THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF FOUR SPIN SYSTEMS

II. Proton Resonance Spectra of Some Para-Disubstituted Benzenes

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ABSTRACT

The spectra of a number of p-disubstituted benzenes were analyzed earlier by Richards and Schaeffer by assuming that the two meta H–H coupling constants are equal and the para H–H coupling constant is zero. In the present work a method for analysing this type of spectra, without making any simplifying assumptions, is proposed. The proton resonance spectra of p-bromochlorobenzene, p-chlorotoluene and p-chloroiodobenzene were obtained and analyzed as examples, and all the parameters were determined in each case. The general form of this type of spectra for different values of chemical shift is discussed.

1. INTRODUCTION

The general theory of the spectra of four spin systems, which can be divided into two pairs of two equivalent nuclei (A₂B₂ type), was discussed by Pople, Bernstein and Schneider. There are twenty-eight transitions in the spectrum out of which four are combination transitions of feeble intensity. The remaining twenty-four transitions occur symmetrically about the centre of the spectrum and therefore the analysis can be completely done if the twelve transitions in a typical half of the spectrum are identified. Explicit expressions in terms of the involved parameters (one chemical shift and four spin-spin coupling constants) can be derived for only six of these twelve transitions, and the spectrum depends on the chemical shift and the spin-spin coupling constants in a rather complicated manner. A straightforward analysis is therefore not usually possible. Pople et al., however, proposed some practical methods of analysis for some special cases of this type of spectra (a) when the two AB coupling constants are equal and (b) when one pair of nuclei are more strongly coupled than the other.

1 Our earlier paper on "H and F Resonance Spectra of 1-fluoro, 2, 4-dinitrobenzene," Proc. Ind. Acad. Sci., 1960, 52 A, 109, is referred to as I.
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The proton resonance spectra of \( p \)-disubstituted benzenes (where the substituents do not interfere in the spectrum) belong to a different case of \( A_2B_2 \) spectra as the nuclei in each pair are strongly coupled to nearly the same extent. Richards and Schaeffer\(^3\) (hereafter referred to as RS) have recently studied the spectra of a number of these compounds at 29.92 mc./sec., and carried out the analysis by making the simplifying assumptions that the coupling constants \( J_A \) and \( J_B \) are equal and that \( J' = 0 \) (see Fig. 1). As shown later in this paper there is no pressing necessity, however, to make these assumptions.

\[ \text{Fig. 1.} \]

We have here studied again the proton resonance spectra of three \( p \)-disubstituted benzenes at 40 mc./sec. A general method for analyzing this type of spectra is proposed, and on this basis all the parameters were obtained in each case.

2. EXPERIMENTAL

All the three compounds studied, viz., \( p \)-bromochlorobenzene, \( p \)-chlorotoluene and \( p \)-chloroiodobenzene were obtained from British Drug House and were used without further purification. \( p \)-chlorotoluene is a liquid and the other two compounds are solids. For \( p \)-bromochlorobenzene a solution in ether and for \( p \)-chloroiodobenzene a solution in ethanol were used.*

The spectra were all obtained on a Varian V-4300 B High Resolution N.M.R. Spectrometer. The general experimental details for the proton resonance studies at 40 mc./sec. were given in I\(^4\). The observed line frequencies are all expressed with respect to the centre of the spectrum to facilitate comparison with the theoretical spectrum (see Table III).

The experimental spectra of \( p \)-bromochlorobenzene, \( p \)-chlorotoluene and \( p \)-chloroiodobenzene are reproduced in Figs. 2(a), 3(a) and 4(a) respectively.

3. METHOD OF ANALYSIS

The complete spin matrix for the \( A_2B_2 \) system and the explicit expressions for the energy levels and the corresponding wave functions, and the

* The solvents are the same as those used by RS for these compounds.
transition energies and relative intensities in cases where these can be derived, were given by Pople et al.\textsuperscript{1, 2} The notation employed by them is freely used throughout this paper without specification. The calculations can be conveniently done in terms of new quantities \( K, L, M \) and \( N \) defined as below:

\[
\begin{align*}
K &= J_A + J_B \\
M &= J_A - J_B \\
N &= J + J' \quad \text{and} \quad L = J - J'.
\end{align*}
\]

Explicit expressions were derived for all but four of the energy levels which were labelled as \( 1s_0', 2s_0', 3s_0' \) and \( 4s_0' \). If we denote the energy values corresponding to these four states as \( E_1, E_2, E_3 \) and \( E_4 \) respectively, these are given by the roots of the fourth power equation (obtained by expanding the corresponding \( 4\times4 \) determinant):

\[
(K + E)\left\{ E^3 + NE^2 - E\left[\frac{3}{4}N^2 + (v_0\delta)^2\right] - \frac{1}{4}N^3 \right\} - \frac{1}{4}L^2\left\{ 3E^2 - \left[\frac{3}{4}N^2 + (v_0\delta)^2\right] \right\} = 0
\] (2)

where \( v_0\delta \) is the chemical shift in cps.

The exact eigenfunctions \( \phi_q (q = 1, \ldots, 4) \) for these four levels can be expressed as linear combinations of the zero order wave functions \( \phi^0_m \) \( (m = 1, \ldots, 4) \) of the four states, \textit{i.e.},

\[
\phi_q = \sum_m a_{qm}\phi^0_m
\] (3)

where the coefficients \( a_{qm} \) may be evaluated in the usual manner\textsuperscript{2, 5} if the parameters are determined.

Six of the twelve 'A' (or 'B') transitions involve these energy levels and the energies of these transitions may tentatively be expressed in terms of \( E_1, E_2, E_3 \) and \( E_4 \). The relative intensities may also be calculated in terms of the coefficients \( a_{qm} \) in Eq. (3). The transition energies and relative intensities of all the twelve transitions are given, in this manner, in Table I.

To proceed with the analysis, taking a typical half of the spectrum, the lines 1 and 3 (line Nos. as in Table I) may first be identified. The identification is easier if an approximate value of \( N \) is known, as the separation between the lines is \( N \).\textsuperscript{*} If these lines are fixed, at least tentatively, \( v_0\delta \) and \( N \) can easily be obtained.

\* In the case of \( p \)-disubstituted benzenes \( N \) is equal to the sum of the ortho and para \( H-H \) coupling constants and its value may be expected to be about 9.0 cps., from the known data on these constants in other compounds. It is reasonable to expect like this as the coupling constants are not, in general, found to be much sensitive to substitution.
**TABLE I***

*Transition energies and relative intensities for the 'A' spectrum*

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Transition</th>
<th>Energy relative to $\frac{1}{2}(v_n + v_a)$</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1s'_1 \rightarrow s_2$</td>
<td>$\frac{1}{2}N + \frac{1}{2}[(\omega_0^2 + N^2)^{\frac{1}{2}}]$</td>
<td>$1 - \sin 2\phi$</td>
</tr>
<tr>
<td>2</td>
<td>$1s'_0 \rightarrow 1s'_1$</td>
<td>$-\frac{1}{2}[(\omega_0^2 + N^2)^{\frac{1}{2}}]$</td>
<td>$[\cos \phi (a_{11} + a_{14}) - \sin \phi \times (a_{12} + a_{14})]_{2}$</td>
</tr>
<tr>
<td>3</td>
<td>$s_{-2} \rightarrow 1s_{-1}'$</td>
<td>$-\frac{1}{2}N + \frac{1}{2}[(\omega_0^2 + N^2)^{\frac{1}{2}}]$</td>
<td>$1 + \sin 2\phi$</td>
</tr>
<tr>
<td>4</td>
<td>$1s_{-1}' \rightarrow 2s'_0$</td>
<td>$E_2 - \frac{1}{2}[(\omega_0^2 + N^2)^{\frac{1}{2}}]$</td>
<td>$[\cos \phi (a_{23} + a_{24}) + \sin \phi \times (a_{31} + a_{34})]_{2}$</td>
</tr>
<tr>
<td>5</td>
<td>$3s'_0 \rightarrow 2s'_1$</td>
<td>$\frac{1}{2}[(\omega_0^2 + N^2)^{\frac{1}{2}}]$</td>
<td>$[\cos \phi (a_{31} + a_{34}) - \sin \phi \times (a_{41} + a_{44})]_{2}$</td>
</tr>
<tr>
<td>6</td>
<td>$2s_{-1}' \rightarrow 4s'_0$</td>
<td>$E_4 + \frac{1}{2}[(\omega_0^2 + N^2)^{\frac{1}{2}}]$</td>
<td>$[\cos \phi (a_{41} + a_{44}) - \sin \phi \times (a_{41} + a_{44})]_{2}$</td>
</tr>
<tr>
<td>7</td>
<td>$4s'_0 \rightarrow 2s'_1$</td>
<td>$\frac{1}{2}[(\omega_0^2 + N^2)^{\frac{1}{2}}]$</td>
<td>$[\cos \phi (a_{41} + a_{44}) + \sin \phi \times (a_{31} + a_{34})]_{2}$</td>
</tr>
<tr>
<td>8</td>
<td>$2s_{-1}' \rightarrow 3s'_0$</td>
<td>$E_3 + \frac{1}{2}[(\omega_0^2 + N^2)^{\frac{1}{2}}]$</td>
<td>$[\cos \phi (a_{31} + a_{34}) - \sin \phi \times (a_{23} + a_{24})]_{2}$</td>
</tr>
<tr>
<td>9</td>
<td>$2a'_0 \rightarrow 2a'_1$</td>
<td>$\frac{1}{2}[(\omega_0^2 + M)^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}]$</td>
<td>$\sin^2 (\theta_a - \psi_\pm)$</td>
</tr>
<tr>
<td>10</td>
<td>$2a_{-1}' \rightarrow 1a'_0$</td>
<td>$\frac{1}{2}[(\omega_0^2 - M)^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}]$</td>
<td>$\cos^2 (\theta_a + \psi_\pm)$</td>
</tr>
<tr>
<td>11</td>
<td>$1a'_0 \rightarrow 2a'_1$</td>
<td>$\frac{1}{2}[(\omega_0^2 + M)^{\frac{1}{2}} - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}]$</td>
<td>$\cos^2 (\theta_a - \psi_\pm)$</td>
</tr>
<tr>
<td>12</td>
<td>$2a_{-1}' \rightarrow 2a'_0$</td>
<td>$\frac{1}{2}[(\omega_0^2 - M)^{\frac{1}{2}} - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}]$</td>
<td>$\sin^2 (\theta_a + f \psi_\pm)$</td>
</tr>
</tbody>
</table>

* The expressions for transitions 1, 3, 9, 10, 11 and 12 are the same as those on p. 144 of reference 2.

In molecules like the $p$-disubstituted benzenes one might expect the value of $M$ to be small, and $N$ and $L$ to be nearly equal. Then the lines 9 and 10 will lie close to 1, and lines 11 and 12 will lie close to 3. Sometimes these lines (9–12) may not be separated sufficiently from lines 1 and 3 to be observed. These transitions may therefore be considered towards the end of the analysis.
We will now be left with the six transitions 2, 4, 5, 6, 7 and 8, and these involve the roots of the Eq. (2), in which the quantities K and L^2 are yet to be determined (ν_0δ and N are already known from the identification of the lines 1 and 3). From Table I it can be seen that the sum of the transition frequencies of 5 and 8 as well as that of 6 and 7 are both equal to [(ν_0δ)^2 + N^2]^1/2. The value of this factor is known, and therefore we can pick up from the rest of the lines in the observed spectrum, two pairs of lines such that the sum of the frequencies of the lines, with respect to 1/2(ν_A + ν_B), in each pair is equal to [(ν_0δ)^2 + N^2]^1/2. If the frequencies of these lines are say ν_5 & ν_8, and ν_6 & ν_7 we find that

\begin{align*}
E_3 &= \pm \frac{\nu_5 - \nu_8}{2} \\
E_4 &= \pm \frac{\nu_6 - \nu_7}{2}.
\end{align*}

(4)

From this identification we therefore get two probable values of E_3 and two for E_4, out of which one is to be discarded in each case. If we substitute these four roots of E in Eq. (2), we get four equations each involving K and L^2.

As mentioned earlier we know that the values of N and L are close to each other, as the para H–H coupling constant is expected to be small.
Fig. 3. $^1$H NMR spectrum of para-chlorotoluene at 40 mc./sec.
(a) Experimental, (b) Calculated: 1 cm. = 3.138 Cps.

Fig. 4. $^1$H NMR spectrum of para-Chloriodobenzene at 40 mc./sec.
(a) Experimental, (b) Calculated: 1 cm. = 3.184 Cps.
So, tentatively putting $L = N$ (N being already) known $K$ may be determined from every one of the four equations obtained above. Now, the roots of $E$, which yield values of $K$ that are positive and close to each other and also lying in the range estimated from the known meta H-H coupling constants should be chosen as the proper roots $E_3$ and $E_4$. The corresponding equations involving $K$ and $L^2$ can then be solved to obtain $K$ and $L$.

Now the other roots $E_1$ and $E_2$ can be readily determined and if the lines 2 and 4, involving these energy levels, are satisfactorily accounted for in the observed spectrum, a check on the identification of lines 5 to 8 is obtained.

Sometimes, it may be possible, in practice, to find more than two pairs of lines satisfying the above condition, or one of the lines in a pair may not be observed if its intensity is very low,* so that an unambiguous assignment is not readily obtained. Some trial and error calculations will then be necessary to decide upon the proper assignment. Further, at two stages in the above procedure, firstly for the identification of lines 1 and 3, and secondly for determining the proper roots $E_3$ and $E_4$, a knowledge of approximate values of the coupling constants is said to be necessary. This, however, does not place any drastic limitation on the method (except that more trial and error calculations may be necessary) as any assignment is ultimately checked completely for internal consistency.

After satisfactorily assigning lines 1 to 8 if some lines in the observed spectrum are still left unassigned, they may be assigned properly to transitions 9 to 12 and the value of $M$ may be calculated.$t$

The relative signs of the coupling constants cannot be determined in this analysis, and all the coupling constants were assumed to be positive for the spectra analyzed.

4. RESULTS

Following the method described in the preceding section the lines in the spectrum of $p$-bromochlorobenzene [Fig. 2(a)] are assigned in the following manner:

* Even if one of the pair of lines is identified the corresponding root of Eq. (2) may be determined.

† It may be noted that the value of $M$ is very sensitive to slight errors in the line positions (even within the limits of experimental error) and therefore an approximate value of $M$ may be estimated such that the calculated frequency agrees with the observed, within experimental error. It is not usually possible to determine the sign of $M$, as this can be done only if the intensities are accurately known, and thus it is difficult to find which of the two meta H-H coupling constants ($J_n$ and $J_o$) is larger.
The lines at 1.50 and 10.40 cps., with respect to the centre of the spectrum, were first assigned to the transitions 3 and 1 respectively. From this we obtain \( N = 8.9 \) cps. and \( [(v_0^0)^2 + N_0^2]^1 = 11.9 \) cps. The two lines at 4.30 and 7.70 cps. were assigned to the transitions 6 and 7 and the line at 0 cps. was taken as one of the transitions 5 and 8.* Finally the line at 9.81 cps. was assigned to the transition 10.

The assignment of lines in the spectra of \( p \)-chlorotoluene and \( p \)-chloroiodobenzene was done in the same manner as above.

The parameters obtained in the analyses of these three spectra are given in Table II. The line frequencies and relative intensities calculated on the basis of these parameters, along with the observed line frequencies for \( p \)-bromochlorobenzene, \( p \)-chlorotoluene and \( p \)-chloroiodobenzene, are given in Table III, while the calculated spectra are shown in Figs. 2 (b), 3 (b) and 4 (b) respectively.

**TABLE II**

*Values of the parameters* obtained from the analyses (the values obtained by RS† are given for comparison)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( v_0^0 )</th>
<th>( J_0^{10} )</th>
<th>( J_m^{10} )</th>
<th>( J_p^{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. <strong>P</strong>-bromochlorobenzene</td>
<td>7.9</td>
<td>8.6</td>
<td>2.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Values of RS</td>
<td>7.1</td>
<td>9.1</td>
<td>(Range 1.5–2.0)</td>
<td>0</td>
</tr>
<tr>
<td>2. <strong>P</strong>-chlorotoluene</td>
<td>8.3</td>
<td>8.3</td>
<td>2.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Values of RS</td>
<td>5.3</td>
<td>9.1</td>
<td>(Range 1.5–2.0)</td>
<td>0</td>
</tr>
<tr>
<td>3. <strong>P</strong>-chloroiodobenzene</td>
<td>20.7</td>
<td>8.4</td>
<td>2.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Values of R. S.</td>
<td>20.8</td>
<td>9.0</td>
<td>1.6</td>
<td>0</td>
</tr>
</tbody>
</table>

* All the values are given in cps. The error involved in any of the parameters is about \( \pm 0.2 \) cps.

† The \( v_0^0 \) values in reference 3 are multiplied by (40/29.92) to compare with the values in the present work.

* The lines at 10.91 and 1.10 also appear to be a probable pair of lines to be assigned to either the transitions 6 and 7 or 5 and 8. But this was finally discarded as the assignment on this basis does not account for the line at 0 cps.
### TABLE III

*Calculated transition frequencies and relative intensities, and observed frequencies* for p-bromochlorobenzene, p-chlorotoluene and p-chloroiodobenzene

<table>
<thead>
<tr>
<th>Transition No.</th>
<th>P-bromochlorobenzene</th>
<th>P-chlorotoluene</th>
<th>P-chloroiodobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_{\text{cal.}}$</td>
<td>$v_{\text{obs.}}$</td>
<td>$I_{\text{cal.}}$</td>
</tr>
<tr>
<td>5</td>
<td>11.90</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>2</td>
<td>11.06</td>
<td>10.91</td>
<td>0.21</td>
</tr>
<tr>
<td>1</td>
<td>10.40</td>
<td>10.78</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>10.40</td>
<td>15.60</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>10.16</td>
<td>0.13</td>
<td>9.97</td>
</tr>
<tr>
<td>10</td>
<td>9.79</td>
<td>9.81</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>7.65</td>
<td>7.70</td>
<td>0.29</td>
</tr>
<tr>
<td>7</td>
<td>4.25</td>
<td>4.30</td>
<td>0.42</td>
</tr>
<tr>
<td>11</td>
<td>1.74</td>
<td>0.87</td>
<td>1.93</td>
</tr>
<tr>
<td>3</td>
<td>1.50</td>
<td>1.50</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>6.89</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1.37</td>
<td>0.85</td>
<td>1.57</td>
</tr>
<tr>
<td>4</td>
<td>1.11</td>
<td>1.10</td>
<td>2.23</td>
</tr>
<tr>
<td>8</td>
<td>0.00</td>
<td>0.00</td>
<td>0.61</td>
</tr>
</tbody>
</table>

(Calculated and observed frequencies are given in cps., for a half of the spectrum, with respect to the centre $\frac{1}{2}(v_A + v_B)$. $I_{\text{cal.}}$ stands for the calculated relative intensity.)

* Average standard deviations for the observed line frequency determinations for p-bromochlorobenzene, p-chlorotoluene and p-chloroiodobenzene are 0.12, 0.07 and 0.13 respectively.

† Nos. as in Table I.

The parameters are all obtained assuming $v_A > v_B$ but it is not possible to determine, from the analysis, which pair of nuclei are shielded more. In the case of p-chloroiodobenzene, however, by comparing with the results obtained by Corio and Dailey on the chemical shifts in monosubstituted
benzenes, the two protons ortho to chlorine may be expected to be shielded more.

Note added in proof.—Schäffer and Schneider (J. Chem. Phys., 1960, 32, 1218) observe that a methyl group gives rise to spin-spin coupling with the ring protons and that this coupling is strongest with the protons ortho to the group, resulting usually in a broadening of the spectrum of these protons, and utilised this fact to identify the transitions of ortho and meta protons in several para-substituted toluenes. On this basis the protons ortho to methyl group in p-chlorotoluene may be taken to be shielded more as the half of this spectrum on the higher field is clearly broadened [see Fig. 3(a)].

5. DISCUSSION

The agreement between the calculated and observed spectra, for all the three cases, as seen from Table III and Figs. 2, 3 and 4, is satisfactory, and the method of analysis therefore appears to be reliable.

The corresponding values of the parameters obtained by RS for all these cases are also given in Table II for comparison.

The ortho-coupling constants \( J_0^{HH} \) obtained by RS are all consistently larger than the corresponding values obtained here. This is because of the assumption made by RS that \( J' = 0 \), and the value of \( J_0^{HH} \) determined by them corresponds to \( N \) in the present analysis. All the meta H–H coupling constants \( J_m^{HH} \) obtained here are outside the range of 1.5 to 2.0 cps. suggested by RS for these molecules. All the coupling constants observed here agree with the values of the ortho, meta and para H–H coupling constants in substituted benzenes determined by earlier workers.

The value of \( v_0^\delta \) for p-chloriodobenzene obtained here agrees very well with the value of RS (Table II). However, there is considerable discrepancy between the \( v_0^\delta \) values determined here and those of RS (converted to 40 mc./sec., as given in Table II) in the case of the other two compounds. The value of \( v_0^\delta \) is small in both these cases and is still smaller at 29.92 mc./sec. used by RS for the work. The assignment of the lines to the transitions is usually rendered difficult when \( v_0^\delta \) is small and this is probably the reason for the low values of \( v_0^\delta \) obtained by RS in these cases. As the present experiments are done at 40 mc./sec. the values reported here are expected to be more reliable than those of RS.

6. DEPENDENCE OF THE SPECTRUM ON THE CHEMICAL SHIFT

In view of the several difficulties involved in arriving at a correct assignment, it was thought worthwhile to calculate the spectra for some typical
values of $v_0\delta$, as the rest of the parameters remain approximately the same for all the $p$-disubstituted benzenes. The manner in which a typical half of the spectrum varies with $v_0\delta$ is schematically represented in Fig. 5. In the

![Diagram](image)

**Fig. 5.** Schematic representation of 'A' spectrum for different values of the chemical shift. (a) in the $A_2X_2$ limit, (b) $v_0\delta = 20.7$ cps., (c) $v_0\delta = 7.9$ cps., (d) $v_0\delta = 4$ cps.

Other parameters are $N = 8.5$ cps., $L = 8.0$ cps., $K = 5.0$ cps., and $M = 0.5$ cps. The numbers correspond to the transitions given in Table I.

limit when $v_0\delta$ is large compared with the coupling constants ($A_2X_2$ case) the half of the spectrum is again symmetrical, in the positions of the lines as well as the intensities, about the centre $v_A$. As $v_0\delta$ decreases the spectrum becomes gradually unsymmetrical with respect to the centre $(v_A)$, and the lines nearer to $\frac{1}{2}(v_A + v_B)$ increase in intensity while those away diminish in intensity, and some of them may even escape detection at small values of $v_0\delta$. The spectra (b) and (c) in Fig. 5 are the same as those of $p$-chloro-iodobenzene and $p$-bromochlorobenzene respectively. The spectrum (d)
in Fig. 5 is calculated for $\nu_0\delta = 4.0$ cps. Other parameters used in the calculation are:

\[
\begin{align*}
K &= 5.0 \text{ cps.} \\
N &= 8.5 \text{ cps.} \\
M &= 0.5 \text{ cps.} \\
L &= 8.0 \text{ cps.}
\end{align*}
\]

These parameters in Eq. (5) are also used in the calculation of the spectrum (a) in the figure.

It can be seen from Fig. 5 that the spectrum depends on the chemical shift in a rather complicated manner, but the schematic variation shown in this diagram may be useful in analyzing spectra of this type.

7. ACKNOWLEDGEMENTS

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8. REFERENCES