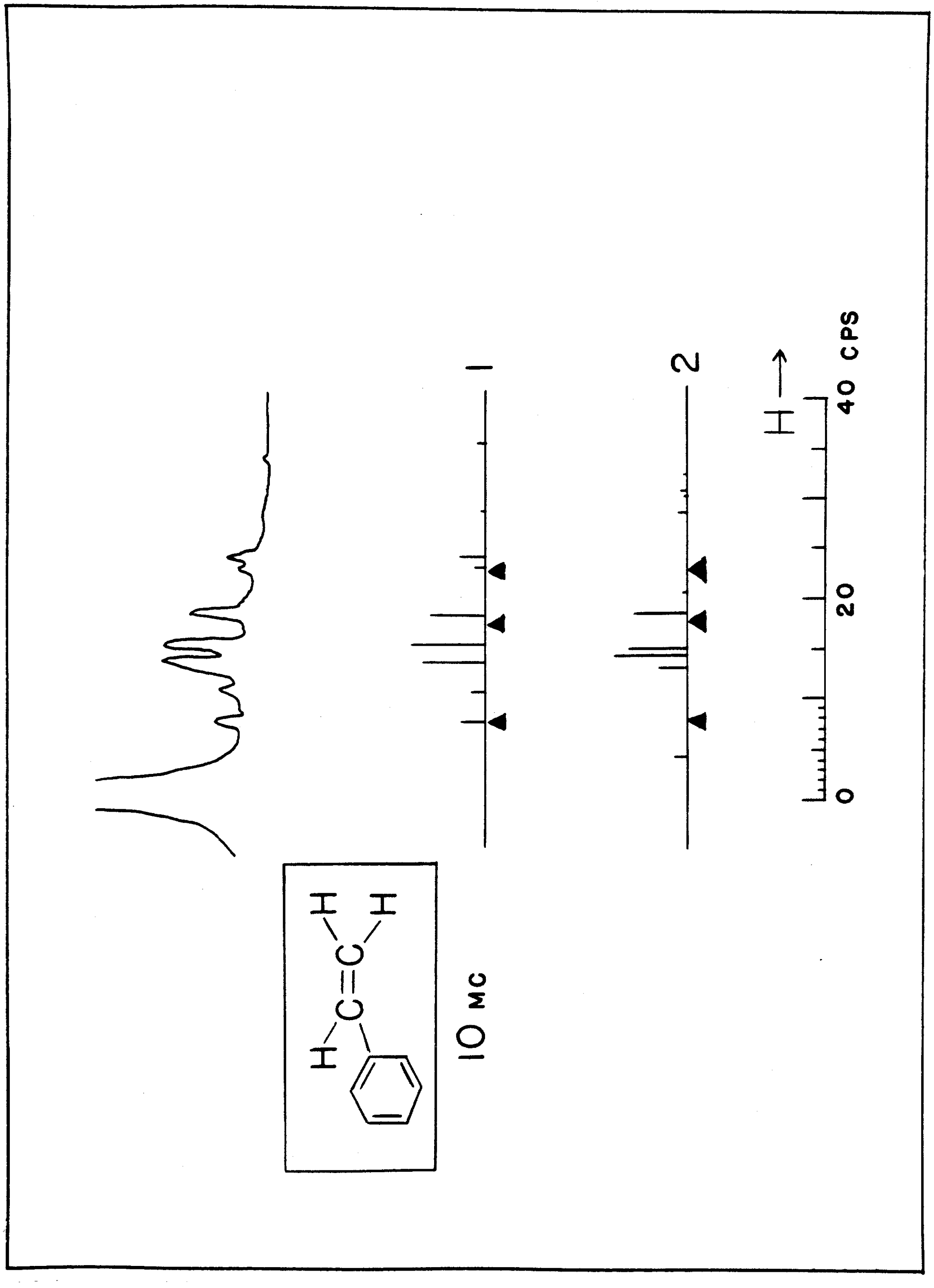


TABLE V

STYRENE - 22.55 Mc.

Transition	Origin	Position		Intensity	
		Observed	Calculated	Observed	Calculated
78	1	3.7	3.38	0.27	0.32
35	1	14.0	13.60	0.27	0.36
46	1	21.2	20.72	0.93	0.93
36	x	27.6	27.20	0.25	0.23
12	1	31.2	30.95	1.80	2.14
68	2	36.3	36.14	1.37	1.11
25	2	38.8	38.81	2.00	2.18
58	3	50.0	49.74	1.59	1.58
26	3	52.4	52.41	1.10	0.95
47	2	53.7	53.48	0.96	0.80
13	2	55.9	56.16	0.13	0.11
37	3	59.9	59.96	0.54	0.52
14	3	62.4	62.64	0.79	0.76

STYRENE - 10 Mc.

78	1	--	-11.95	--	0.11
45	x	--	-6.26	--	0.09
46	1	--	1.43	--	0.05
36	x	7.9	8.03	0.87	1.09
68	2	10.8	10.81	0.84	0.59
12	1	13.5	13.72	3.50	2.67
25	2	15.1	15.41	3.11	3.20
58	3	18.6	18.50	2.03	2.30
26	3	23.1	23.09	0.59	0.45
47	2	24.2	24.19	0.89	1.10
13	2	28.7	28.79	0.10	0.10
14	3	35.4	35.39	0.17	0.23

and illustrating the value of having data corresponding to more than one value of the magnetic field.

The assignment of transitions to lines at 40 Mc. is given with the line frequencies in Table IV. Figure 6 then correlates the lines observed at several frequencies and shows the relationship of the spectra. It also shows which lines remain with nonzero intensity in the limit of no chemical shift. The line which corresponds to the transition ν_{36}, the one observable combination line at 40 Mc., is seen to be one of the five largest lines at 10 Mc. It has intensity 1.00 in the limit of no chemical shift.

Assignment #1 corresponds to all A_{ij} positive. The assignment #2, which also fits closely at 40 Mc., is also given in the table. This new assignment has interchanged all labeling of lines separated by the splitting corresponding to A_{12}. Now, there is a negative value for A_{12} and the parameters are:

$\delta_2 - \delta_1 = 0.99$ ppm.

$\delta_3 - \delta_1 = 1.51$

$A_{12} = -17.8$ cps.

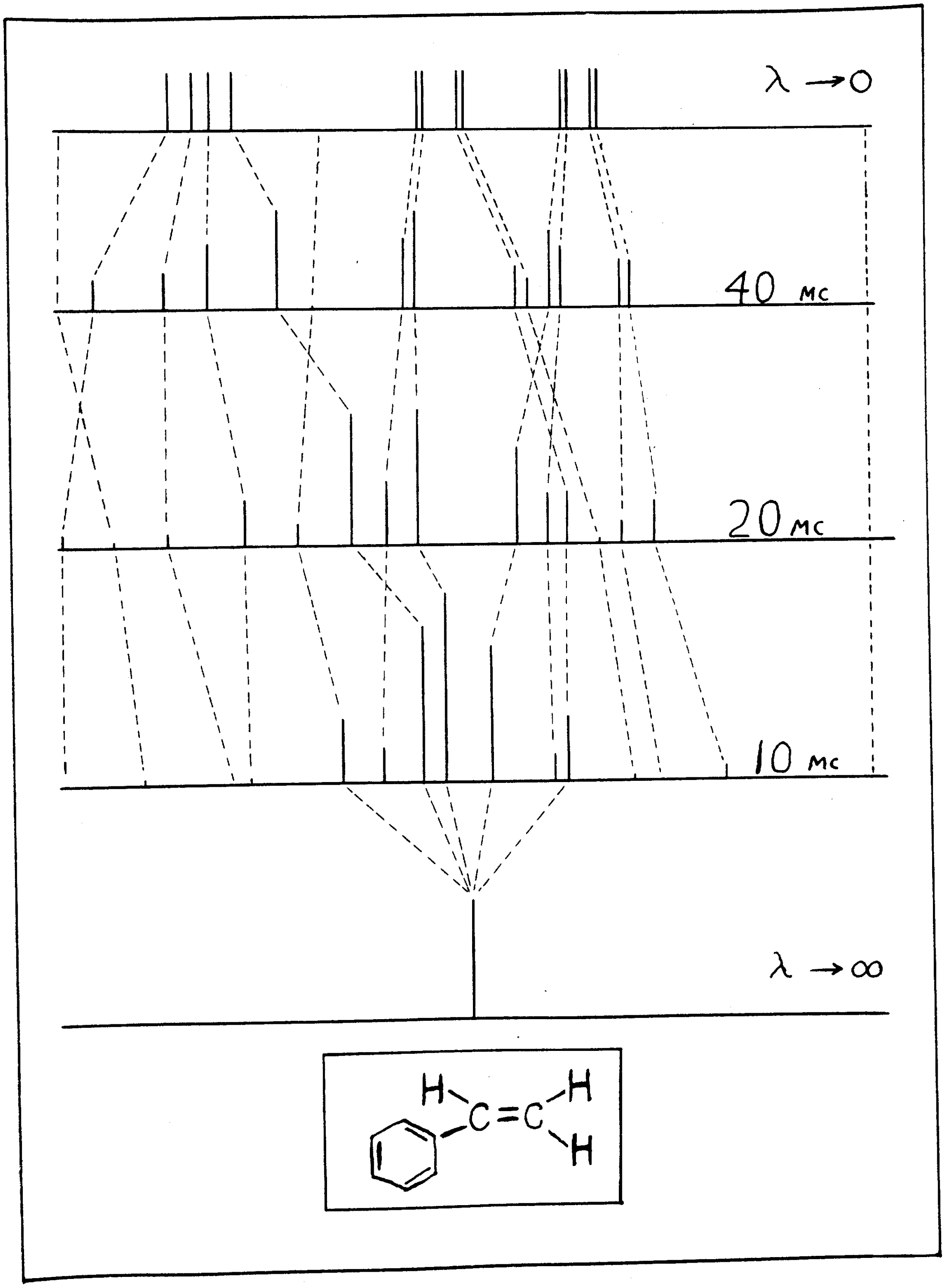
$A_{13} = 11.3$

$A_{23} = 1.4$

As was mentioned earlier, this set is incorrect since it does not at all agree with experiment at 10 Mc.

It is interesting to note what occurred in changing from $A_{12} > 0$ to $A_{12} < 0$. The changes made in the other parameters are small, but are necessary to get the best fit of the line positions. The assignments #3 and #4 are based upon sets of parameters with $A_{13} < 0$ and $A_{23} < 0$. These two can be rejected even at 40 Mc. That all assignments corresponding to some A_{ij} negative have been eliminated has shown that the relative signs of the three coupling constants must be the same. There is no other assignment with different mag-

FIGURE 6

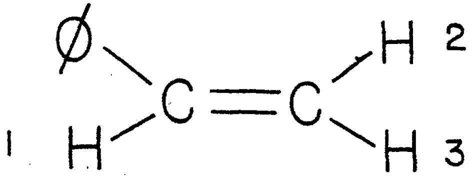


nitudes of ν's and A's possible at 40 Mc., because there is no other with the proper repeated spacings.

In Appendix B are given some details pertaining to the calculation of the spectrum at 22.55 Mc. It demonstrates vividly the effects of the spin-spin couplings in mixing the zero order wave functions.

The values of the parameters calculated from the spectrum of styrene are rather unusual. Proton 1 is far removed from the position usually associated with ethylenic hydrogens (37). Also A_{23} is extremely small. These values should be examined more closely. The chemical shifts, relative to the center of the line due to the ring hydrogens, are $\nu_1' = 25$, $\nu_2' = 65$, and $\nu_3' = 85$ cps. Using as model compounds α-methyl styrene and trans-β-methyl styrene (prepared by C. Bumgardner), numbers 1, 2, and 3 can be assigned to particular protons in the vinyl group. In α-methyl styrene the protons have chemical shifts of about 72 and 86 cps., relative to the ring. If it is assumed that the ring differs by only a small amount between these compounds, which is certainly correct to the degree of accuracy needed here, then the #1 proton is evidently the α one in styrene. Therefore, the unusual chemical shift of this proton is probably connected with the well known ability of the ring to conjugate with the α position.

In trans-β-methyl styrene the spectrum is complicated by coupling of the methyl protons to one ethylenic proton. No complete analysis has been made, but there appears to be a coupling between the two vinyl hydrogens of 17 ± 1 cps. It would appear that the 17.8 cps. coupling in styrene is that between trans hydrogens. This is in accord with the observation that in several compounds, the coupling between H^1 and F^{19} is larger if they are trans, instead of cis, on a double bond (25). The assignment then is:



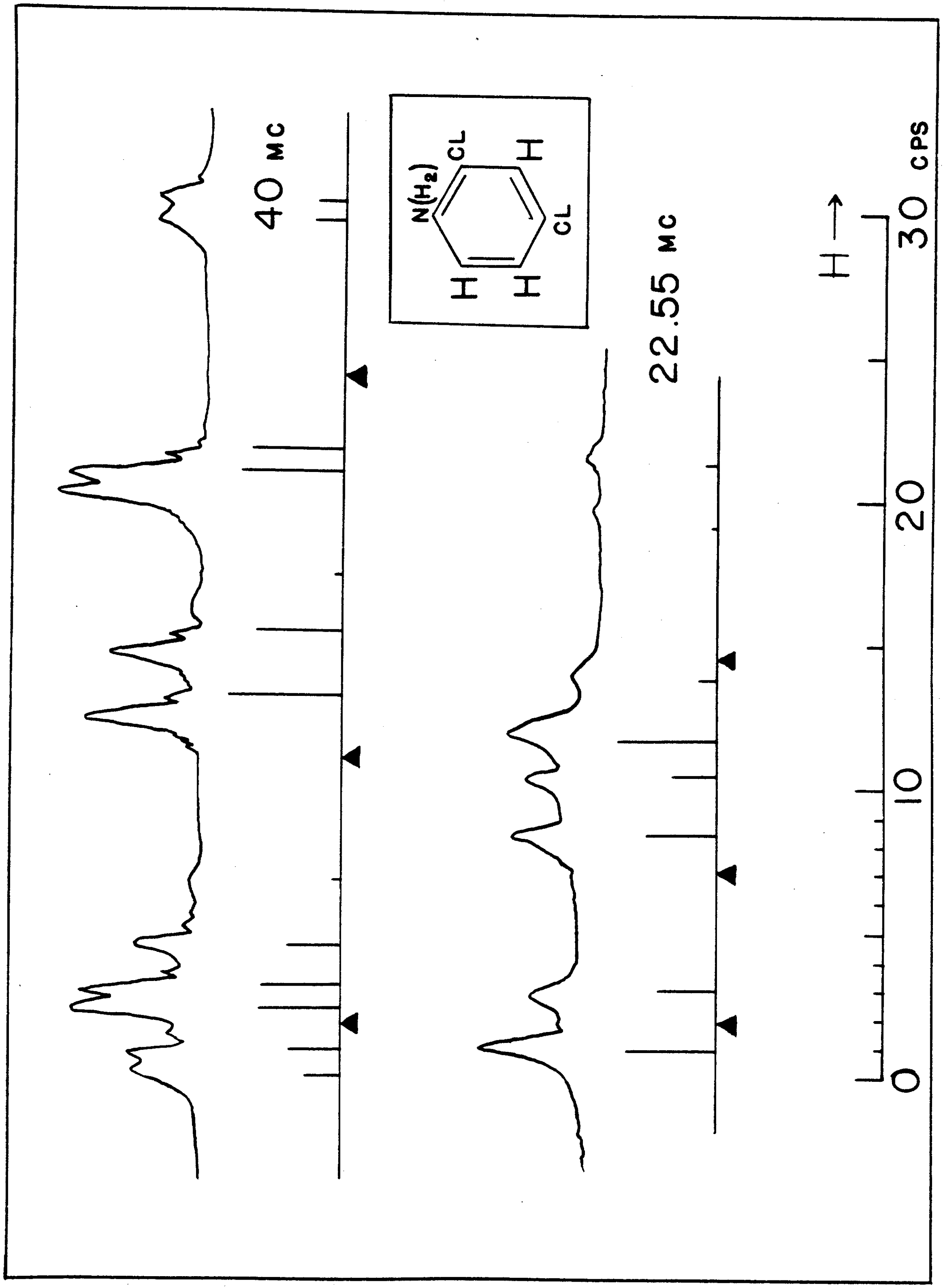
The same small coupling constant exists for the two protons in $CH_2=CF_2$ (24) and for the analogous pair in 1,1,1 tri-methyl-propene-(2), $(CH_3)_3-CH=CH_2$ (1). (In this case all the coupling constants have values similar to those found for styrene, and have been shown to have the same sign.)

The very small value of this coupling constant is puzzling when compared to the coupling between protons on the same carbon when that carbon is saturated (19, 27). In this case, the constant is of the order of 10--12 cps. If the methods used by Gutowsky and his group (19) predict this small coupling constant in ethylene or its derivatives, then some physical insight might be forthcoming. At present, however, it is unexplained.

2,4-dichloroaniline

Figure 7 shows spectra for this compound at 40 and 22.55 Mc. As before, the 22.55 Mc. spectrum was calculated from the parameters found at 40 Mc. Here, too, the experimental errors and deviations between calculated and experimental spectra are essentially the same. The errors in line positions are about 0.10 cps.; the errors in intensities are about 5 %. The deviations between experimental and calculated line intensities are 5 % at 40 Mc., but nearly 20 % at 22.55 Mc. This rather large deviation is probably due to the uncertainty in determining the level of the base line with the poorer resolution, and to the fact that the observed

FIGURE 7



lines are the approximate superposition of several, and the heights may not be additive.

The solid triangles again give the chemical shifts. The proton numbering is 1, 2, 3 toward the right. Table VI gives the assignments, and calculated and observed positions and intensities. At 40 Mc. all first order lines are observed. In addition, it should be pointed out that the small line in the upper spectrum, at about 17 on the scale, is a combination line. Table VI shows that in the 22.55 Mc. spectrum there are two combination lines, although they occur in conjunction with other first order lines. In the latter spectrum, one first order line is not experimentally observable.

The parameters which give the best fit at 40 Mc. are:

$$\delta_2 - \delta_1 = 0.230 \pm 0.007 \text{ ppm.}$$

$$\delta_3 - \delta_1 = 0.570 \pm 0.007$$

$$A_{12} = 2.4 \pm 0.4 \text{ cps.}$$

$$A_{13} = 0.4 \pm 0.3$$

$$A_{23} = 8.8 \pm 0.4$$

No assignments were tried for any A_{ij} negative because lines such as those for transitions 78 and 35 are not at all completely resolved. These pairs would have to be separated to use any of the tests which are useful for rejecting incorrect assignments, such as those involving the intensities of certain groups of lines. Because there is good agreement at the two frequencies, it is highly probable that the set of parameters is the correct one, neglecting the possibility of others with different signs of the A's.

The splitting of the pairs 78 and 35, 46 and 12, 58 and 37, and 26 and 14 is about 0.6 cps. in the experimental spectrum. If $A_{13} = 0$ is used in the calculation, there remains a residual splitting at 40 Mc. of about 0.4 cps.

TABLE VI

2,4-DICHLOROANILINE - 40 Mc.

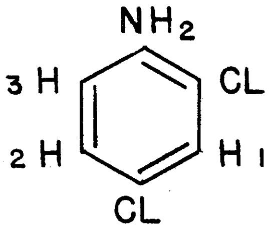
Transition	Origin	Position		Intensity	
		Observed	Calculated	Observed	Calculated
78	1	0.6	0.29	1.50	0.57
35	1	1.2	1.03		0.82
46	1	2.6	2.53	2.50	1.29
12	1	3.2	3.28		1.24
68	2	4.8	4.65	0.95	0.84
47	2	7.0	6.89	0.20	0.13
25	2	13.2	13.25	1.67	1.77
13	2	15.5	15.50	1.27	1.33
36	x	17.1	17.45	0.11	0.08
58	3	21.1	21.07	3.01	1.59
37	3	21.7	21.81		1.43
26	3	29.9	29.67	0.84	0.46
14	3	30.5	30.42		0.42

2,4-DICHLOROANILINE - 22.55 Mc.

Transition	Origin	Position		Intensity	
		Observed	Calculated	Observed	Calculated
46	1	0.8	0.90	3.23	0.84
35	1		0.94		0.73
68	2		1.05		1.11
12	1	2.8	3.01	1.53	1.41
47	2		3.12		0.35
25	2	8.3	8.47	2.27	2.14
13	2	10.3	10.54	1.69	1.38
36	x	12.1	11.63	2.31	1.12
58	3		11.74		1.80
37	3	14.0	13.85	0.55	0.53
26	3	19.5	19.06	0.16	0.14
14	3	21.3	21.27	0.27	0.21
27	x		21.38		0.13

If A_{13} = .4 cps. is included, then the splitting is .75 cps., approximately the observed splitting. This splitting is not accurately known so the A_{13} is subject to some error.

To decide which of the chemical shifts corresponds to which of the hydrogens in the molecule, it is necessary to extimate what the values for A_o, A_m, and A_p are. (A_o means the coupling constant between two protons ortho to one another on a benzene ring, etc.). McConnell (22) calculates that the contribution to the coupling constant by the π electron system of a ring is of the order of 1 cps. or less for all pairs of protons. Therefore, the coupling constants should behave as in most other compounds and decrease with increased separation of the hydrogens. Gutowsky (15) makes this assumption and finds that for several systems studied $A_o \cong 8$, $A_m \cong 2.5$, and $A_p < 1$. If the same assumption is made here, then the numbering is



Proton 3 is shifted toward the right (more shielded), presumably because it is ortho to the NH_2 group. This shift has been observed to exist for the center of gravity of the spectrum of the ring in aniline, although the spectrum is very complex, and it is not possible to give the numerical values for the chemical shifts (as was incorrectly done by Corio and Dailey (11)).

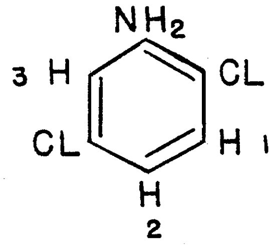
2,5-dichloroaniline

Experimental and calculated spectra at 40 and 22.55 Mc. are shown in Figure 8. The probable error in a line position is about 0.08 cps. at both frequencies, and that in an intensity is about 5 %. The deviations in fit of the calculated line positions are 0.08 cps. at 40 Mc. and 0.20 cps. at 22.55 Mc; for intensities, they are 5 % at 40 Mc. and 10 % at 22.55 Mc. The larger deviation in the calculated spectrum at 22.55 Mc. is presumably because of the fact that some pairs of lines at 40 Mc. are nearly degenerate and no accurate method of arriving at the corresponding A_{ij} is available. The agreement is considered to be excellent in this third case also. Table VII gives observed and calculated positions and intensities and the assignments.

In both the spectra for this compound there occur two combination lines, separately observable, in addition to the first order lines. The parameters found are:

$$\delta_2 - \delta_1 = 0.478 \pm 0.007 \text{ ppm.}$$
$$\delta_3 - \delta_1 = 0.490 \pm 0.007$$
$$A_{12} = 8.6 \pm 0.4 \text{ cps.}$$
$$A_{13} = 0.6 \pm 0.5$$
$$A_{23} = 2.6 \pm 0.4$$

The numbering in the structure is:



Here both ortho and para protons are more shielded that the meta.

FIGURE 8

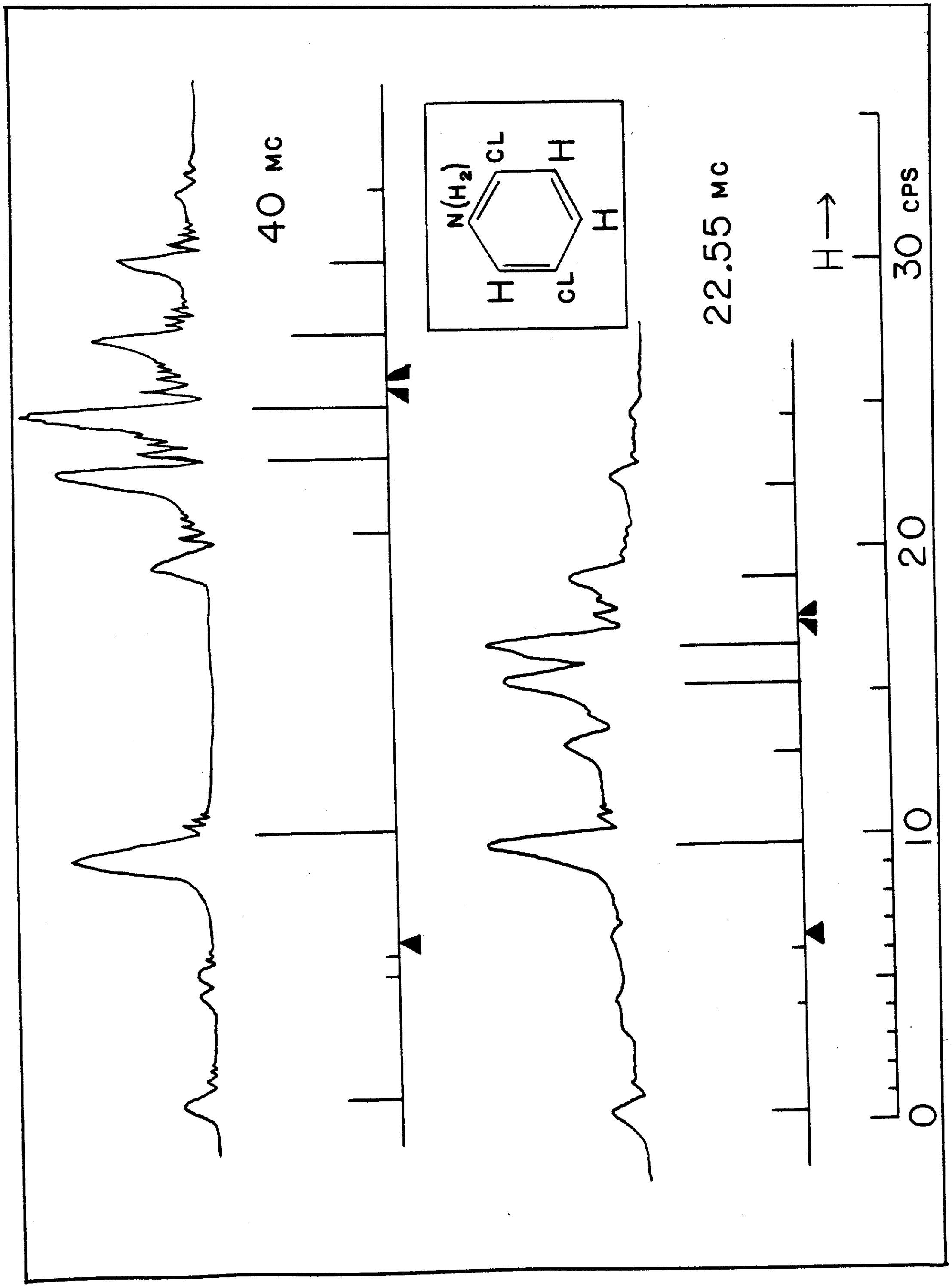


TABLE VII

2,5-DICHLOROANILINE - 40 Mc.

Transition	Origin	Position		Intensity	
		Observed	Calculated	Observed	Calculated
35	1	0.8	0.65	0.90	0.40
78	1		0.74		0.57
36	x	5.0	5.00	0.31	0.25
45	x	5.7	5.74	0.28	0.26
12	1	9.9	10.01	2.48	1.47
46	1		10.08		1.04
68	2	20.4	20.41	0.75	0.65
25	2	22.7	22.93	2.12	2.13
37	3	24.7	24.67	2.22	0.61
58	3		24.76		1.78
14	3	27.1	27.21	1.65	1.26
26	3		27.28		0.37
47	2	29.8	29.75	1.01	0.96
13	2	32.2	32.29	0.31	0.27

2,5-DICHLOROANILINE - 22.55 Mc.

78	1	0.65	0.28	0.65	0.35
35	1		0.30		0.25
36	x	4.15	4.02	0.18	0.19
45	x	6.35	5.91	0.20	0.24
46	1	9.65	9.63	2.67	1.19
12	1		9.65		1.78
68	2	13.05	12.78	0.97	0.65
25	2	15.15	15.21	2.35	2.51
58	3	16.45	16.50	2.63	2.00
37	3		16.52		0.74
26	3	18.55	18.93	1.42	0.27
14	3		18.95		1.03
47	2	22.25	22.13	0.66	0.61
13	2	24.25	24.56	0.25	0.19

It is curious to note that here if one takes $A_{13} = 0$, the residual splitting "corresponding" to A_{13} is 0.4 cps., but that introducing $A_{13} = .4$ reduces the splitting, contrary to what happened in the case of 2,4-dichloroaniline. This agrees with experiment in that with the existing resolution there is no splitting of the appropriate lines. The difference in the two cases is connected in detail with the special values of the parameters.

This case also demonstrates that the values of λ_{ij} between pairs of nuclei do not individually determine the mixing of the wave functions and therefore the departure from a first order spectrum. The value of λ_{23} is 6.5 at 40 Mc. However because there is a great difference between A_{12} and A_{13}, the effects, such as the disappearance of some lines for protons 2 and 3, which occur when $A_{12} = A_{13}$, do not appear. This is explained qualitatively by saying that the inequality of A_{12} and A_{13} disturbs the coupling of protons 2 and 3 -- which would exist if $A_{12} = A_{13}$ -- into singlet and triplet states (uncouples them). It is worthwhile to point this out since, although most workers in the field undoubtedly recognize this phenomenon and at least one illustration has appeared in print (5), it is foreign to the usual first order theory which is often applied in preliminary discussions of spectra.

V. CONCLUSION

Although it is possible that there will be essential deviations between experimental and calculated spectra when it becomes possible to measure the experimental spectra more accurately, the present work indicates that even for systems which depart greatly from first order behavior there is a unique set of parameters which can describe the system over a range of magnetic fields in accord with equation 1. For styrene at 10 Mc., for instance, the values of λ_{ij} are 1.8, .75, and .25, indicating a great departure from first order behavior. Here the agreement between calculated and experimental spectra is excellent, indicating that there is indeed a set of parameters which describes the system at this field. Lest this seem to be a fatuous statement, it should be remarked again that no test of the spin Hamiltonian to this accuracy has heretofore been given. In addition, this is the same set which was determined at a much higher field (appropriate to 40 Mc.). Indirectly then, it shows that the ν_i' vary linearly with the magnetic field and that the A_{ij} are independent of field.

Consideration of the spectra given at the lower frequencies indicates that interpretation of these spectra is very difficult. If no aids, such as those shown in Section II involving the form of the spectrum, were known, it is highly likely that it would be impossible to get a trial starting set of parameters, The correlation diagram for styrene, Figure 6, helps to illustrate this difficulty. It is easy to group the lines at 40 Mc. into three groups, one for each nucleus. Although the proper groupings at 10 Mc. can be seen in the diagram, it would be exceedingly difficult to reproduce them from an experimental spectrum.

The method given by McConnell and Anderson (23) for determining some of the parameters from experimental first, second, and higher moments of the spectrum does not change the above statements very much. The higher moments (fourth and above) which are necessary to determine the coupling constants are always very inaccurately known because of experimental errors. It was found, in collaboration with Dr. D.M. Graham, that for 2,4-dichloroaniline at 40 Mc. an intelligent guess was as close to the correct parameters as the results of the method of moments. The moment method is nonetheless useful in determining a set of approximate parameters in the cases with greater mixing.

The present work is the first in which combination lines have been observed experimentally. Many of the papers dealing with the analysis of spectra (7, 15, 30) seem to convey the general feeling that combination lines are always weak. The correlation diagram shows that this is not the case, and that at low fields one combination line, the one which appears in the spectrum even at 40 Mc., grows to unit intensity. At 10 Mc., for instance, it is much larger than all but four first order lines. The fact that the same eight energy levels which describe the first order lines also give the correct positions for the observable combination lines is further proof that the methods used for describing the spectra are correct.

Finally, the example of styrene shows that at least in favorable cases the relative signs of the coupling constants can be determined unambiguously. The methods given here can also determine the correct signs without a complete analysis. The one case in which the signs were determined showed that the coupling constants were all of the same sign, in accord with theory (16, 21, 33).

VI. INTRODUCTION: INTERNAL ROTATION

Several workers have observed that the high resolution nuclear resonance spectra of certain ethane-like substances contain more lines than can be explained by assuming completely free rotation about the carbon-carbon bond (14, 27, 30). In addition, a strong temperature dependence has been observed for the chemical shift in one compound (12). This dependence was originally ascribed to changing amplitudes of torsional oscillation of a particular isolated rotational isomer. The correct explanation for all these observations appears to be that internal rotation, even when rapid, may give rise to unequivalences among nuclei when some internal configurations are energetically more favorable than others. In addition, the temperature dependence of a spin-spin splitting between a pair of lines, which must exist if this explanation is correct, has been demonstrated by Graham and Waugh (14).

It is extremely desirable that such cases be examined further to substantiate the theory, and to connect in detail the temperature dependence with the energetics of the internal rotation. This connection must exist, but in the cases studied so far its quantitative elucidation has been difficult. Such a quantitative connection would be of great value because it would provide a new means of measuring the energy differences between rotational isomers, and thereby shed light on the general problem of internal rotation, in which considerable theoretical interest already exists (26).

VII. THEORY OF ROTATIONAL AVERAGING

The usual description of the potential energy of a substituted ethane as a function of the azimuthal angle ϕ around the carbon-carbon axis is one with potential minima when the substituents are separated by approximately 60° (staggered) and maxima when they are separated by 0° (eclipsed). If the further assumption is made that the height of the maxima is several times the differences between minima, there will be two extremes which are of interest. In one case the barrier is high enough compared to kT so that the lifetime of the molecule in one configuration is long compared with $\frac{1}{\delta\omega}$ where $\delta\omega$ is a chemical shift or spin-spin coupling. In this case any fine structure resulting from $\delta\omega$ is observable for each of the several configurations which may be present. If the lifetimes are short with respect to $\frac{1}{\delta\omega}$, then a time-averaged Hamiltonian should be used to describe the system. For the substances of interest here, the latter case is appropriate at room temperature since the spectra observed are attributable to a single molecular species and not to superposition of several spectra. In addition, some instances have been reported in which, by going to lower temperatures (-80° C.), it was possible to increase the lifetimes enough so that spectra of the several distinct isomers appeared (27, 28). The fact that this time averaging is necessary was recognized independently by Nair and Roberts (27), Shoolery and Crawford (36), Graham and Waugh (14), Gutowsky *et al*.(15), and Pople (29). Two cases where it was appropriate, but was not recognized, have also appeared (12, 20).

The simplest possible model which contains all of the necessary features is the following: the lifetimes of the rotational isomers are short and the time average state of a molecule is just a superposition of the three staggered isomers taken in proportion to single Boltzman factors for these states. In saying this it is assumed that the time spent in transitions between states is small and that each isomer occupies no more than one torsional oscillation level.

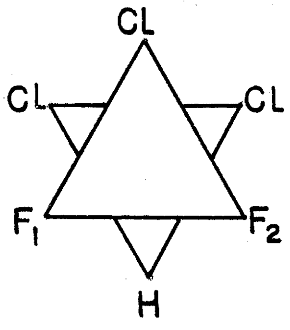
There are two classes of compounds with different symmetries which Shoolery and Crawford discuss (36); however, it is convenient to break down one of these further. Class I includes molecules of the sort CX_2R-$CR'R''Y$, where X and Y may or may not be the same, and R, R', and R" do not have magnetic nuclei which interact with X and Y. Here the two nuclei X can have different chemical shifts and coupling constants to Y, as will be seen later. Class IIA includes molecules such as CX_2RCY_2R', in which there can be no chemical shift between the two X nuclei or between the two Y nuclei because, given one gauche isomer in which the X's (or Y's) have different chemical shifts, there is another isomer of equal energy, hence probability, in which the X's are simply interchanged. These two must average to give no chemical shift. In this case, however, there can be two values of A_{XY}, indicating a nonequivalence of the X's and Y's. The spectrum will show this nonequivalence in that, instead of a triplet of intensity 1:2:1 for X or Y, the center line is split into four components. (The lines usually occur in pairs, however). Shoolery and Crawford (36) and Graham and Waugh (14) observed this splitting in several cases.

Class IIB includes molecules such as $CXR_2CR'Y_2$, in which the spectrum shows no effects of nonequivalence, but the parameters involved can change with temperature as do those in the other cases.

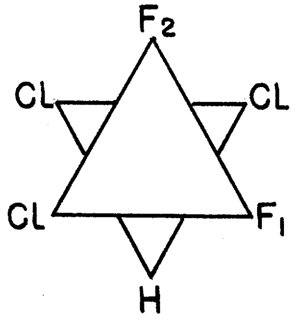
To demonstrate the correctness of the simple theory, it is advisable to show that the spectra depend upon temperature in a manner consistent with the predicted Boltzman factors. Graham and Waugh(14) have shown that a temperature dependence exists in the spectrum of CH_2BrCF_2Br, and have obtained a consistent interpretation in terms of energy differences of ~300 calories/mole. Two more cases have been studied in the present work: $CHCl_2CClF_2$ and $CF_2BrCHClBr$.

1,1,2-trichloro-, 2,2-difluoroethane ($CHCl_2$-$CClF_2$)

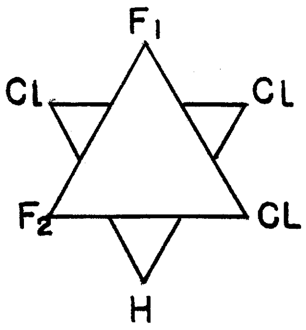
The three rotational isomers of $CHCl_2$-$CClF_2$ can be represented as follows, looking along the C-C bond:



A



B



C

B and C are related by a mirror plane or by inversion, either of which exchanges F_1 and F_2. They have the same total energies (26) and the same chemical shifts and spin-spin couplings for corresponding nuclei, and will have equal weightings in the time average.

Let H = 1, F_1 = 2, and F_2 = 3, and let ν_1, $\nu_2 = \nu_3 = \nu$, $A_{12} = A_{13} = A$, and $A_{23} = A_2$ be the parameters for form A, and ν_1', ν', ν'', A', A'', A_2' be the parameters for form B.

$$\begin{aligned}\langle \mathcal{H} \rangle_{\text{time}} &= \frac{n_A}{n}\ \nu_1 I_{z_1} + \nu I_{z_2} + \nu I_{z_3} + A(\underline{I}_1\cdot\underline{I}_2 + \underline{I}_1\cdot\underline{I}_3) + A_2\underline{I}_2\cdot\underline{I}_3 \\ &+ \frac{n_B}{n}\ \nu_1' I_{z_1} + \nu' I_{z_2} + \nu'' I_{z_3} + A'\underline{I}_1\cdot\underline{I}_2 + A''\underline{I}_1\cdot\underline{I}_3 + A_2'\underline{I}_2\cdot\underline{I}_3 \\ &+ \frac{n_C}{n}\ \nu_1' I_{z_1} + \nu'' I_{z_2} + \nu' I_{z_3} + A''\underline{I}_1\cdot\underline{I}_2 + A'\underline{I}_1\cdot\underline{I}_3 + A_2'\underline{I}_2\cdot\underline{I}_3\end{aligned}$$

where the equivalence between B and C has been included, and

$$\frac{n_A}{n} = \frac{e^{-E_A/kT}}{\sum_i e^{-E_i/kT}} = f_A$$

collecting terms,

$$\begin{aligned}\langle \mathcal{H} \rangle &= (f_A\nu_1 + 2f_B\nu')I_{z_1} + f_A\nu + f_B(\nu' + \nu'')\ (I_{z_1} + I_{z_2}) \\ &+ \ f_A A + f_B(A' + A'')\ \underline{I}_1\cdot\underline{I}_2 \\ &+ \ f_A A + f_B(A' + A'')\ \underline{I}_1\cdot\underline{I}_3 \\ &+ \ f_A A_2 + 2f_B A_2' \ \ \underline{I}_2\cdot\underline{I}_3\end{aligned}$$

The chemical shift of 2 and 3, and the coupling constants of 2 and 3 to 1 are the same, therefore 2 and 3 are equivalent and the term in $\underline{I}_2\cdot\underline{I}_3$ can be omitted (16). This spectrum has the same form as that for a <u>rigid</u> array of one proton and two equivalent fluorines, containing a doublet fluorine resonance and a triplet hydrogen resonance. The coupling constant is in general, however, a function of the absolute temperature, T, since f_A and f_B are. In the limit of large T, $f_A = f_B = 1/3$ and there will be no changes with temperature, however if this is not the case and f_A and f_B differ from 1/3, then changes of the coupling constant with temperature will be observed. (Except if, by chance, $A' + A'' = 2A$.)

The chemical shifts of H and F presumably vary with temperature also, but an external reference and an accurate method of measurement would be necessary to verify this. For this work the spin coupling can be measured more accurately in any case, so it alone has been studied.

The relation for the H-F spin-spin coupling is

$$A_{obs} = f_A A + f_B(A' + A'')$$

where if $\frac{E_B - E_A}{RT} = X$,

then $\frac{f_B}{f_A} = e^{-X}$, $f_B = f_A e^{-X}$, and $f_A + 2f_B = 1$

so $f_A + 2f_A e^{-X} = 1$, $f_A = \frac{1}{1 + 2e^{-X}}$, $f_B = \frac{e^{-X}}{1 + 2e^{-X}}$

Then if $A' + A'' \equiv 2A + 2g$, $A_{obs} = f_A A + f_B(2A + 2g)$

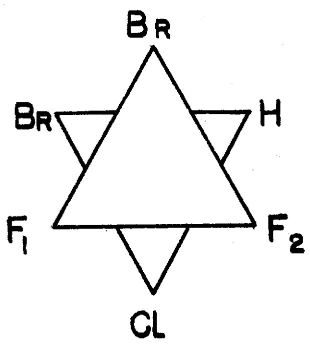
$$= A + 2gf_B$$

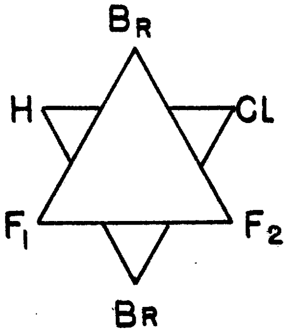
So the change in A_{obs} is proportional to f_B if g is a constant. The value of g will be constant if there are no changes in the values A, A', and A" with temperature. Such changes could be produced by changes in population of torsional oscillation states, by modification of the wave functions, by changes in population of vibrational states, and by changes in intermolecular interactions. It will be assumed that these changes are of a smaller order than the one produced by changing rotational averaging, since they have never been observed.

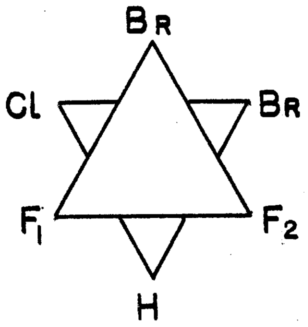
A plot of A_{obs} against f_B for different values of $\frac{E_B-E_A}{R}$, which connects X and $\frac{1}{T}$, should give a straight line for the proper value of $\frac{E_B-E_A}{R}$. A more complete analysis is not possible because there is at present no way of predicting what values A, A', and A" should have.

1-chloro-, 1,2-dibromo-, 2,2-difluoroethane ($CHClBrCBrF_2$)

For the molecule $CHClBrCBrF_2$ there are three rotational isomers for both the right and left handed forms.







Since the properties of interest here are the same for the corresponding rotational isomers of each enantiomorph, only one need be considered. The parameters for the rotational isomers A, B, and C will be designated ν_1, ν_1', ν_1'', etc. With H = (1), F_1 = (2), and F_2 = (3), the time averaged Hamiltonian, found as in the first case, is

$$
\begin{aligned}
\langle \mathcal{H} \rangle = {} & (f_A\nu_1 + f_B\nu_1' + f_C\nu_1'')\, I_{z_1} \\
& + (f_A\nu_2 + f_B\nu_2' + f_C\nu_2'')\, I_{z_2} \\
& + (f_A\nu_3 + f_B\nu_3' + f_C\nu_3'')\, I_{z_3} \\
& + (f_A A_{23} + f_B A_{23}' + f_C A_{23}'')\, \underline{I}_2 \cdot \underline{I}_3 \\
& + (f_A A_{12} + f_B A_{12}' + f_C A_{12}'')\, \underline{I}_1 \cdot \underline{I}_2 \\
& + (f_A A_{13} + f_B A_{13}' + f_C A_{13}'')\, \underline{I}_1 \cdot \underline{I}_3
\end{aligned}
$$

In this case the averaged Hamiltonian has the same form as that for any single rotational isomer. There is no reason to expect 2 and 3 to have the same chemical shift or the same spin-spin coupling to 1. Here there is a large number of parameters involved in describing the average spin system and there are three different energies involved, rather than two. There are enough unknowns so that little can be done except to show that the values $(A_{12})_{obs}$, $(A_{13})_{obs}$, and $(\nu_3-\nu_2)_{obs}$ change with temperature.

VIII. THEORY OF THE CASE ABX

For the analysis of the spectrum of one of the substituted ethanes, a treatment of the case ABX is needed. Here A and B are fluorine nuclei and X a proton. This treatment can be done as a special case of the results given in part II. This case has also been treated by Bernstein, Pople, and Schneider (7) and Gutowsky et al. (15), and alternately their results can be used. For the present problem it is convenient to simplify these results since certain approximations can be made. If the following definitions are made: 1 = H, 2,3 = F,

$$A_{23} = A_F \qquad \tfrac{1}{4}(A_{12} + A_{13}) = a \qquad \tfrac{1}{4}(-A_{12} + A_{13}) = b$$

$$\nu_3' - \nu_2' = \nu_F' \qquad \nu_2' - \nu_1' = M$$

then following the notation of part II, the energies will be as given in Table VIII. To put the energies in the most convenient form, the square roots can be expanded. The spectrum for which this treatment will be used indicates that

$$\nu_F' \cong A_F \cong 100 \text{ cps.} \quad \text{and } a \cong 1,$$

so that $a^2 \ll \nu_F a \ll \frac{1}{4} A_F^{\,2}$.

Using $$(1 + \tfrac{m}{n})^{\frac{1}{2}} = 1 + \tfrac{1}{2}\tfrac{m}{n} - \tfrac{1}{8}(\tfrac{m}{n})^2 + \text{---} \qquad \text{for } \tfrac{m}{n} \ll 1,$$

it follows that, to a good approximation,

$$\sqrt{A_F^{\,2} + \nu_F'^{\,2} + 4\nu_F a + 4a^2} = \sqrt{A_F^{\,2} + \nu_F'^{\,2}} + \frac{2a}{\sqrt{1 + (\frac{A_F}{\nu_F'})^2}} .$$

This expansion is used to give the approximate energies shown also in Table VIII, with $a' = \dfrac{a}{\sqrt{1 + (\frac{A_F}{\nu_F})^2}}$.

TABLE VIII

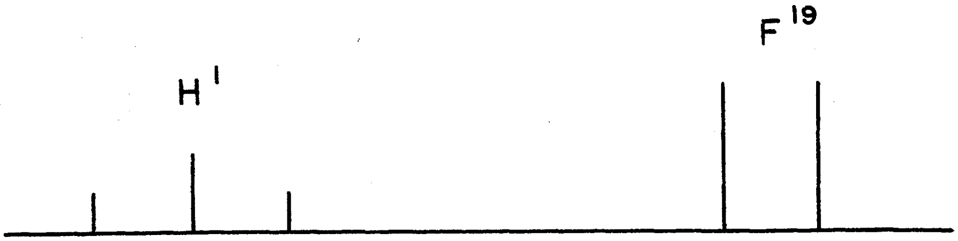
ENERGY LEVELS FOR THE CASE ABX

Level	E exact	E approximate
1	$-(M + \frac{1}{2} \nu_F') - \frac{A_F}{2} - b$	
2	$-(M + \frac{1}{2} \nu_F') - \frac{A_F}{2} + b$	
3	$-\frac{1}{2}\sqrt{A_F{}^2 + \nu_F{}^2 + 4\nu_F a + 4a^2} + \frac{A_F}{4}$	$-\frac{1}{2}\sqrt{A_F{}^2 + \nu_F'^2} + \frac{A_F}{4} - a'$
4	$+\frac{1}{2}\sqrt{A_F{}^2 + \nu_F{}^2 + 4\nu_F a + 4a^2} + \frac{A_F}{4}$	$+\frac{1}{2}\sqrt{A_F{}^2 + \nu_F'^2} + \frac{A_F}{4} + a'$
5	$-\frac{1}{2}\sqrt{A_F{}^2 + \nu_F{}^2 - 4\nu_F' a + 4a^2} + \frac{A_F}{4}$	$-\frac{1}{2}\sqrt{A_F{}^2 + \nu_F'^2} + \frac{A_F}{4} + a'$
6	$+\frac{1}{2}\sqrt{A_F{}^2 + \nu_F{}^2 - 4\nu_F' a + 4a^2} + \frac{A_F}{4}$	$+\frac{1}{2}\sqrt{A_F{}^2 + \nu_F'^2} + \frac{A_F}{4} - a'$
7	$M + \frac{1}{2} \nu_F' - \frac{A_F}{4} + b$	
8	$M + \frac{1}{2} \nu_F - \frac{A_F}{4} - b$	

The spectrum is given in Figure 9. The F^{19} spectrum is essentially that for AB with splittings because of the coupling of the fluorines to the proton. The H^1 spectrum is similar to that of a proton coupled differently to two other nuclei. The intensities, although not discussed in detail, are qualitatively as given in the figure. The references (7) and (15) can be consulted for exact values.

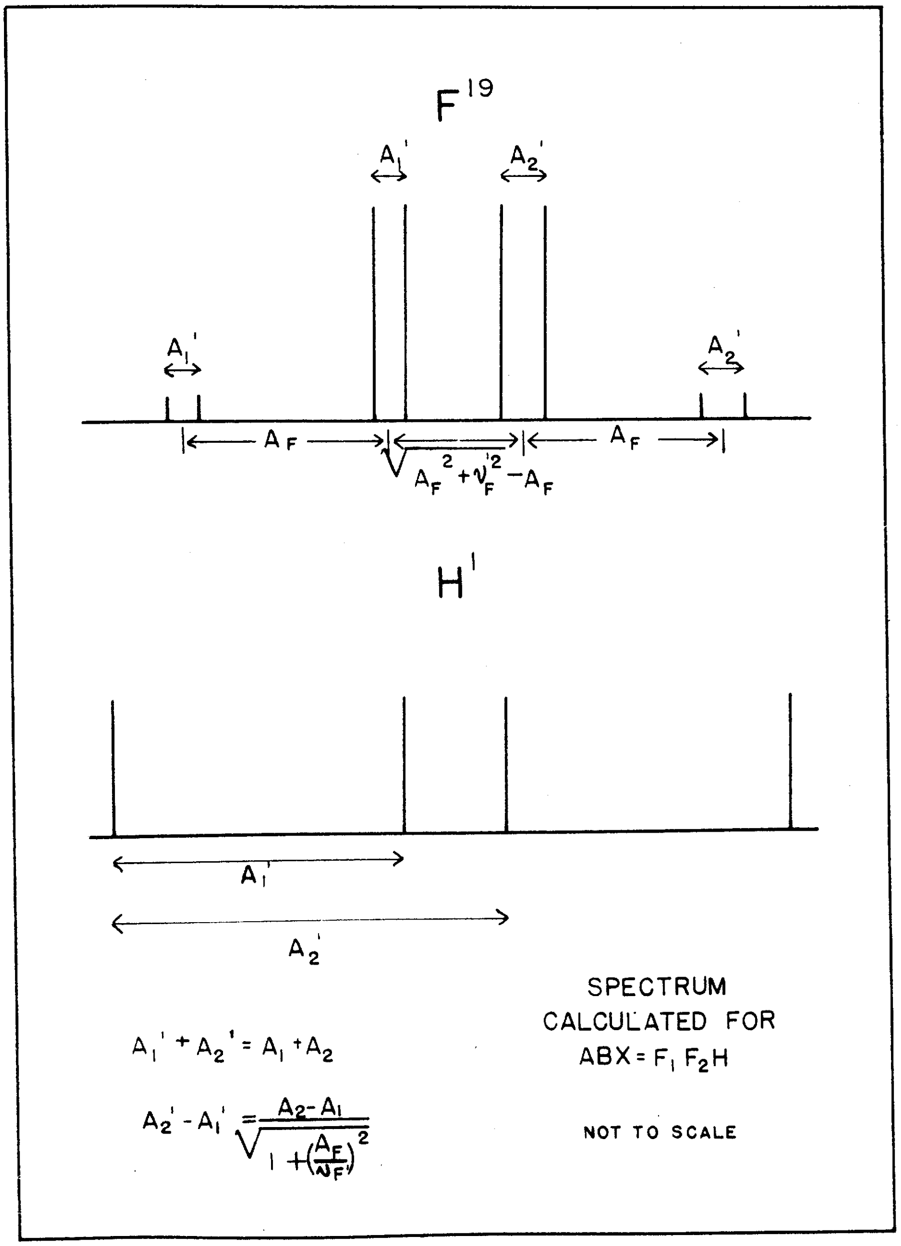
It is obvious that if $\frac{A_F}{\nu_F'} \cong 1$, the splittings in these spectra are not just the coupling constants which first order theory would predict. Even in this case then, caution must be used in trying to apply first order theory or else the values for the coupling constants will be in error.

Using the results for ABX it is possible to display a case in which there are two alternate sets of parameters which lead to the same spectrum. Here 1 = H, 2,3 = F. Let $A_{23} = 16$, $A_{13} = 4$, $A_{12} = 0$, and $\nu_3' - \nu_2' = 0$. The spectrum consists of:



There are some very small lines not ordinarily detectable and the two F^{19} lines are not truly degenerate, but each is composed of a pair with a splitting of about .12 cps. Experimentally it is not possible to distinguish this from a doublet for F^{19} of splitting 2 cps. and a triplet for H^1 of intensity ratio 1:2:1, also of splitting 2 cps. The parameters chosen are not actually very likely; however, the possibility exists that a spectrum of this type could be obtained, and emphasizes the dangers of over-casual interpretation of spectra.

FIGURE 9


F^{19}
A_1'
A_2'
A_1'
A_2'
A_F
$\sqrt{A_F^2+\nu_F'^2}-A_F$
A_F
H^1
A_1'
A_2'
SPECTRUM CALCULATED FOR $ABX = F_1 F_2 H$
$A_1' + A_2' = A_1 + A_2$
$A_2' - A_1' = \frac{A_2 - A_1}{\sqrt{1+\left(\frac{A_F}{\nu_F'}\right)^2}}$
NOT TO SCALE

IX EXPERIMENTAL

The 1,1,2-trichloro-, 2,2-difluoroethane was prepared by adding chlorine to 1-chloro-, 2,2-difluoroethylene (procured from General Chemicals Division, Allied Chemical and Dye Corporation) in the gas phase. To increase the speed of the reaction an ordinary 150 watt light bulb was placed near the reaction vessel. The light bulb was operated from a Variac to control its actinic output, and therefore the rate of the reaction. The progress of the reaction was observed by means of the pressure in the reaction vessel (1/2 atmosphere) as indicated by a manometer. The chlorine was added as the reaction progressed so that the $CF_2=CHCl$ was always in excess, in order to reduce the amount of substitution and to prevent the reaction from proceeding too rapidly. The nuclear resonance spectrum, just a doublet for F^{19} and a triplet for H^1, gave no indication of more than one product, assuring that no substitution had occurred. A distillation in vacuo easily isolated the product because it boils (at one atmosphere) at about 70° C., whereas the reactants boil considerably below 0° C. The sample was sealed into a 5 mm. O. D. Pyrex tube while under vacuum.

The 1-chloro-, 1,2-dibromo-, 2,2-difluoroethane was prepared by adding bromine to 1-chloro-, 2,2-difluoroethylene (same source as above). In this case, the 150 watt light bulb was operated at about 140 volts. The whole amount of bromine was added initially and allowed to react. The amount was adjusted so that it reacted completely, allowing easy separation of the product. Again the spectrum indicated that essentially one compound was present. The sample was sealed into a 5 mm. O. D. tube.

Both samples exhibited boiling points near those reported in the literature. 1,1,2-trichloro-, 2,2-difluoroethane boiled near 70° C. (literature value 72° (18)). The freezing point for this compound, observed by the disappearance of all narrow lines in the nuclear resonance spectrum, was -60° C. ± 10°. The other compound was found to boil near 120° C. (literature, 118° (18)), and the freezing point was observed to be -70° C. ± 10°.

All the spectra were taken at 40 Mc. with conventional Varian equipment. The slow passage measurements were all done by the side band technique mentioned earlier (Section III). Here two audio frequencies were mixed and used to produce side bands. In this way it is possible to record only a portion of the spectrum containing two side bands bracketing the other lines of interest. The known frequency difference between the two side bands serves as an accurate calibration of sweep rate. In this way it is possible to scan only a small portion of the spectrum and to reduce considerably errors due to changes in the sweep rate. Some care must be exercised to identify correctly all the lines recorded.

For the measurements of line separations of the order of 5 cycles per second, Reilly's "wiggle beat" method is used (35). (This letter shows some excellent experimental traces.) In this method the pair of lines of interest is scanned rapidly and the resulting signal recorded on the Sanborn recorder with a chart speed of 25 or 50 mm./sec. The signal consists of two superimposed trains of damped oscillations, following the main signal from the pair of lines. The frequency difference of the two oscillations will be just the frequency difference of the two line positions. This frequency difference appears as the envelope of the resulting train of "wiggles". The separation between the lines is found, therefore, by comparing the envelope wave length with the distance between seconds markers on the chart. It is found by analyzing the errors occurring in a series of measurements that the probable error in the measurement of a line spacing can be reduced to .01 cps. or less (in favorable cases) by averaging 10 or more measurements. The error in the spacing of the timing markers is about the same, 1 part in 500, because the markers are derived from the power line frequency. It is not known whether there are any systematic errors which increase the absolute error. However, some of the results presented later indicate that there may be none.

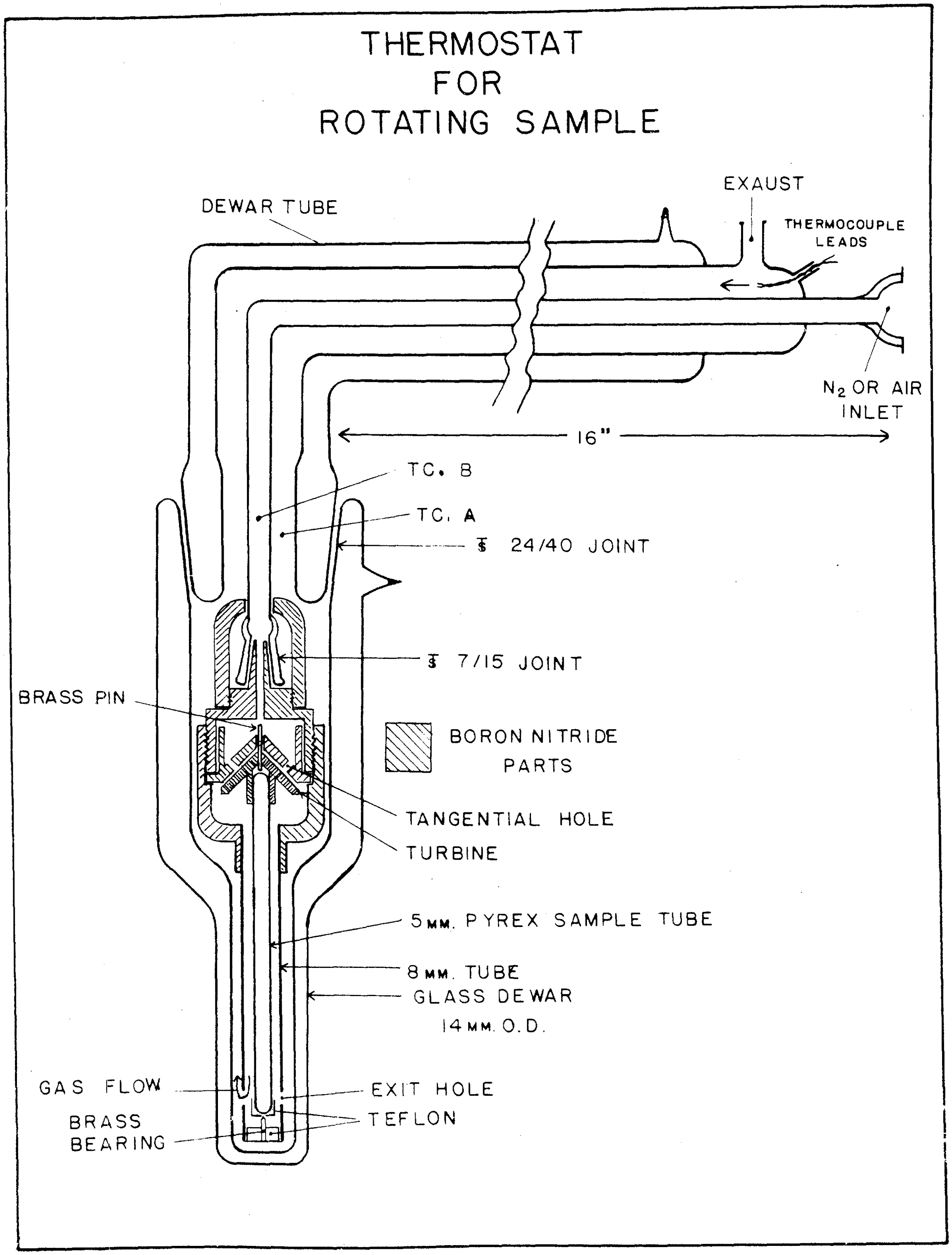
The spectra recorded at other than room temperature were taken with the sample in the thermostat shown in Figure 10. To get the resolution desired, the sample must be rotated about the vertical axis. The rotation is accomplished by passing the air which maintains the temperature through a small turbine similar to that used at room temperature with the Varian probe.

The temperature range which can be covered is about -100° to 200° C. It is possible to reach lower temperatures if the sample is not spun.

The operation of the thermostat is as follows. The air (or tank nitrogen) is passed through either a heater or cooler, depending upon the temperature desired, into the thermostat. Because the inlet must be outside the magnet gap, a rather long dewar tube is provided to carry the gas to and from the sample. Inside the body of the thermostat the gas passes through four tangential holes and onto the surface of the conical turbine, providing enough torque to spin the sample at 1000 to 2000 r.p.m. The gas then passes down over the sample, through the exit holes, up inside the main dewar, and out through the dewar tube.

To operate above room temperature the compressed air from a laboratory supply line is passed through a heater before entering the thermostat. The heater consists simply

FIGURE 10


THERMOSTAT
FOR
ROTATING SAMPLE
EXAUST
DEWAR TUBE
THERMOCOUPLE
LEADS
N_2 OR AIR
INLET
16"
TC. B
TC. A
§ 24/40 JOINT
§ 7/15 JOINT
BRASS PIN
▨ BORON NITRIDE
PARTS
TANGENTIAL HOLE
TURBINE
5 MM. PYREX SAMPLE TUBE
8 MM. TUBE
GLASS DEWAR
14 MM. O.D.
GAS FLOW
EXIT HOLE
BRASS
BEARING
TEFLON

of a coil of nichrome wire inside a glass tube. The wire is heated by current from a Variac, thereby providing a means of temperature control. No provision has been made for automatically regulating the temperature. About 1/2 hour is necessary to reach temperature equilibrium.

Below room temperature, tank nitrogen is passed through a cooler and then through a small heater similar to that described above. The cooler is a four liter nitrogen storage dewar equipped with a two-hole cork and containing liquid nitrogen through which the tank nitrogen is bubbled. The operation is very similar to that of a bubbler for washing gases. The only important difference is that the inlet tube is a dewar tube with a small spiral of copper tubing on the end. The dewar tube prevents the incoming gas from warming that leaving at the top of the flask and the copper tube presumably allows good heat exchange. The amount of glass wool insulation on the tubes carrying the cold gas to the thermostat and the current provided to the small heater are used for providing temperature control, because the gas flow rate must unfortunately be fixed to obtain proper operation of the turbine spinning the sample.

The temperature of the sample is measured by copper-constantan thermocouples at points A and B indicated in the drawing. The potentials were measured on a recording potentiometer and are accurate to about the equivalent of $\pm 1^{\circ}$ C. At the extremes of temperature there exists a difference of about 10° between the two points. The temperature of the sample was assumed to be the average of the two. The error is estimated to be about 1/4 of the temperature difference between points A and B.

The resolution which can be achieved while using the thermostat is not as good as that possible without it, probably because there is departure from cylindrical symmetry in the thermostat which allows the differing diamagnetic susceptibilities of its various parts to produce gradients in the magnetic field (the most important factor controlling the resolution achievable).

X. RESULTS AND DISCUSSION

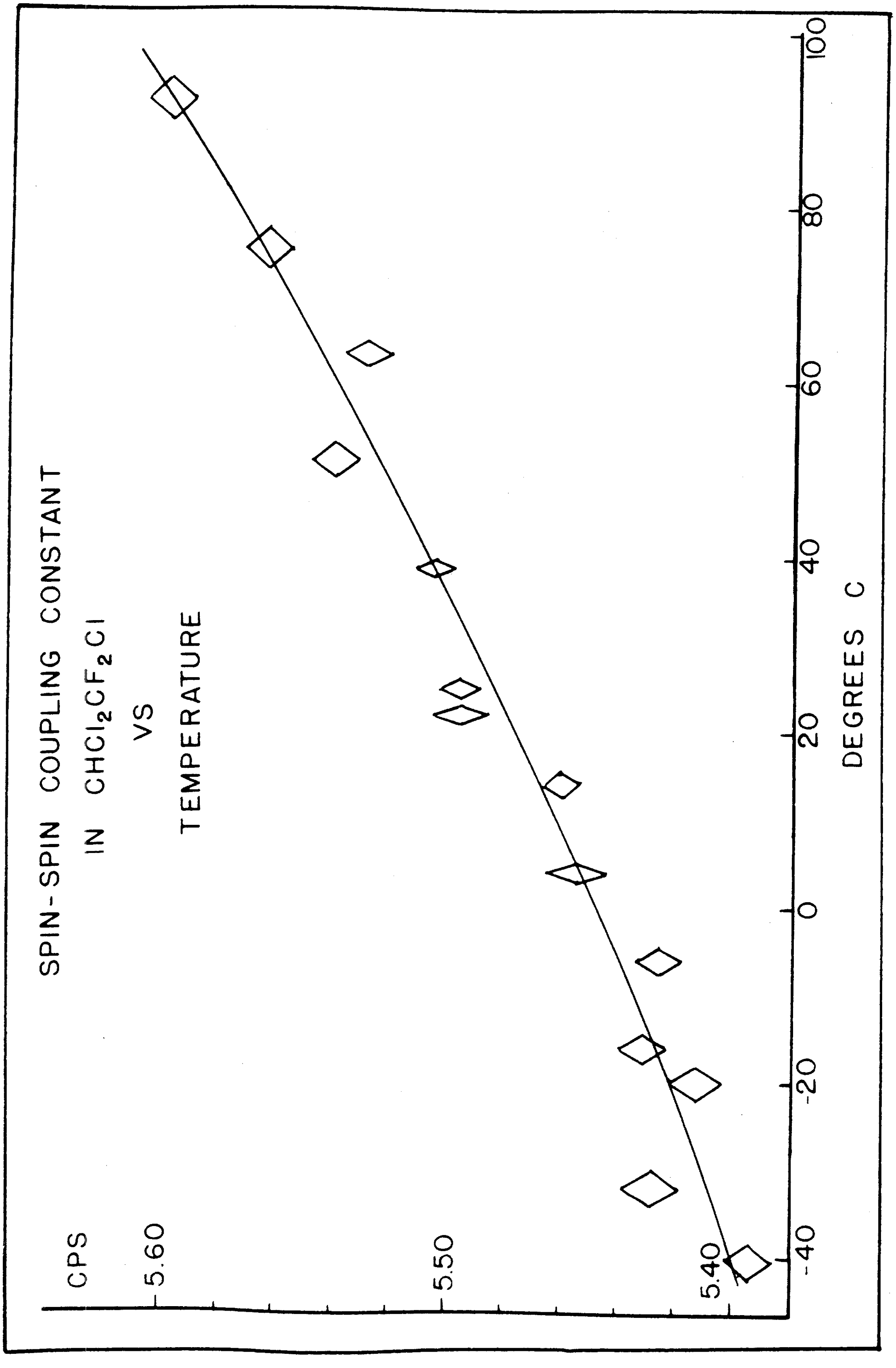
1,1,2-trichloro-, 2,2-difluoroethane

As was expected, the spectrum for this compound showed a simple doublet for the F^{19} and a triplet of intensity ratio 1:2:1 for H^1. The spacing of the doublet was measured by the "wiggle beat" method at temperatures between about -30° C. and 90° C. Below -30° the lines became too wide for the method to work well. (The wiggle train became damped so that only a few cycles of the "beat" were observable.) The widening of the lines can be explained in part, at least, by a decreased relaxation time, T_1, because of the lower rate of molecular motions (9); it could also be caused by the lifetimes of particular rotational isomers approaching $\frac{1}{A_{HF}}$. Further work is necessary to decide whether the latter is correct. At the highest temperature the vapor pressure of the sample was about two atmospheres and it seemed unwise to exceed this.

For each temperature the results of ten or more traces were averaged; each trace consisted of a train of 8--15 beats. The fairly large number of beats reduced the error introduced in deciding where the maxima (or minima) of the beats occurred. The probable error in the average of these measurements was usually of the order of .01 cps. A probable error of .005 cps., arising from variations in power line frequency, should be included in addition to this. Figure 11 shows the results of the series of measurements. The heights and widths of the diamonds representing the individual points are the probable errors.

The one point taken for H^1 (25° C.) agrees very well with those for F^{19}. Because the magnetic field inhomogeneities controlling the line shape are different for the

FIGURE 11


SPIN-SPIN COUPLING CONSTANT
IN $CHCl_2CF_2Cl$
VS
TEMPERATURE
CPS
5.60
5.50
5.40
-40
-20
0
20
40
60
80
100
DEGREES C

two magnetic fields involved, this agreement seems to indicate that the results of this method of measurement do not depend upon the line shape in any very important way. Results with the compound discussed later substantiate this.

Unfortunately, the change in $(A_{HF})_{obs}$ is rather small; however, it is enough larger than the errors involved to be meaningful. If the theory of rotational averaging given in Section VII is accepted, a plot of $(A_{HF})_{obs}$ against f_B, with the correct value of $\Delta E = E_B - E_A$ used in determining f_B, should be a straight line, within the experimental error. In the case being discussed here, by choosing different values of ΔE it is possible to get curves which change from concave upwards to concave downwards, or vice versa, depending on the sign of ΔE. Figures 12 and 13 show plots of (A_{HF}) obs versus f_B (labeled F_B in the figures) for $\Delta E > 0$ and $\Delta E < 0$; the curves are labeled with 2, 3, or 4, the value of $\frac{E}{RT}$ for $T = 365^\circ$ K. The corresponding values of ΔE are 1450, 2200, and 2900 calories/mole. For either sign of ΔE the curve labeled 3 is chosen as the best straight line, for the reason that the proper one seems to lie between 2 and 4. The absolute value of ΔE is then 2200 ± 700 cal./mole. Unfortunately, the energy differences for this molecule have not been determined by other methods.

If $\Delta E > 0$ the slope is $2g = +5$; if $\Delta E < 0$ the slope is $2g = -20$. To make a comparison with some other results, the assumption can be made that $A' = A$, then $2g = A'' - A$. Now, in $CH_2BrCBrF_2$ there are two greatly differing coupling constants (14, 36). Also the results for substituted olefins (25) indicate that A_{HF}(trans) $>$ A_{HF}(cis), and it can be assumed that A''(trans) $>$ A(gauche). If the same were true for $CHCl_2CClF_2$, 2g would be positive, and $\Delta E = +2200$ would be the proper choice. However, no information exists which can tell whether A and A" are of the same sign, as was implicitly assumed above. Because of this fact and

FIGURE 12

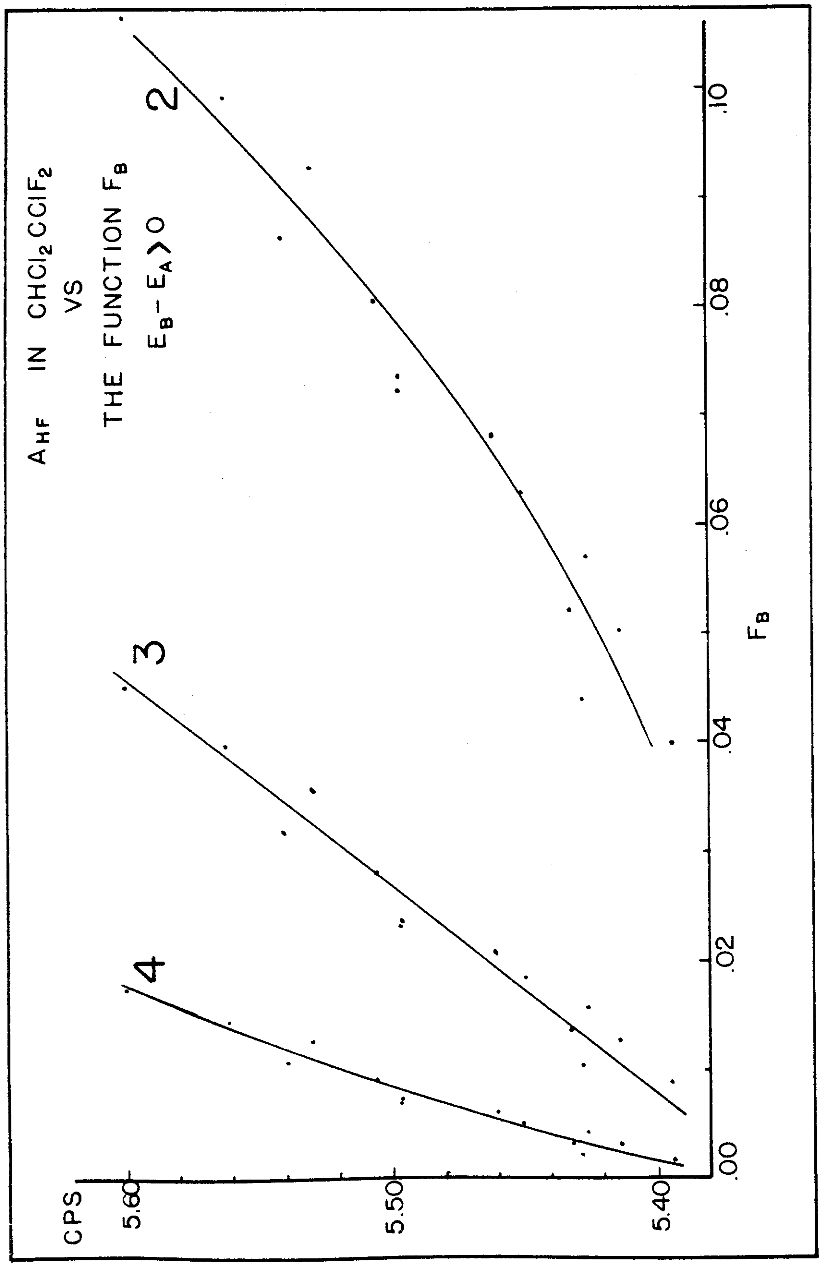
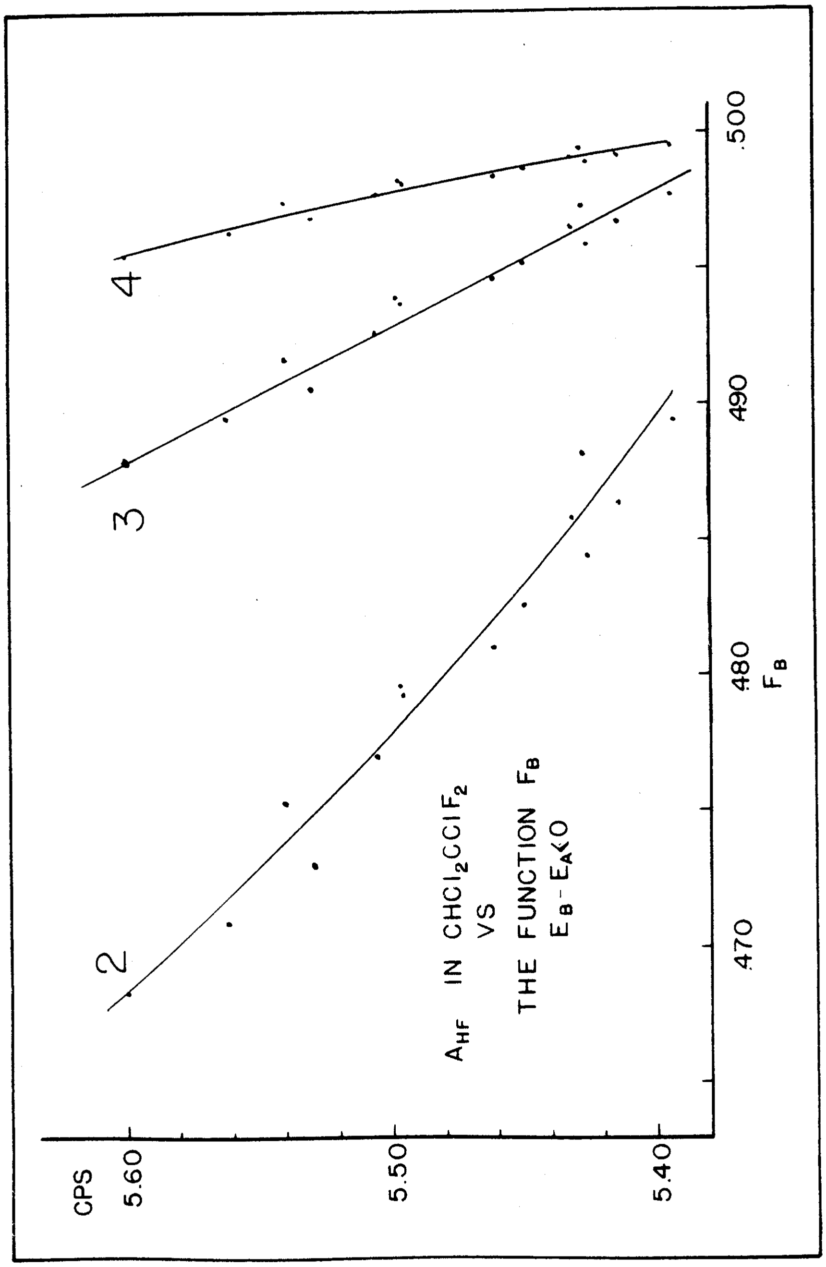

A_{HF} IN $CHCl_2CClF_2$
VS
THE FUNCTION F_B
$E_B - E_A > 0$
CPS
5.60
5.50
5.40
.00
.02
.04
.06
.08
.10
F_B
2
3
4

FIGURE 13


CPS
5.60
5.50
5.40
470
480
490
.500
F_B
2
3
4
A_{HF} IN $CHCl_2CClF_2$
VS
THE FUNCTION F_B
$E_B - E_A < 0$

because of the number of other assumptions made, it is better not to attempt to judge which sign for ΔE is proper.

In fact, the change in $(A_{HF})_{obs}$ is so small that some doubt may easily be entertained as to the appropriateness of the model. On the scale involved, it has never been shown, for instance, that the spin coupling constants are independent of temperature, even when internal rotation is not a factor. A further investigation is indicated in order to settle this point.

1-chloro-, 1,2-dibromo-, 2,2-difluoroethane

The spectrum for this compound is just that expected for a case ABX, and is like that shown schematically in Figure 9.

The measurements needed to find the relative chemical shift of the two fluorines and the value of A_F were made by the side band method. The estimated error is .4 cps., including uncertainty in calibrating the audio oscillator. Figure 14 shows the chemical shift of the two fluorines as a function of temperature; at the four temperatures -17°, 27°, 85° and 117° C., the value for A_F was constant at $161.0 \pm .4$ cps., and is assumed to be the same at the other temperatures. The two spacings A_1' and A_2' were measured by the wiggle beat method, using the center two pairs of lines in the F^{19} spectrum. Ten to fifteen measurements were averaged at each temperature. The sum, $A_2' + A_1'$, and the difference, $A_2' - A_1'$, are shown in Figure 15 as functions of temperature. The measured values of $\nu_{F_2}' - \nu_{F_1}'$ and A_F were used to calculate the values shown for A_1 and A_2, the true parameters. (The calculation is that described in Section VIII.) In addition, the value $A_2' - A_1'$ was measured in the H^1 spectrum; these values are also shown in the figure. A good agreement exists between the

FIGURE 14

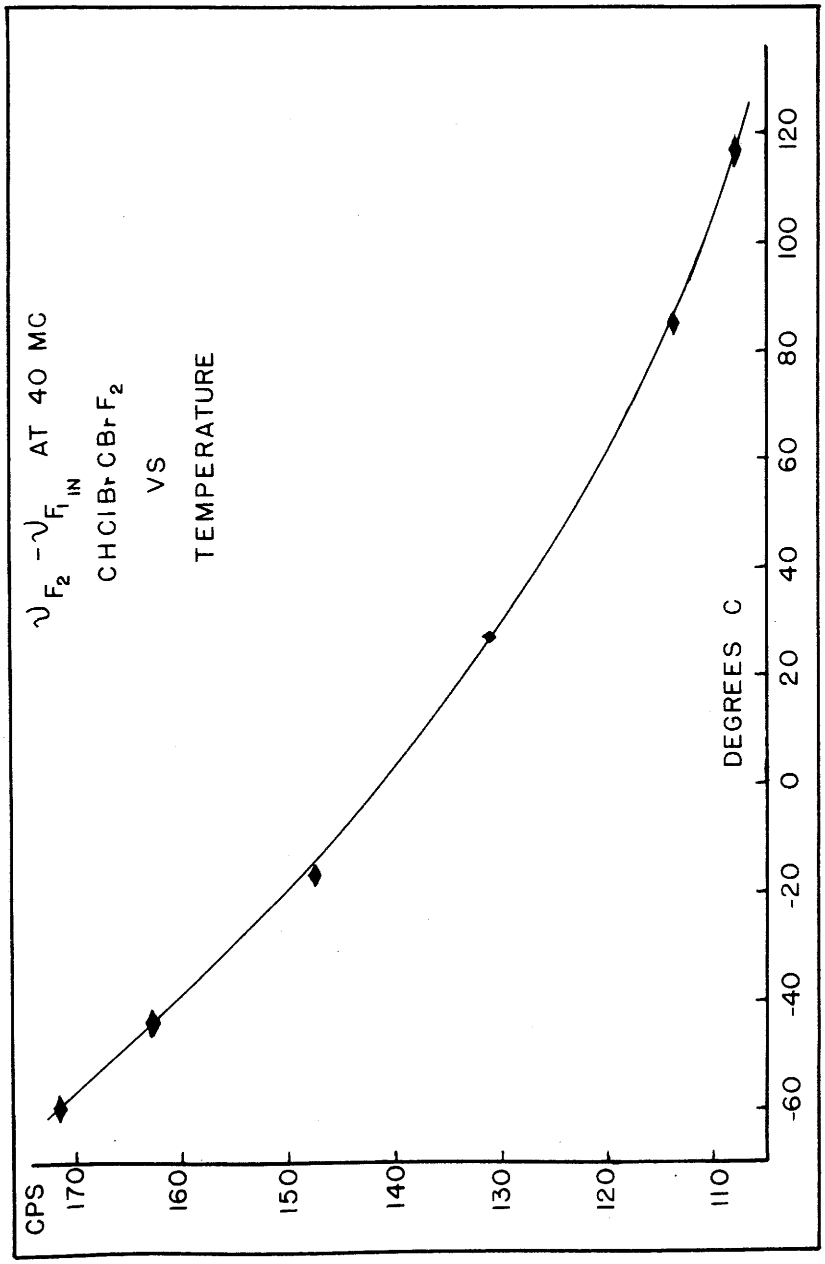
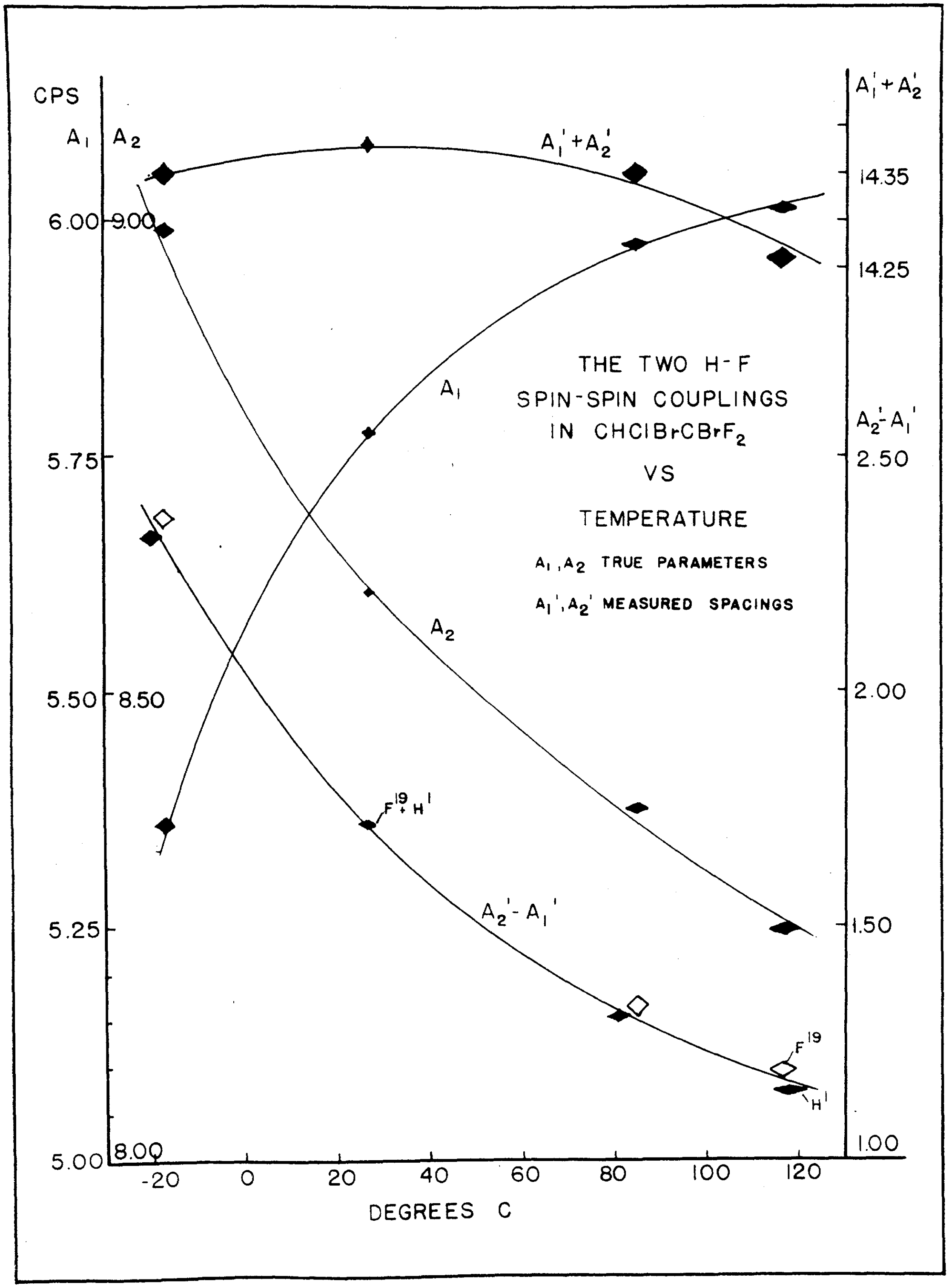

$\nu_{F_2} - \nu_{F_{1_{IN}}}$ AT 40 MC
CHClBrCBrF$_2$
VS
TEMPERATURE
CPS
170
160
150
140
130
120
110
-60
-40
-20
0
20
40
60
80
100
120
DEGREES C

FIGURE 15


CPS
A₁
A₂
6.00
9.00
5.75
5.50
8.50
5.25
5.00
8.00
-20
0
20
40
60
80
100
120
DEGREES C
A₁' + A₂'
14.35
14.25
A₂' - A₁'
2.50
2.00
1.50
1.00
A₁
A₂
F¹⁹ + H¹
F¹⁹
H¹
THE TWO H-F SPIN-SPIN COUPLINGS IN CHClBrCBrF₂ VS TEMPERATURE
A₁, A₂ TRUE PARAMETERS
A₁', A₂' MEASURED SPACINGS

two sets of measurements, which adds a great deal to one's confidence in the extreme accuracy of the wiggle beat method, because in one case a 6 or 8 cps. difference is being measured, and in the other a 1 to 2 cps. difference is being detected. Apparently any systematic errors involved do not depend on the size of the spacings.

The observed change in the chemical shift is qualitatively the same as that reported for some similar compounds by W.D. Phillips (28). Because there is no information on the energy differences in this molecule, or alternatively, because no values for the parameters ν_1', ν_2'', A_{23}'', etc. are known, little can be done at present in the way of interpretation except to state that the change exists. A similar situation holds for the values of the spin-spin couplings, except here the effect has been observed in only one other case (14). The cases reported here seem to be somewhat more advantageous because the absolute values of the coupling constants can be found, whereas in the case reported by Graham and Waugh the absolute values cannot be determined. (They involve the two quantities A_{FF} and A_{HH} which are theoretically, but not experimentally, measurable, at least for the present.) Much of this advantage, if not all, is lost for the case which shows the larger temperature dependence, by the larger set of parameters needed to describe this less symmetric molecule.

XI. CONCLUSION

Probably the most conspicuous result shown here is that, although the chemical shifts and spin-spin couplings show effects ascribable to rotational isomerism, quantitative interpretation at this time is very difficult. Because two more compounds have been found which demonstrate effects consistent with the theory of rotational averaging, the theory would seem to be substantiated somewhat. Unfortunately, no quantitative check can be made, so that is nearly equivalent to <u>not</u> finding a case which is <u>not</u> in accord with the theory.

Changes is observed spin-spin coupling constants have been shown to be of somewhat more common occurrence than was previously supposed. This work, in addition to that of Graham and Waugh, demonstrates a new temperature effect in nuclear resonance spectra.

Although these nuclear resonance spectra show obvious effects of internal rotation, the quantitative interpretation seems nearly impossible. There are several reasons for this. The manner in which the spectra depend upon temperature is such that experimentally it is impossible to observe limiting values corresponding to the limits, T very large and very small. Even more important, the theory which is applied connects two functions of internal configuration, $A=A(\phi)$, the spin-spin coupling, and $V=V(\phi)$, the potential energy, which are not known, either experimentally or theoretically. A good theory of either one would immediately make possible an accurate and detailed study of the other.

As an experimental note, the "wiggle beat" method of measuring small line spacings has yielded exceedingly precise results. In particular, the difference between the measurements of two splittings and the measurement of that difference itself, as it appeared in another part of the spectrum, agreed to within the experimental error. This agreement should help dispel any doubts that the accuracy of the method is the same as its precision.

APPENDIX A

INVARIANCE OF A NUCLEAR RESONANCE SPECTRUM UPON CHANGING THE SIGNS OF ALL A_{ij}

Anderson has pointed out (2) that by observing a nuclear resonance spectrum, the absolute sign of a nuclear spin-spin coupling constant A_{ij} cannot be determined, although in certain cases the relative signs in a set of A_{ij} for a molecule can. It is instructive to see how the former assertion is proved, since no justification of this important point seems to have been made in the literature.

The Hamiltonian for a system of nuclear spins (I=1/2) can be written as

$$\mathcal{H} = \mathcal{H}^{(o)} + \mathcal{H}^{(1)}$$

where $$\mathcal{H}^{(o)} = -h \sum_i \nu_i I_{zi}$$

$$\mathcal{H}^{(1)} = -h \sum_{i<j} A_{ij} \underline{I}_i \cdot \underline{I}_j$$

This will be called case I. The matrix elements $(\psi_m|\mathcal{H}|\psi_n)$, where ψ_m, ψ_n are product wave functions of the form $\alpha(1)\ \beta(2)$ ---, are

$$(\psi_m|\mathcal{H}^{(o)}|\psi_m) = -\tfrac{1}{2} h \sum_i \nu_i S_i$$

$$(\psi_m|\mathcal{H}^{(1)}|\psi_m) = -\tfrac{1}{4} h \sum_{i<j} A_{ij} T_{ij}$$

$m \neq n$ $$(\psi_m|\mathcal{H}^{(o)}|\psi_n) = 0$$

$$(\psi_m|\mathcal{H}^{(1)}|\psi_n) = -\tfrac{1}{2} h A_{ij} U_{ij}$$

and $S_i = \pm 1$ as nucleus i is in the α or β state,

$T_{ij} = \pm 1$ as nuclei i and j are parallel or anti-parallel,

$U_{ij} = 1$ if ψ_m and ψ_n differ by interchange of i and j spins only, and is zero otherwise.

The secular equation is then

$$\left| H_{mn} - E\delta_{mn} \right| = 0$$

The quantity $F_z = \sum_i I_{zi}$ is a good quantum number, so there is no mixing between states of different F_z. The secular equation is seem to factor into

$$\prod_{\text{all } F_z} \left| H_{mn} - E\delta_{mn} \right|_{F_z} = 0$$

One factor will be considered,

$$\left| H_{mn} - E\delta_{mn} \right|_G = 0$$

Reversing the signs of all the A_{ij} gives a new Hamiltonian $\mathcal{H}'$, with

$$(\psi_m | \mathcal{H}' | \psi_m) = -h\left\{ \tfrac{1}{2} \sum_i \nu_i S_i - \tfrac{1}{4} \sum_{i<j} A_{ij} T_{ij} \right\}$$

$$= (\psi_m | \mathcal{H}^{(o)} | \psi_m) - (\psi_m | \mathcal{H}^{(1)} | \psi_m)$$

$$(\psi_m | \mathcal{H}' | \psi_n) = -h A_{ij} U_{ij} = -(\psi_m | \mathcal{H}^{(1)} | \psi_n)$$

This situation will be called Case II. Here ψ_m and ψ_n denote the same wave functions as in Case I.

Let the product wave functions be renumbered so that ψ_p is just ψ_m with all spins inverted, and ψ_q and ψ_n are similarly related. With these wave functions

$$(\psi_p|\mathcal{H}'|\psi_p) = -(\psi_m|\mathcal{H}^{(o)}|\psi_m) - (\psi_m|\mathcal{H}^{(1)}|\psi_m)$$

$$(\psi_p|\mathcal{H}'|\psi_q) = -(\psi_m|\mathcal{H}^{(1)}|\psi_n)$$

The factor of the secular equation which should now be considered is

$$\left|H'_{pq} - E'\delta_{pq}\right|_{-G} = 0$$

All the H'_{pq} are the negatives of the H_{mn}, so if $E'' = -E'$, there results

$$(-1)^{\#\text{rows}}\left|H_{mn} - E''\delta_{mn}\right|_{-G} = 0$$

with the same roots E'' as in Case I,

or $\quad E''_{-G} = E_G = -E'_{-G}.$

Using the correspondence demonstrated earlier (Section II) between H_{mm} and a particular root, E_m, this is

$$(E_m)_G = -(E'_p)_{-G}.$$

The selection rule is $\Delta F_z = \pm 1$ (-1 for absorption) so the observed frequencies in the spectrum for Case I are

$$(E_r)_{G-1} - (E_m)_G = \nu_i$$

For Case II the frequencies are of the same form and

$$(E'_p)_{-G} - (E'_s)_{-G+1} = \nu_i'$$

or $\quad -(E_m)_G - (-E_r)_{G-1} = (E_r)_{G-1} - (E_m)_G$

so $\nu_i' = \nu_i$. Thus both spectra have the same frequencies.

To find the intensity of any transition, the stationary state wave functions for Cases I and II must be found. This is done as follows for Case I. A proper wave function is

$$\phi_m = \sum_k a_{mk} \psi_k$$

with the a_{mk} given by a set of homogensous equations

$$\sum_k (H_{m'k} - E_m \delta_{m'k})\, a_{mk} = 0 \qquad \text{for each } m'$$

Because of the correspondence between states of F_z of opposite sign in Cases I and II, there is a proper wave function for Case II given by

$$\phi_p = \sum_k a'_{pk} \psi'_k$$ where the ψ'_k are the ψ_k with all spins inverted.

The a'_{pk} are given by

$$\sum_k (H'_{p'k} - E_p \delta_{p'k})\, a'_{pk} = 0 \qquad \text{for all } p'.$$

But all the elements $H'_{p'k} = -H_{m'k}$ and $E_p = -E_m$, as seen in calculating the E_p. Hence,

$$(-1) \sum_k (H_{m'k} - E_m \delta_{m'k})\, a'_{pk} = 0$$

or the a'_{pk} are just the a_{mk}.

The intensity of a transition in Case I is proportional to

$$(\phi_r | I_x | \phi_m)^2 = \left[\sum_{k,\ell} a_{mk} a_{r\ell} (\psi_\ell | I_x | \psi_k) \right]^2$$

The corresponding transition for Case II is $\phi_S \longrightarrow \phi_P$, and the intensity is

$$(\phi_p | I_x | \phi_s)^2 = \left[\sum_{k,\ell} a'_{sk} a'_{p\ell} (\psi'_k | I_x | \psi'_\ell) \right]^2$$

If $(\psi_\ell|I_x|\psi_k) = 1$ (ψ_ℓ and ψ_k differ in spin of one nucleus only)

then $(\psi'_\ell|I_x|\psi'_k) = (\psi'_k|I_x|\psi'_\ell) = 1$ also.

The a'_{sk} are the same as the $a_{r\ell}$ in Case I, etc.

$$(\phi_p|I_x|\phi_s)^2 = (\phi_r|I_x|\phi_m)^2$$

and the transitions have identical intensity as well as frequency.

One further comment is necessary. If a group of nuclei are equivalent, the symmetry of that group will be evident in the mixing of certain of the trial wave functions, i.e., the factors in the wave functions for those nuclei will appear in the proper symmetry species: transitions involving that group will have the proper intensities in that there are no transitions between differing symmetry species. It is obvious that if signs of all the A_ij are changed, ϕ_p will have the same symmetry that ϕ_m had in Case I, since the a_{mk} or a'_{pk} are the same and the ψ_k or ψ'_k differ only by inversion of all spins. Thus the analogous transitions will also have the same relaxation times, since the relaxation times apparently depend only upon the symmetry of the wave function, the properties of individual spins, and the dynamics of the molecular environment (2).

APPENDIX B

SAMPLE CALCULATION

Styrene, 22.55 Mc.

The parameters given here to illustrate the calculation were not those originally used, but differ by a scale factor, applied in order that the calculated spectra may be compared with the experimental one immediately. To make sure that all the matrix elements, energies, etc., are consistent, four places after the decimal point have been retained. For beginning a calculation, accuracy to only two decimal places would be adequate. The parameters to be used are:

$\nu_1' = -33.8197$ cps.
$\nu_2' = -11.6828$
$\nu_3' = 0.0$
$A_{12} = 17.8165$
$A_{13} = 11.2726$
$A_{23} = 1.1633$

Our reference frequency is obviously the chemical shift of nucleus 3.

Following the procedure of Section II, the matrix elements are (omitting the ν_o term):

$H_{11} = E_1 = 15.1882$
$H_{88} = E_8 = -30.3144$

$$\text{and } (H_{mn})_{m,n=2,3,4} = \begin{bmatrix} -4.0870 & -8.9083 & -5.6363 \\ -8.9083 & 12.9953 & -0.5817 \\ -5.6363 & -0.5817 & 21.4061 \end{bmatrix}$$

$$\text{and } (H_{mn})_{m,n=5,6,7} = \begin{bmatrix} -24.0964 & -0.5817 & -5.6363 \\ -0.5817 & -9.1416 & -8.9083 \\ -5.6363 & -8.9083 & 18.0499 \end{bmatrix}$$

The two equations $|H_{mn} - E\delta_{mn}| = 0$ are,

$$E^3 - 30.3144E^2 + 26.1161E + 3305.5214 = 0, \text{ for } m,n=2,3,4$$

and $$E^3 + 15.1881E^2 - 491.1270E - 6114.1498 = 0, \text{ for } m,n=5,6,7$$

The solution of these cubic equations is readily performed on a desk calculator by repeated substitution of trial solutions and interpolation between them. Remembering the correspondence between H_{mm} and E_m, there results:

$$\begin{aligned} E_2 &= -8.8585 & E_5 &= -25.0504 \\ E_3 &= 16.3470 & E_6 &= -11.4516 \\ E_4 &= 22.8256 & E_7 &= 21.3138 \end{aligned}$$

Now, following the outline in Section II, the coefficients giving the proper wave functions can be found. The submatrices (a_{mn}) which result for this case are:

$$\underset{m,n=2,3,4}{\begin{bmatrix} .9098 & .3756 & .1764 \\ -.3253 & .9069 & -.2582 \\ -.2575 & .1772 & .9498 \end{bmatrix}} \qquad \underset{m,n=5,6,7}{\begin{bmatrix} .9806 & .1217 & .1533 \\ -.1585 & .9531 & .2575 \\ -.1148 & -.2769 & .9539 \end{bmatrix}}$$

If the energies are arranged

$$\begin{array}{ccc} & E_1 & \\ E_2 & E_3 & E_4 \\ E_5 & E_6 & E_7 \\ & E_8 & \end{array}$$

the frequencies of the fifteen transitions allowed by the selection rule $\Delta F_z = \pm 1$ will be given by the differences between energies occupying adjacent rows. Transition $\emptyset_6 \rightarrow \emptyset_3$ of frequency ν_{36} is then $E_3 - E_6$, this frequency is in addition to that of the reference ν_o. As a further example, the intensity of this transition will be calculated. The intensity is given by

$$I_{36} = \left[\sum_{\ell} \sum_{k} a_{3\ell} a_{6k} \, (\psi_\ell | I_x | \psi_k) \right]^2$$

Now the matrix elements $(\psi_\ell | I_x | \psi_k)$ are

$$(\psi_1 | I_x | \psi_m) = 1 \qquad m = 2,3,4$$

$$(\psi_m | I_x | \psi_8) = 1 \qquad m = 5,6,7$$

$$(\psi_m | I_x | \psi_n) = 1 \qquad \begin{matrix} m = 2,3,4 \\ n = 5,6,7 \end{matrix}$$

except $(\psi_4 | I_x | \psi_5) = (\psi_3 | I_x | \psi_6) = (\psi_2 | I_x | \psi_7) = 0$

Therefore, there are six terms involved.

$$I_{36} = \left[a_{32}a_{65} + a_{32}a_{66} + a_{33}a_{65} + a_{33}a_{67} + a_{34}a_{66} + a_{34}a_{67} \right]^2 = 0.23$$

The other intensities are found in a similar manner, except that those such as I_{12} involve only three terms

$$I_{12} = \left[a_{22} + a_{23} + a_{24} \right]^2$$

The results for this spectrum are given below.

Transition	-(Frequency)	Intensity
ν_{12}	-24.05	2.14
ν_{13}	1.16	0.11
ν_{14}	7.64	0.76
ν_{58}	-5.26	1.58
ν_{68}	-18.86	1.11
ν_{78}	-51.62	0.32
ν_{25}	-16.19	2.18
ν_{26}	-2.59	0.95
ν_{27}	30.17	0.006
ν_{35}	-41.40	0.36
ν_{36}	-27.80	0.23
ν_{37}	4.96	0.52
ν_{45}	-47.88	0.032
ν_{46}	-34.28	0.93
ν_{47}	-1.52	0.80

The values have now been rounded off to be only somewhat more accurate than the experimental ones. To get the values given in Table V, an arbitrary number, 55.00, was added to all frequencies. This spectrum is plotted in Figure 4.

It is useful to note at this time that several checks upon the calculation exist. These are useful because they can give a high degree of certainty that no computational errors were made. The checks will be listed.

1. The traces are preserved

$$E_2 + E_3 + E_4 = H_{22} + H_{33} + H_{44} = -H_{88}$$

$$E_5 + E_6 + E_7 = H_{55} + H_{66} + H_{77} = -H_{11}$$

2. It is required that the new wave functions be

normalized, or that in the 3x3 matrices, $\sum_k a_{ik}^2 = 1$, for i = 2,3,4,5,6,or 7 and k over the columns. It also follows that these matrices are unitary and

$$\sum_i a_{ik}a_{i\ell} = \delta_{k\ell}$$

$$\sum_i a_{ki}a_{\ell i} = \delta_{k\ell}$$

where i goes over rows or columns. This gives a sensitive check on not only the a_{mn}, but also on the energy values used in finding them.

3. Certain intensity relations

$$I_{12} + I_{13} + I_{14} = 3$$

$$I_{58} + I_{68} + I_{78} = 3$$

$$\sum_{\text{all lines}} I_{ij} = 12$$

If these relations are all satisfied to a degree commesurate with the number of figures retained in the calculation, it can be said that in all probability there are no computational errors. Here, for instance,

for check 1:

$$H_2 + H_3 + H_4 = 30.3144 = -H_8$$

$$E_2 + E_3 + E_4 = 30.3141$$

for check 2:

$$a_{22}^2 + a_{32}^2 + a_{42}^2 = .99986$$

These results are highly satisfactory.

The energy values for this case differ from the diagonal elements of $\mathcal{H}$ by considerable amounts in some cases; however, the wave functions retain most of their identity as some ψ_i , as evidenced by the a_{mm} which are all larger than 0.9. It is important to note that the line intensities do change drastically nevertheless. The intensity of transition ν_{13} is only 0.11, compared to the first order value of 1.00. The intensities are thus very sensitive indicators of the amount of mixing of the first order wave functions.

It should be pointed out that combination lines are not always weak; in the present case, they are of intensity comparable to that of some first order lines. Bernstein, Pople, and Schneider (7) have made the statement that in the case ABX, the combination lines are generally weak. This statement might be interpreted as indicating that in the case ABC this is true also. By studying the correlation diagram, Figure 6, it is seen that ν_{36}, a combination line, is one of the lines remaining at small field. It should be added that this line is of intensity 1.00 at this limit, certainly not a weak line.

Finally, it is useful to show how the line intensities can help determine which of the assignments corresponding to different signs of the A's can be allowed. If for styrene, the assignment for all $A_{ij} > 0$ is made, then the sums of intensities which should give 3.00 are:

1. $I_{12} + I_{13} + I_{14} = 3.00$
   $I_{78} + I_{68} + I_{58} = 3.00$

If this labeling of the lines is retained, the sums corresponding to $A_{12} < 0$ are:

2. $I_{35} + I_{25} + I_{14}$
   $I_{46} + I_{47} + I_{58}$

And for $A_{13} < 0$ and $A_{23} < 0$:

3. $$\begin{gathered} I_{46} + I_{13} + I_{26} \\ I_{35} + I_{68} + I_{37} \end{gathered}$$

and

4. $$\begin{gathered} I_{12} + I_{47} + I_{37} \\ I_{78} + I_{25} + I_{26} \end{gathered}$$

If the indicated operations are performed on the experimental data for styrene at 22.55 Mc., there results:

Assignment	Experimental Spectrum		Calculated Spectrum	
	S_1	S_2	S_1	S_2
1	2.72	3.23	3.01	3.01
2	3.06	3.48	3.30	3.31
3	2.16	2.18	1.99	1.99
4	3.30	3.37	3.46	3.45

It is apparent that #3 must be rejected and that although #2 and #4 can probably be allowed, these do not check as well as #1, particularly if the two sums are required to add to 6.00. If the intensity criterion alone were to be used, it might be possible to get better experimental intensity data to allow all but #1 to be rejected on this basis. (At 40 Mc. also, #3 is rejected easily.)

If the parameters used were exact and the experimental errors small, and if #1 were indeed the correct assignment, the second two columns would give the values of the sums. Comparison of these with the experimental ones indicates the kind of errors to be expected in the sums. No reason for the equality of the two sums in all cases (although they do not now equal 3.00) has been found, but this fact and the deviations between ideal and observed sums would strongly suggest that # 1 is the only assignment which can be accepted.

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Richard Warren Fessenden, son of Mr. and Mrs. Richard William Fessenden, was born on January 22, 1934, in Northampton, Massachusetts. He attended the public schools of Amherst, Massachusetts, graduating from high school in June, 1951.

He attended the University of Massachusetts from June, 1951, to February, 1955, during which time he was selected as Phi Kappa Phi Class Scholar in three sucessive years and as Phi Beta Kappa Class Scholar, and was elected a member of Phi Kappa Phi and Sigma Xi. He graduated Summa cum laude with a B. S. Degree in June, 1955.

In February, 1955, he enrolled as a candidate for the degree of Doctor of Philosophy in Physical Chemistry at the Massachusetts Institute of Technology. He held a National Science Foundation Fellowship in the academic years 1956-1957 and 1957-1958. While at M. I. T. he was elected a full member of Sigma Xi. He accepted a National Science Foundation Postdoctoral Fellowship for study at the California Institute of Technology for a year, starting in September, 1958.