Analysis of I-I Coupling Fine Structures in Nuclear Magnetic Resonance Spectra of Simple Organic Molecules,II.Para-Difluorobenzene

Analysis of I-I Coupling Fine Structures in Nuclear Magnetic Resonance Spectra of Simple Organic Molecules. II. Para-Difluorobenzene

By

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We have analyzed the spin-spin coupling fine structures of the proton and the fluorine magnetic resonance spectra in para-difluorobenzene as a six-spin system having a symmetry V_h, considering ortho proton-proton, ortho fluorine-proton, meta fluorine-proton and para fluorine-fluorine spin coupling constants.

We have found that ten spectral lines in the proton resonance and nineteen in the fluorine are expected in general, but some of them have weak intensities. And also, we have seen that it is necessary to observe either the relative intensities of the intense spectral lines or the energy shifts of the weak spectral lines in order to determine each coupling constant individually.

It is probable that the observation of the weak spectral lines is more advantageous than the measurements of the relative intensities of the intense spectral lines, experimentally.

1. INTRODUCTION

High resolution nuclear magnetic resonance spectra of fluorine substituted benzenes were reported early by Gutowsky, Meyer and McCall[1] and by Baker[2], and they interpreted their experimental spectra in consequence of chemical equivalence of nuclei in each group of protons and fluorines. Thereafter, the resolving power of nuclear magnetic resonance experiments has been improving and the detailed work on a large number of substituted benzenes was reported by Gutowsky, Holm, Saika and Williams[3]. They concluded that the coupling constants depend somewhat upon the substituents but the values of them are determined mainly by the atomic species themselves and by their relative positions in benzene ring. Bak, Shoolery and Williams[4] carried out the experiments on deuterium substituted fluorobenzenes and reported that the ortho and the meta fluorine-proton coupling constants have different values. Further, many works were appeared about the spin-spin couplings in benzene derivatives.[5]~[9]

In para-difluorobenzene, it seems that two fluorine nuclei and four protons are chemically equivalent, but as far as the values of the coupling constants between the group of the fluorine nuclei and that of the protons are not the same, the spectra in this molecule are to show complicated fine structures.[10]

There are six spin-spin coupling constants in this molecule. We have distinguished the ortho and the meta fluorine-proton coupling constants and taken up the ortho proton-proton and the para fluorine-fluorine coupling constants, and analyzed the spectra as a six-spin system of A_2B_4 type with a symmetry V_h. We have ignored the para proton-proton coupling constant here, because this was reported[3] to be less than 0.5 cps and it seemed that this value was smaller than the other coupling constants. Although the meta proton-proton coupling constant was reported[3],[6] to be approximately 2 cps, we have found that this does not affect the spectra so far as this is treated as a perturbation.

2. ANALYSIS OF FINE STRUCTURES

The Hamiltonian for para-difluorobenzene can be written as[3],[10]~[14]

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)};$$
$$\mathcal{H}^{(0)} = \mathcal{H}^{(0)}(H) + \mathcal{H}^{(0)}(F),$$
$$\mathcal{H}^{(0)}(H) = (\gamma_H/2\pi)H_H I_z(H),$$
$$\mathcal{H}^{(0)}(F) = (\gamma_F/2\pi)H_F I_z(F);$$
$$\mathcal{H}^{(1)} = \mathcal{H}^{(1)}(HH) + \mathcal{H}^{(1)}(FH) + \mathcal{H}^{(1)}(FF),$$
$$\mathcal{H}^{(1)}(HH) = J_o(HH)[I(H_1)\cdot I(H_2) + I(H_3)\cdot I(H_4)],$$
$$\mathcal{H}^{(1)}(FH) = J_o(FH)[I(F_1)\cdot I(H_{1,3}) + I(F_2)\cdot I(H_{2,4})]$$
$$+ J_m(FH)[I(F_1)\cdot I(H_{2,4}) + I(F_2)\cdot I(H_{1,3})],$$
$$\mathcal{H}^{(1)}(FF) = J_p(FF)[I(F_1)\cdot I(F_2)];$$

where protons and fluorine nuclei are labeled according to Fig. 1, and

$$I_z(F) = I_z(F_1) + I_z(F_2),$$
$$I_z(H) = I_z(H_1) + I_z(H_2) + I_z(H_3) + I_z(H_4),$$
$$I(H_{i,j}) = I(H_i) + I(H_j).$$

In the equations given above, energy is expressed in units of cps and $I(i)$ is the spin angular momentum vector in units of $\hbar$ of nucleus i, and $I_z(i)$, its z-component. H_i represents the local magnetic field at nucleus i and γ_i, the gyromagnetic ratio of nucleus i. $J_o(HH)$, $J_o(FH)$, $J_m(FH)$ and $J_p(FF)$ are the ortho proton-proton, the ortho fluorine-proton, the meta fluorine-proton and the para fluorine-fluorine coupling constants, respectively.

We have treated $\mathcal{H}^{(1)}$ as a perturbation to the Zeeman Hamiltonian $\mathcal{H}^{(0)}$. In order to find the matrix elements of $\mathcal{H}^{(1)}$, we have chosen the zero-order spin wave functions utilizing the irreducible representations A, B_1, B_2 and B_3 of V_h symmetry, where z-axis perpendicular to the molecular plane and x-axis parallel to the F–F axis were taken. These sixty four zero-order spin wave functions
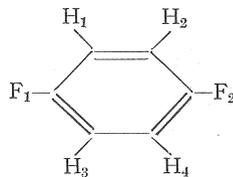
Fig. 1

are shown in Table I. In the designations of the spin states employed in Table I, numbers written in front of the irreducible representations of V_h symmetry are introduced in order to distinguish the degenerate spin states and the former and the latter of the subscripts represent the eigen-values, $M(F)$ and $M(H)$, of $I_z(F)$ and $I_z(H)$, respectively. The zero-order spin wave functions in Table I are expressed according to the following scheme:

$|\, \mathbf{I}(F),\ M(F);\ \mathbf{I}(H_{1,3}),\ M(H_{1,3});\ \mathbf{I}(H_{2,4}),\ M(H_{2,4})\rangle.$

TABLE I. Zero-order spin wave functions for para-difluorobenzene.

Designation	Spin wave function	Designation	Spin wave function
$(A)_{1,2}$	$|1,1;\,1,1;\,1,1\rangle$	$(A)_{-1,-2}$	$|1,-1;\,1,-1;\,1,-1\rangle$
$(A)_{1,1}$	$\frac{1}{\sqrt{2}}[|1,1;\,1,0;\,1,1\rangle+|1,1;\,1,1;\,1,0\rangle]$	$(A)_{-1,-1}$	$\frac{1}{\sqrt{2}}[|1,-1;\,1,0;\,1,-1\rangle+|1,-1;\,1,-1;1,0\rangle]$
$(B_1)_{1,1}$	$\frac{1}{\sqrt{2}}[|1,1;\,0,0;\,1,1\rangle-|1,1;\,1,1;\,0,0\rangle]$	$(B_1)_{-1,-1}$	$\frac{1}{\sqrt{2}}[|1,-1;\,0,0;\,1,-1\rangle-|1,-1;\,1,-1;0,0\rangle]$
$(B_2)_{1,1}$	$\frac{1}{\sqrt{2}}[|1,1;\,1,0;\,1,1\rangle-|1,1;\,1,1;\,1,0\rangle]$	$(B_2)_{-1,-1}$	$\frac{1}{\sqrt{2}}[|1,-1;\,1,0;\,1,-1\rangle-|1,-1;\,1,-1;1,0\rangle]$
$(B_3)_{1,1}$	$\frac{1}{\sqrt{2}}[|1,1;\,0,0;\,1,1\rangle+|1,1;\,1,1;\,0,0\rangle]$	$(B_3)_{-1,-1}$	$\frac{1}{\sqrt{2}}[|1,-1;\,0,0;\,1,-1\rangle+|1,-1;\,1,-1;0,0\rangle]$
$1(A)_{1,0}$	$\frac{1}{\sqrt{2}}[|1,1;\,1,-1;\,1,1\rangle+|1,1;\,1,1;\,1,-1\rangle]$	$1(A)_{-1,0}$	$\frac{1}{\sqrt{2}}[|1,-1;\,1,-1;\,1,1\rangle+|1,-1;\,1,1;1,-1\rangle]$
$2(A)_{1,0}$	$|1,1;\,1,0;\,1,0\rangle$	$2(A)_{-1,0}$	$|1,-1;\,1,0;\,1,0\rangle$
$3(A)_{1,0}$	$|1,1;\,0,0;\,0,0\rangle$	$3(A)_{-1,0}$	$|1,-1;\,0,0;\,0,0\rangle$
$(B_1)_{1,0}$	$\frac{1}{\sqrt{2}}[|1,1;\,1,0;\,0,0\rangle-|1,1;\,0,0;\,1,0\rangle]$	$(B_1)_{-1,0}$	$\frac{1}{\sqrt{2}}[|1,-1;\,1,0;\,0,0\rangle-|1,-1;\,0,0;1,0\rangle]$
$(B_2)_{1,0}$	$\frac{1}{\sqrt{2}}[|1,1;\,1,-1;\,1,1\rangle-|1,1;\,1,1;\,1,-1\rangle]$	$(B_2)_{-1,0}$	$\frac{1}{\sqrt{2}}[|1,-1;\,1,-1;\,1,1\rangle-|1,-1;\,1,1;1,-1\rangle]$
$(B_3)_{1,0}$	$\frac{1}{\sqrt{2}}[|1,1;\,1,0;\,0,0\rangle+|1,1;\,0,0;\,1,0\rangle]$	$(B_3)_{-1,0}$	$\frac{1}{\sqrt{2}}[|1,-1;\,1,0;\,0,0\rangle+|1,-1;\,0,0;1,0\rangle]$
$(A)_{1,-1}$	$\frac{1}{\sqrt{2}}[|1,1;\,1,0;\,1,-1\rangle+|1,1;\,1,-1;\,1,0\rangle]$	$(A)_{-1,1}$	$\frac{1}{\sqrt{2}}[|1,-1;\,1,0;\,1,1\rangle+|1,-1;\,1,1;1,0\rangle]$
$(B_1)_{1,-1}$	$\frac{1}{\sqrt{2}}[|1,1;\,0,0;\,1,-1\rangle-|1,1;\,1,-1;\,0,0\rangle]$	$(B_1)_{-1,1}$	$\frac{1}{\sqrt{2}}[|1,-1;\,0,0;\,1,1\rangle-|1,-1;\,1,1;0,0\rangle]$
$(B_2)_{1,-1}$	$\frac{1}{\sqrt{2}}[|1,1;\,1,0;\,1,-1\rangle-|1,1;\,1,-1;\,1,0\rangle]$	$(B_2)_{-1,1}$	$\frac{1}{\sqrt{2}}[|1,-1;\,1,0;\,1,1\rangle-|1,-1;\,1,1;1,0\rangle]$
$(B_3)_{1,-1}$	$\frac{1}{\sqrt{2}}[|1,1;\,0,0;\,1,-1\rangle+|1,1;\,1,-1;\,0,0\rangle]$	$(B_3)_{-1,1}$	$\frac{1}{\sqrt{2}}[|1,-1;\,0,0;\,1,1\rangle+|1,-1;\,1,1;0,0\rangle]$
$(A)_{1,-2}$	$|1,1;\,1,-1;\,1,-1\rangle$	$(A)_{-1,2}$	$|1,-1;\,1,1;\,1,1\rangle$
$(A)_{0,2}$	$|1,0;\,1,1;\,1,1\rangle$	$(A)_{0,-2}$	$|1,0;\,1,-1;\,1,-1\rangle$
$(B_2)_{0,2}$	$|0,0;\,1,1;\,1,1\rangle$	$(B_2)_{0,-2}$	$|0,0;\,1,-1;\,1,-1\rangle$
$1(A)_{0,1}$	$\frac{1}{\sqrt{2}}[|1,0;\,1,1;\,1,0\rangle+|1,0;\,1,0;\,1,1\rangle]$	$1(A)_{0,-1}$	$\frac{1}{\sqrt{2}}[|1,0;\,1,-1;\,1,0\rangle+|1,0;\,1,0;1,-1\rangle]$
$2(A)_{0,1}$	$\frac{1}{\sqrt{2}}[|0,0;\,1,1;\,1,0\rangle-|0,0;\,1,0;\,1,1\rangle]$	$2(A)_{0,-1}$	$\frac{1}{\sqrt{2}}[|0,0;\,1,-1;\,1,0\rangle-|0,0;\,1,0;1,-1\rangle]$
$1(B_1)_{0,1}$	$\frac{1}{\sqrt{2}}[|1,0;\,1,1;\,0,0\rangle-|1,0;\,0,0;\,1,1\rangle]$	$1(B)_{0,-1}$	$\frac{1}{\sqrt{2}}[|1,0;\,1,-1;\,0,0\rangle-|1,0;\,0,0;1,-1\rangle]$
$2(B_1)_{0,1}$	$\frac{1}{\sqrt{2}}[|0,0;\,1,1;\,0,0\rangle+|0,0;\,0,0;\,1,1\rangle]$	$2(B_1)_{0,-1}$	$\frac{1}{\sqrt{2}}[|0,0;\,1,-1;\,0,0\rangle+|0,0;\,0,0;1,-1\rangle]$
$1(B_2)_{0,1}$	$\frac{1}{\sqrt{2}}[|1,0;\,1,1;\,1,0\rangle-|1,0;\,1,0;\,1,1\rangle]$	$1(B_2)_{0,-1}$	$\frac{1}{\sqrt{2}}[|1,0;\,1,-1;\,1,0\rangle-|1,0;\,1,0;1,-1\rangle]$
$2(B_2)_{0,1}$	$\frac{1}{\sqrt{2}}[|0,0;\,1,1;\,1,0\rangle+|0,0;\,1,0;\,1,1\rangle]$	$2(B_2)_{0,-1}$	$\frac{1}{\sqrt{2}}[|0,0;\,1,-1;\,1,0\rangle+|0,0;\,1,0;1,-1\rangle]$
$1(B_3)_{0,1}$	$\frac{1}{\sqrt{2}}[|1,0;\,1,1;\,0,0\rangle+|1,0;\,0,0;\,1,1\rangle]$	$1(B_3)_{0,-1}$	$\frac{1}{\sqrt{2}}[|1,0;\,1,-1;\,0,0\rangle+|1,0;\,0,0;1,-1\rangle]$
$2(B_3)_{0,1}$	$\frac{1}{\sqrt{2}}[|0,0;\,1,1;\,0,0\rangle-|0,0;\,0,0;\,1,1\rangle]$	$2(B_3)_{0,-1}$	$\frac{1}{\sqrt{2}}[|0,0;\,1,-1;\,0,0\rangle-|0,0;\,0,0;1,-1\rangle]$

Desig-nation	Spin wave function	Desig-nation	Spin wave function
$1(A)_{0,0}$	$\frac{1}{\sqrt{2}}[\lvert 1,0;1,-1;1,1\rangle+\lvert 1,0;1,1;1,-1\rangle]$	$1(B_2)_{0,0}$	$\frac{1}{\sqrt{2}}[\lvert 0,0;1,-1;1,1\rangle+\lvert 0,0;1,1;1,-1\rangle]$
$2(A)_{0,0}$	$\lvert 1,0;1,0;1,0\rangle$	$2(B_2)_{0,0}$	$\lvert 0,0;1,0;1,0\rangle$
$3(A)_{0,0}$	$\lvert 1,0;0,0;0,0\rangle$	$3(B_2)_{0,0}$	$\lvert 0,0;0,0;0,0\rangle$
$4(A)_{0,0}$	$\frac{1}{\sqrt{2}}[\lvert 0,0;1,-1;1,1\rangle-\lvert 0,0;1,1;1,-1\rangle]$	$4(B_2)_{0,0}$	$\frac{1}{\sqrt{2}}[\lvert 1,0;1,-1;1,1\rangle-\lvert 1,0;1,1;1,-1\rangle]$
$1(B_1)_{0,0}$	$\frac{1}{\sqrt{2}}[\lvert 0,0;1,0;0,0\rangle+\lvert 0,0;0,0;1,0\rangle]$	$1(B_3)_{0,0}$	$\frac{1}{\sqrt{2}}[\lvert 1,0;1,0;0,0\rangle+\lvert 1,0;0,0;1,0\rangle]$
$2(B_1)_{0,0}$	$\frac{1}{\sqrt{2}}[\lvert 1,0;1,0;0,0\rangle-\lvert 1,0;0,0;1,0\rangle]$	$2(B_3)_{0,0}$	$\frac{1}{\sqrt{2}}[\lvert 0,0;1,0;0,0\rangle-\lvert 0,0;0,0;1,0\rangle]$

We have employed the representation that the group of the protons and that of the fluorine nuclei were space-quantized independently, because the matrix elements for $\Delta M(F)=\pm1$ and $\Delta M(H)=\mp1$ are the order of $J^2/[(\gamma_H H_H-\gamma_F H_F)\cdot(2\pi)^{-1}]\sim0.5\times10^{-4}$ which is negligible small compared with our observable quantities.

Utilizing the zero-order spin wave functions given in Table I, the 64×64 secular determinant for this case has been factored into thirty six 1×1, eight 2×2 and four 3×3 determinants. Eight 2×2 determinants were occurred from the degeneracies of the following states: $1(A)_{0,\pm1}$ and $2(A)_{0,\pm1}$; $1(B_1)_{0,\pm1}$ and $2(B_1)_{0,\pm1}$; $1(B_2)_{0,\pm1}$ and $2(B_2)_{0,\pm1}$; $1(B_3)_{0,\pm1}$ and $2(B_3)_{0,\pm1}$; and four 3×3 determinants from $1(A)_{\pm1,0}$, $2(A)_{\pm1,0}$ and $3(A)_{\pm1,0}$; $1(A)_{0,0}$, $2(A)_{0,0}$ and $3(A)_{0,0}$; $1(B_2)_{0,0}$, $2(B_2)_{0,0}$ and $3(B_2)_{0,0}$. These 3×3 determinants have been able to solve exactly but further degeneracies still remained.

For these twelve sets of the degenerate spin wave functions, we have been able to choose the new mixed spin wave functions as the eigen-functions of $\mathcal{H}$, as shown in Table II.

We must see the selection rule using these spin wave functions but this calculation is comparatively easy by the reason that the only transitions between the states which belong

TABLE II.   The new spin wave functions for twelve degenerate sets.

$$1'(A)_{\pm1,0}=\frac{1}{\sqrt{2}}2(A)_{\pm1,0}+\frac{1}{\sqrt{2}}3(A)_{\pm1,0}$$

$$2'(A)_{\pm1,0}=\frac{1}{\sqrt{2}}1(A)_{\pm1,0}+\frac{1}{2}2(A)_{\pm1,0}-\frac{1}{2}3(A)_{\pm1,0}$$

$$3'(A)_{\pm1,0}=\frac{1}{\sqrt{2}}1(A)_{\pm1,0}-\frac{1}{2}2(A)_{\pm1,0}+\frac{1}{2}3(A)_{\pm1,0}$$

$$1'(A)_{0,0}=\frac{1}{\sqrt{2}}2(A)_{0,0}+\frac{1}{\sqrt{2}}3(A)_{0,0}$$

$$2'(A)_{0,0}=\frac{1}{\sqrt{2}}1(A)_{0,0}+\frac{1}{2}2(A)_{0,0}-\frac{1}{2}3(A)_{0,0}$$

$$3'(A)_{0,0}=\frac{1}{\sqrt{2}}1(A)_{0,0}-\frac{1}{2}2(A)_{0,0}+\frac{1}{2}3(A)_{0,0}$$

$$1'(B_2)_{0,0}=\frac{1}{\sqrt{2}}2(B_2)_{0,0}+\frac{1}{\sqrt{2}}3(B_2)_{0,0}$$

$$2'(B_2)_{0,0}=\frac{1}{\sqrt{2}}1(B_2)_{0,0}+\frac{1}{2}2(B_2)_{0,0}-\frac{1}{2}3(B_2)_{0,0}$$

$$3'(B_2)_{0,0} = \frac{1}{\sqrt{2}} 1(B_2)_{0,0} - \frac{1}{2} 2(B_2)_{0,0} + \frac{1}{2} 3(B_2)_{0,0}$$

$$1'(A)_{0,\pm1} = C_1 1(A)_{0,\pm1} - C_2 2(A)_{0,\pm1}$$

$$2'(A)_{0,\pm1} = C_2 1(A)_{0,\pm1} + C_1 2(A)_{0,\pm1}$$

$$1'(B_1)_{0,\pm1} = C_3 1(B_1)_{0,\pm1} - C_4 2(B_1)_{0,\pm1}$$

$$2'(B_1)_{0,\pm1} = C_4 1(B_1)_{0,\pm1} + C_3 2(B_1)_{0,\pm1}$$

$$1'(B_2)_{0,\pm1} = C_3 1(B_2)_{0,\pm1} - C_4 2(B_2)_{0,\pm1}$$

$$2'(B_2)_{0,\pm1} = C_4 1(B_2)_{0,\pm1} + C_3 2(B_2)_{0,\pm1}$$

$$1'(B_3)_{0,\pm1} = C_1 1(B_3)_{0,\pm1} - C_2 2(B_3)_{0,\pm1}$$

$$2'(B_3)_{0,\pm1} = C_2 1(B_3)_{0,\pm1} + C_1 2(B_3)_{0,\pm1}$$

$$C_1^2 = [J_o(FH) - J_m(FH)]^2 / [\{J_o(HH) + J_p(FF) - J_+\}^2 + \{J_o(FH) - J_m(FH)\}^2]$$

$$C_2^2 = [J_o(HH) + J_p(FF) - J_+]^2 / [\{J_o(HH) + J_p(FF) - J_+\}^2 + \{J_o(FH) - J_m(FH)\}^2]$$

$$C_3^2 = [J_o(HH) - J_p(FF) - J_-]^2 / [\{J_o(HH) - J_p(FF) - J_-\}^2 + \{J_o(FH) - J_m(FH)\}^2]$$

$$C_4^2 = [J_o(FH) - J_m(FH)]^2 / [\{J_o(HH) - J_p(FF) - J_-\}^2 + \{J_o(FH) - J_m(FH)\}^2]$$

$$J_\pm = [J_o(HH) \pm J_p(FF)]^2 + [J_o(FH) - J_m(FH)]^2$$

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to the same symmetry species and satisfy $\Delta M(F) = \pm1$ for the fluorine resonance or $\Delta M(H) = \pm1$ for the proton resonance, are allowed.

The energy shifts in cps and the relative intensities for the allowed transitions, we have obtained theoretically, are summarized in Table III and Table IV for the proton and the fluorine resonances, respectively.

3. DISCUSSION

As seen from the results tabulated in Table III and Table IV, it is expected that ten spectral lines in the proton resonance and nineteen in the fluorine are to observe theoretically, but some of them have weak intensities and can be hardly observed.

We have carried out the preliminary experiments on the proton resonance and obtained the spectra shown in Fig. 2, but from our data with much wiggle, we have not been able to determine each spin-spin coupling constant uniquely.

First, using the average values for each coupling constant, reported[3]~[9] in many varieties of benzene derivatives, we have tried to reproduce the theoretical patterns as shown in Fig. 3 and Fig. 4 for the proton and the fluorine resonances, respectively. In these calculations, the values of the spin-spin coupling constants used are $J_o(HH) = 8.0$ cps, $J_o(FH) = 9.1$ cps, $J_m(FH) = 6.0$ cps and $J_p(FF) = 13.2$ cps.
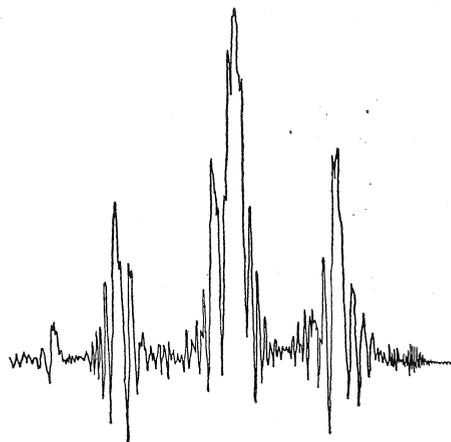

Fig. 2. Proton resonance spectra in para-difluorobenzene.

From this estimation, we have seen that the difference of $J_o(FH)$ and $J_m(FH)$, which is able to find by observation of either the relative intensities of the intense spectral lines or the energy shifts of the weak ones, is required in order to determine each spin-spin coupling constant uniquely.

It seems to be rather advantageous than to measure the relative intensities of the intense spectral lines, to find the energy shifts of the weak ones, in high resolution nuclear magnetic resonance experiments.

More precise experiments on this molecule are in progress for both the proton and the fluorine resonances.

TABLE III. Theoretical energy shifts (in cps) and intensities for proton resonance spectra in para-difluorobenzene.

	Transition	Energy shift	Relative intensity	
A	$(B_2)_{0,2} \longleftrightarrow 1'(B_2)_{0,1}$	$\frac{1}{2}[J_o(HH)-J_p(FF)]-\frac{1}{2}J_-$	C_3^2	$4C_3^2$
	$2'(B_1)_{0,1} \longleftrightarrow 2'(B_1)_{0,0}$		$\frac{1}{2}C_3^2$	
	$2'(B_2)_{0,1} \longleftrightarrow 4(B_2)_{0,0}$		$\frac{1}{2}C_3^2$	
	$1'(B_1)_{0,0} \longleftrightarrow 1'(B_1)_{0,-1}$		$\frac{1}{2}C_3^2$	
	$1'(B_2)_{0,0} \longleftrightarrow 1'(B_2)_{0,-1}$		$\frac{1}{2}C_3^2$	
	$2'(B_2)_{0,0} \longleftrightarrow 1'(B_2)_{0,-1}$		C_3^2	
B	$(B_2)_{0,2} \longleftrightarrow 2'(B_2)_{0,1}$	$\frac{1}{2}[J_o(HH)-J_p(FF)]+\frac{1}{2}J_-$	C_4^2	$4C_4^2$
	$1'(B_1)_{0,1} \longleftrightarrow 2'(B_1)_{0,0}$		$\frac{1}{2}C_4^2$	
	$1'(B_2)_{0,1} \longleftrightarrow 4(B_2)_{0,0}$		$\frac{1}{2}C_4^2$	
	$1'(B_1)_{0,0} \longleftrightarrow 2'(B_1)_{0,-1}$		$\frac{1}{2}C_4^2$	
	$1'(B_2)_{0,0} \longleftrightarrow 2'(B_2)_{0,-1}$		$\frac{1}{2}C_4^2$	
	$2'(B_2)_{0,0} \longleftrightarrow 2'(B_2)_{0,-1}$		C_4^2	
C	$(A)_{0,2} \longleftrightarrow 1'(A)_{0,1}$	$\frac{1}{2}[J_o(HH)+J_p(FF)]-\frac{1}{2}J_+$	C_1^2	$4C_1^2$
	$2'(A)_{0,1} \longleftrightarrow 4(A)_{0,0}$		$\frac{1}{2}C_1^2$	
	$2'(B_3)_{0,1} \longleftrightarrow 2'(B_3)_{0,0}$		$\frac{1}{2}C_1^2$	
	$1'(A)_{0,0} \longleftrightarrow 1'(A)_{0,-1}$		$\frac{1}{2}C_1^2$	
	$2'(A)_{0,0} \longleftrightarrow 1'(A)_{0,-1}$		C_1^2	
	$1'(B_3)_{0,0} \longleftrightarrow 1'(B_3)_{0,-1}$		$\frac{1}{2}C_1^2$	

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	Transition	Energy shift	Relative intensity	
D	$(A)_{0,2} \longleftrightarrow 2'(A)_{0,1}$	$\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]+\frac{1}{2}J+$	C_2^2	$4C_2^2$
	$1'(A)_{0,1} \longleftrightarrow 4(A)_{0,0}$		$\frac{1}{2}C_2^2$	
	$1'(B_3)_{0,1} \longleftrightarrow 2'(B_3)_{0,0}$		$\frac{1}{2}C_2^2$	
	$1'(A)_{0,0} \longleftrightarrow 2'(A)_{0,-1}$		$\frac{1}{2}C_2^2$	
	$2'(A)_{0,0} \longleftrightarrow 2'(A)_{0,-1}$		C_2^2	
	$1'(B_3)_{0,0} \longleftrightarrow 2'(B_3)_{0,-1}$		$\frac{1}{2}C_2^2$	
E	$(A)_{1,2} \longleftrightarrow (A)_{1,1}$	$\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$	1	8
	$(A)_{1,1} \longleftrightarrow 1'(A)_{1,0}$		$\frac{1}{2}$	
	$(A)_{1,1} \longleftrightarrow 2'(A)_{1,0}$		1	
	$(B_1)_{1,1} \longleftrightarrow (B_1)_{1,0}$		$\frac{1}{2}$	
	$(B_2)_{1,1} \longleftrightarrow (B_2)_{1,0}$		$\frac{1}{2}$	
	$(B_3)_{1,1} \longleftrightarrow (B_3)_{1,0}$		$\frac{1}{2}$	
	$1'(A)_{1,0} \longleftrightarrow (A)_{1,-1}$		$\frac{1}{2}$	
	$2'(A)_{1,0} \longleftrightarrow (A)_{1,-1}$		1	
	$(B_1)_{1,0} \longleftrightarrow (B_1)_{1,-1}$		$\frac{1}{2}$	
	$(B_2)_{1,0} \longleftrightarrow (B_2)_{1,-1}$		$\frac{1}{2}$	
	$(B_3)_{1,0} \longleftrightarrow (B_3)_{1,-1}$		$\frac{1}{2}$	
A'	$1'(B_1)_{0,1} \longleftrightarrow 1'(B_1)_{0,0}$	$-\frac{1}{2}[J_o(\mathrm{HH})-J_p(\mathrm{FF})]+\frac{1}{2}J-$	$\frac{1}{2}C_3^2$	$4C_3^2$
	$1'(B_2)_{0,1} \longleftrightarrow 1'(B_2)_{0,0}$		$\frac{1}{2}C_3^2$	
	$1'(B_2)_{0,1} \longleftrightarrow 2'(B_2)_{0,0}$		C_3^2	
	$2'(B_1)_{0,0} \longleftrightarrow 2'(B_1)_{0,-1}$		$\frac{1}{2}C_3^2$	
	$4(B_2)_{0,0} \longleftrightarrow 2'(B_2)_{0,-1}$		$\frac{1}{2}C_3^2$	
	$1'(B_2)_{0,-1} \longleftrightarrow (B_2)_{0,-2}$		C_3^2	
B'	$2'(B_1)_{0,1} \longleftrightarrow 1'(B_1)_{0,0}$	$-\frac{1}{2}[J_o(\mathrm{HH})-J_p(\mathrm{FF})]-\frac{1}{2}J-$	$\frac{1}{2}C_4^2$	$4C_4^2$
	$2'(B_2)_{0,1} \longleftrightarrow 1'(B_2)_{0,0}$		C_4^2	
	$2'(B_2)_{0,1} \longleftrightarrow 2'(B_2)_{0,0}$		$\frac{1}{2}C_4^2$	
	$2'(B_1)_{0,0} \longleftrightarrow 1'(B_1)_{0,-1}$		$\frac{1}{2}C_4^2$	

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	Transition	Energy shift	Relative intensity	
	$4(B_2)_{0,0} \longleftrightarrow 1'(B_2)_{0,-1}$		$\frac{1}{2}C_4^2$	
	$2'(B_2)_{0,}{}^-{}_1 \longleftrightarrow (B_2)_{0,-2}$		C_4^2	
C'	$1'(A)_{0,1} \longleftrightarrow 1'(A)_{0,0}$		$\frac{1}{2}C_1^2$	
	$1'(A)_{0,1} \longleftrightarrow 2'(A)_{0,0}$		C_1^2	
	$1'(B_3)_{0,1} \longleftrightarrow 1'(B_3)_{0,0}$	$-\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]+\frac{1}{2}J+$	$\frac{1}{2}C_1^2$	$4C_1^2$
	$4(A)_{0,0} \longleftrightarrow 2'(A)_{0,-1}$		$\frac{1}{2}C_1^2$	
	$2'(B_3)_{0,0} \longleftrightarrow 2'(B_3)_{0,-1}$		$\frac{1}{2}C_1^2$	
	$1'(A)_{0,-1} \longleftrightarrow (A)_{0,-2}$		C_1^2	
D'	$2'(A)_{0,1} \longleftrightarrow 1'(A)_{0,0}$		$\frac{1}{2}C_2^2$	
	$2'(A)_{0,1} \longleftrightarrow 2'(A)_{0,0}$		C_2^2	
	$2'(B_3)_{0,1} \longleftrightarrow 1'(B_3)_{0,0}$	$-\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]-\frac{1}{2}J+$	$\frac{1}{2}C_2^2$	$4C_2^2$
	$4(A)_{0,0} \longleftrightarrow 1'(A)_{0,-1}$		$\frac{1}{2}C_2^2$	
	$2'(B_3)_{0,0} \longleftrightarrow 1'(B_3)_{0,-1}$		$\frac{1}{2}C_2^2$	
	$2'(A)_{0,-1} \longleftrightarrow (A)_{0,-2}$		C_2^2	
E'	$(A)_{-1,2} \longleftrightarrow (A)_{-1,1}$		1	
	$(A)_{-1,1} \longleftrightarrow 1'(A)_{-1,0}$		$\frac{1}{2}$	
	$(A)_{-1,1} \longleftrightarrow 2'(A)_{-1,0}$		1	
	$(B_1)_{-1,1} \longleftrightarrow (B_1)_{-1,0}$		$\frac{1}{2}$	
	$(B_2)_{-1,1} \longleftrightarrow (B_2)_{-1,0}$		$\frac{1}{2}$	
	$(B_3)_{-1,1} \longleftrightarrow (B_3)_{-1,0}$	$-\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$	$\frac{1}{2}$	8
	$1'(A)_{-1,0} \longleftrightarrow (A)_{-1,-1}$		$\frac{1}{2}$	
	$2'(A)_{-1,0} \longleftrightarrow (A)_{-1,-1}$		1	
	$(B_1)_{-1,0} \longleftrightarrow (B_1)_{-1,-1}$		$\frac{1}{2}$	
	$(B_2)_{-1,0} \longleftrightarrow (B_2)_{-1,-1}$		$\frac{1}{2}$	
	$(B_3)_{-1,0} \longleftrightarrow (B_3)_{-1,-1}$		$\frac{1}{2}$	
	$(A)_{-1,-1} \longleftrightarrow (A)_{-1,-2}$		1	

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TABLE IV. Theoretical energy shifts (in cps) and intensities for fluorine resonance spectra in para-difluorobenzene.

	Transition	Energy shift	Relative intensity	
A	$1'(A)_{1,0} \longleftrightarrow 1'(A)_{0,0}$	0	$\frac{1}{2}$	6
	$2'(A)_{1,0} \longleftrightarrow 2'(A)_{0,0}$		$\frac{1}{2}$	
	$3'(A)_{1,0} \longleftrightarrow 3'(A)_{0,0}$		$\frac{1}{2}$	
	$(B_1)_{1,0} \longleftrightarrow 2'(B_1)_{0,0}$		$\frac{1}{2}$	
	$(B_2)_{1,0} \longleftrightarrow 4(B_2)_{0,0}$		$\frac{1}{2}$	
	$(B_3)_{1,0} \longleftrightarrow 1'(B_3)_{0,0}$		$\frac{1}{2}$	
	$1'(A)_{0,0} \longleftrightarrow 1'(A)_{-1,0}$		$\frac{1}{2}$	
	$2'(A)_{0,0} \longleftrightarrow 2'(A)_{-1,0}$		$\frac{1}{2}$	
	$3'(A)_{0,0} \longleftrightarrow 3'(A)_{-1,0}$		$\frac{1}{2}$	
	$2'(B_1)_{0,0} \longleftrightarrow (B_1)_{-1,0}$		$\frac{1}{2}$	
	$4(B_2)_{0,0} \longleftrightarrow (B_2)_{-1,0}$		$\frac{1}{2}$	
	$1'(B_3)_{0,0} \longleftrightarrow (B_3)_{-1,0}$		$\frac{1}{2}$	
B	$(A)_{1,2} \longleftrightarrow (A)_{0,2}$	$J_o(\mathrm{FH}) + J_m(\mathrm{FH})$	$\frac{1}{2}$	1
	$(A)_{0,2} \longleftrightarrow (A)_{-1,2}$		$\frac{1}{2}$	
C	$(A)_{1,1} \longleftrightarrow 2'(A)_{0,2}$	$\frac{1}{2}[J_o(\mathrm{FH}) + J_m(\mathrm{FH})]$	$\frac{1}{2}C_2^2$	C_2^2
	$(B_3)_{1,1} \longleftrightarrow 2'(B_3)_{0,1}$	$+\frac{1}{2}[J_o(\mathrm{HH}) + J_p(\mathrm{FF})] + \frac{1}{2}J_+$	$\frac{1}{2}C_2^2$	
D	$(A)_{1,1} \longleftrightarrow 1'(A)_{0,1}$	$\frac{1}{2}[J_o(\mathrm{FH}) + J_m(\mathrm{FH})]$	$\frac{1}{2}C_1^2$	C_1^2
	$(B_3)_{1,1} \longleftrightarrow 1'(B_3)_{0,1}$	$+\frac{1}{2}[J_o(\mathrm{HH}) + J_p(\mathrm{FF})] - \frac{1}{2}J_+$	$\frac{1}{2}C_1^2$	
E	$1'(B_1)_{0,1} \longleftrightarrow (B_1)_{-1,1}$	$\frac{1}{2}[J_o(\mathrm{FH}) + J_m(\mathrm{FH})]$	$\frac{1}{2}C_4^2$	C_4^2
	$1'(B_2)_{0,1} \longleftrightarrow (B_2)_{-1,1}$	$+\frac{1}{2}[J_o(\mathrm{HH}) - J_p(\mathrm{FF})] + \frac{1}{2}J_-$	$\frac{1}{2}C_4^2$	
F	$2'(B_1)_{0,1} \longleftrightarrow (B_1)_{-1,1}$	$\frac{1}{2}[J_o(\mathrm{FH}) + J_m(\mathrm{FH})]$	$\frac{1}{2}C_3^2$	C_3^2
	$2'(B_2)_{0,1} \longleftrightarrow (B_2)_{-1,1}$	$+\frac{1}{2}[J_o(\mathrm{HH}) - J_p(\mathrm{FF})] - \frac{1}{2}J_-$	$\frac{1}{2}C_3^2$	

	Transition	Energy shift	Relative intensity	
G	$(B_1)_{1,1} \longleftrightarrow 2'(B_1)_{0,1}$ $(B_2)_{1,1} \longleftrightarrow 2'(B_2)_{0,1}$	$\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $-\frac{1}{2}[J_o(\mathrm{HH})-J_p(\mathrm{FF})]+\frac{1}{2}J_-$	$\frac{1}{2}\mathrm{C}_3^2$ $\frac{1}{2}\mathrm{C}_3^2$	C_3^2
H	$(B_1)_{1,1} \longleftrightarrow 1'(B_1)_{0,1}$ $(B_2)_{1,1} \longleftrightarrow 1'(B_2)_{0,1}$	$\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $-\frac{1}{2}[J_o(\mathrm{HH})-J_p(\mathrm{FF})]-\frac{1}{2}J_-$	$\frac{1}{2}\mathrm{C}_4^2$ $\frac{1}{2}\mathrm{C}_4^2$	C_4^2
I	$1'(A)_{0,1} \longleftrightarrow (A)_{-1,1}$ $1'(B_3)_{0,1} \longleftrightarrow (B_3)_{-1,1}$	$\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $-\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]+\frac{1}{2}J_+$	$\frac{1}{2}\mathrm{C}_1^2$ $\frac{1}{2}\mathrm{C}_1^2$	C_1^2
J	$2'(A)_{0,1} \longleftrightarrow (A)_{-1,1}$ $2'(B_3)_{0,1} \longleftrightarrow (B_3)_{-1,1}$	$\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $-\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]-\frac{1}{2}J_+$	$\frac{1}{2}\mathrm{C}_2^2$ $\frac{1}{2}\mathrm{C}_2^2$	C_2^2
B'	$(A)_{1,-2} \longleftrightarrow (A)_{0,-2}$ $(A)_{0,-2} \longleftrightarrow (A)_{-1,-2}$	$-[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$	$\frac{1}{2}$ $\frac{1}{2}$	1
C'	$2'(A)_{0,-1} \longleftrightarrow (A)_{-1,-1}$ $2'(B_3)_{0,-1} \longleftrightarrow (B_3)_{-1,-1}$	$-\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $-\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]-\frac{1}{2}J_+$	$\frac{1}{2}\mathrm{C}_2^2$ $\frac{1}{2}\mathrm{C}_2^2$	C_2^2
D'	$1'(A)_{0,-1} \longleftrightarrow (A)_{-1,-1}$ $1'(B_3)_{0,-1} \longleftrightarrow (B_3)_{-1,-1}$	$-\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $-\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]+\frac{1}{2}J_+$	$\frac{1}{2}\mathrm{C}_1^2$ $\frac{1}{2}\mathrm{C}_1^2$	C_1^2
E'	$(B_1)_{1,-1} \longleftrightarrow 1'(B_1)_{0,-1}$ $(B_2)_{1,-1} \longleftrightarrow 1'(B_2)_{0,-1}$	$-\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $-\frac{1}{2}[J_o(\mathrm{HH})-J_p(\mathrm{FF})]-\frac{1}{2}J_-$	$\frac{1}{2}\mathrm{C}_4^2$ $\frac{1}{2}\mathrm{C}_4^2$	C_4^2
F'	$(B_1)_{1,-1} \longleftrightarrow 2'(B_1)_{0,-1}$ $(B_2)_{1,-1} \longleftrightarrow 2'(B_2)_{0,-1}$	$-\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $-\frac{1}{2}[J_o(\mathrm{HH})-J_p(\mathrm{FF})]+\frac{1}{2}J_-$	$\frac{1}{2}\mathrm{C}_3^2$ $\frac{1}{2}\mathrm{C}_3^2$	C_3^2
G'	$2'(B_1)_{0,-1} \longleftrightarrow (B_1)_{-1,-1}$ $2'(B_2)_{0,-1} \longleftrightarrow (B_2)_{-1,-1}$	$-\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$ $+\frac{1}{2}[J_o(\mathrm{HH})-J_p(\mathrm{FF})]-\frac{1}{2}J_-$	$\frac{1}{2}\mathrm{C}_3^2$ $\frac{1}{2}\mathrm{C}_3^2$	C_3^2
H'	$1'(B_1)_{0,-1} \longleftrightarrow (B_1)_{-1,-1}$ $1'(B_2)_{0,-1} \longleftrightarrow (B_2)_{-1,-1}$	$-\frac{1}{2}[J_o(\mathrm{FH})+J_m\mathrm{FH})]$ $+\frac{1}{2}[J_o(\mathrm{HH})-J_p(\mathrm{FF})]+\frac{1}{2}J_-$	$\frac{1}{2}\mathrm{C}_4^2$ $\frac{1}{2}\mathrm{C}_4^2$	C_4^2

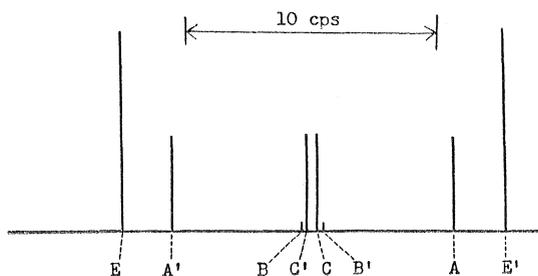|	Transition		Energy shift	Relative intensity	
I'	$(A)_{1,-1} \longleftrightarrow 1'(A)_{0,-1}$		$-\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$	$\frac{1}{2}C_1^2$	C_1^2
	$(B_3)_{1,-1} \longleftrightarrow 1'(B_3)_{0,-1}$		$+\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]-\frac{1}{2}J+$	$\frac{1}{2}C_1^2$	
J'	$(A)_{1,-1} \longleftrightarrow 2'(A)_{0,-1}$		$-\frac{1}{2}[J_o(\mathrm{FH})+J_m(\mathrm{FH})]$	$\frac{1}{2}C_2^2$	C_2^2
	$(B_3)_{1,-1} \longleftrightarrow 2'(B_3)_{0,-1}$		$+\frac{1}{2}[J_o(\mathrm{HH})+J_p(\mathrm{FF})]+\frac{1}{2}J+$	$\frac{1}{2}C_2^2$	

Fig. 3. Calculated proton spectra in para–difluorobenzene, by using the average values of the reported spin coupling constants.
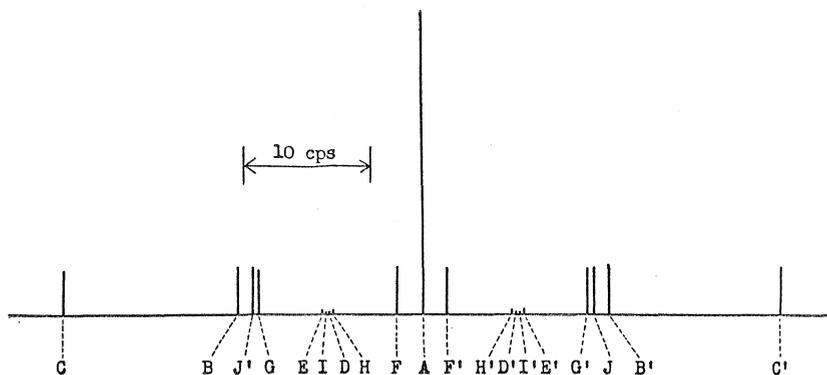

Fig. 4. Calculated fluorine spectra in para–difluorobenzene, by using the average values of the reported spin coupling constants.

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