

264. *The Nuclear Magnetic Resonance Spectra of Triphosphonitrilic 1,1-Difluoride 3,3,5,5-Tetrachloride.*

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The phosphorus and fluorine nuclear magnetic resonance spectra of triphosphonitrilic 1,1-difluoride 3,3,5,5-tetrachloride have been analysed as an AB_2X_2 system, by the full secular determinant method of Pople, Schneider, and Bernstein. The fluorine spectrum was obtained at two field strengths to provide a check on the assignments and to confirm the relative signs of the three spin-coupling constants. The appearance of positive and negative coupling constants in this molecule may have some bearing on the assumed $d\pi-p\pi$ -aromatic delocalisation in the phosphonitrilic halide systems.

It has recently been shown¹ that the compound $P_3N_3Cl_4F_2$ is triphosphonitrilic 1,1-difluoride 3,3,5,5-tetrachloride. In nuclear magnetic resonance spectroscopy this compound provides an example of an AB_2X_2 spin system in which there are three different spin-coupling constants J_{AX} , J_{BX} , and J_{AB} (defined as shown in Fig. 1) together with a

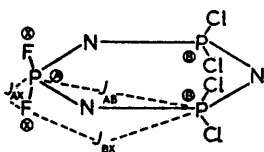


FIG. 1. *Spin-coupling constants in the AB_2X_2 system $P_3N_3Cl_4F_2$.*

field-dependent phosphorus chemical shift. The expected transition energies and relative intensities for this system may be obtained explicitly by an analysis similar to that used for simpler cases by Pople, Schneider, and Bernstein.²

The 32 basic symmetry functions for this system may be written down in such a way that they are products of the symmetry functions for the sets AB_2 and X_2 . Because two of the interacting nuclei are of a different kind from the other three the secular determinant may be factorised in such a way that the maximum order of any subdeterminant is only two. This means that explicit expressions can be found for all the phosphorus and fluorine transition energies and relative intensities. In order to do this it is necessary to introduce the following auxiliary quantities D_i and θ_i , using the notation described in ref. 2.

¹ Chapman, Paine, Searle, Smith, and White, in the press.

² Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance Spectroscopy," McGraw-Hill, New York, 1959.

$$D_i \sin^2 \theta_i = J_{AB}/\sqrt{2}, i = 1, 2 \dots 6$$

$$\begin{aligned} D_1 \cos 2\theta_1 &= \frac{1}{2}v_0(\sigma_B - \sigma_A) - \frac{1}{2}J_{BX} + \frac{1}{4}J_{AB} + \frac{1}{2}J_{AX} \\ D_2 \cos 2\theta_2 &= \frac{1}{2}v_0(\sigma_B - \sigma_A) - \frac{1}{2}J_{BX} - \frac{1}{4}J_{AB} + \frac{1}{2}J_{AX} \\ D_3 \cos 2\theta_3 &= \frac{1}{2}v_0(\sigma_B - \sigma_A) + \frac{1}{4}J_{AB} \\ D_4 \cos 2\theta_4 &= \frac{1}{2}v_0(\sigma_B - \sigma_A) - \frac{1}{4}J_{AB} \\ D_5 \cos 2\theta_5 &= \frac{1}{2}v_0(\sigma_B - \sigma_A) + \frac{1}{2}J_{BX} + \frac{1}{4}J_{AB} - \frac{1}{2}J_{AX} \\ D_6 \cos 2\theta_6 &= \frac{1}{2}v_0(\sigma_B - \sigma_A) + \frac{1}{2}J_{BX} - \frac{1}{4}J_{AB} - \frac{1}{2}J_{AX} \end{aligned}$$

The quantities D_i are usually positive and may always be so chosen but in the present case it is convenient to have the quantities D_1 and D_2 positive and the remainder negative, together with corresponding changes in the signs of the θ_i . This arises because the single phosphorus atom A is more shielded than the two atoms B, that is $\frac{1}{2}v_0(\sigma_B - \sigma_A)$ is negative

TABLE 1. Fluorine transitions in $P_3N_3Cl_4F_2$.

Transition energies	Relative intensities	Transition energies	Relative intensities
X transitions relative to $v_0(1 - \sigma_X)$ as origin		Combination transitions	
$-\frac{1}{2}J_{BX} + D_2 - D_4$	$2 \cos^2(\theta_2 - \theta_4)$	$\frac{1}{2}J_{BX} - D_3 - D_5$	$2 \sin^2(\theta_3 - \theta_5)$
$\frac{1}{2}J_{BX} + D_1 - D_3$	$2 \cos^2(\theta_1 - \theta_3)$	$-\frac{1}{2}J_{BX} - D_4 - D_6$	$2 \sin^2(\theta_4 - \theta_6)$
$-\frac{1}{2}J_{BX} + D_4 - D_6$	$2 \cos^2(\theta_4 - \theta_6)$	$\frac{1}{2}J_{BX} - D_1 - D_3$	$2 \sin^2(\theta_1 - \theta_3)$
$\frac{1}{2}J_{AX}$	4	$-\frac{1}{2}J_{BX} + D_2 + D_4$	$2 \sin^2(\theta_2 - \theta_4)$
$\frac{1}{2}J_{BX} + D_3 - D_5$	$2 \cos^2(\theta_3 - \theta_5)$	$-\frac{1}{2}J_{BX} - D_2 - D_4$	$2 \sin^2(\theta_2 - \theta_4)$
$\frac{1}{2}J_{AX} + J_{BX}$	4	$\frac{1}{2}J_{BX} + D_1 + D_3$	$2 \sin^2(\theta_1 - \theta_3)$
$-\frac{1}{2}J_{AX} - J_{BX}$	4	$-\frac{1}{2}J_{BX} + D_4 + D_6$	$2 \sin^2(\theta_4 - \theta_6)$
$-\frac{1}{2}J_{BX} + D_6 - D_4$	$2 \cos^2(\theta_4 - \theta_6)$	$\frac{1}{2}J_{BX} + D_3 + D_5$	$2 \sin^2(\theta_3 - \theta_5)$
$-\frac{1}{2}J_{AX}$	4		
$\frac{1}{2}J_{BX} - D_3 + D_5$	$2 \cos^2(\theta_3 - \theta_5)$		
$-\frac{1}{2}J_{BX} - D_2 + D_4$	$2 \cos^2(\theta_2 - \theta_4)$		
$\frac{1}{2}J_{BX} - D_1 + D_3$	$2 \cos^2(\theta_1 - \theta_3)$		

TABLE 2. Phosphorus transitions in $P_3N_3Cl_4F_2$.

Transition energies	Relative intensities
A transitions relative to $v_0(1 - \sigma_A)$	
$\frac{1}{2}v_0(\sigma_A - \sigma_B) + \frac{1}{2}J_{BX} - \frac{3}{4}J_{AB} + \frac{1}{2}J_{AX} + D_2$	$(\cos \theta_2 + \sqrt{2} \sin \theta_2)^2$
$v_0(\sigma_A - \sigma_B) + J_{BX} + D_1 + D_2$	$[\cos \theta_1 \cos \theta_2 + \sqrt{2} \sin(\theta_1 - \theta_2)]^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) + \frac{1}{2}J_{BX} + \frac{3}{4}J_{AB} + \frac{1}{2}J_{AX} + D_1$	$(\cos \theta_1 - \sqrt{2} \sin \theta_1)^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) - \frac{3}{4}J_{AB} + D_4$	$2(\cos \theta_4 + \sqrt{2} \sin \theta_4)^2$
$v_0(\sigma_A - \sigma_B) + D_3 + D_4$	$2[\cos \theta_3 \cos \theta_4 + \sqrt{2} \sin(\theta_3 - \theta_4)]^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) + \frac{3}{4}J_{AB} + D_3$	$2(\cos \theta_3 - \sqrt{2} \sin \theta_3)^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) - \frac{1}{2}J_{BX} - \frac{3}{4}J_{AB} - \frac{1}{2}J_{AX} + D_6$	$(\cos \theta_6 + \sqrt{2} \sin \theta_6)^2$
$-J_{AX}$	1
$v_0(\sigma_A - \sigma_B) - J_{BX} + D_5 + D_6$	$[\cos \theta_5 \cos \theta_6 + \sqrt{2} \sin(\theta_5 - \theta_6)]^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) - \frac{1}{2}J_{BX} + \frac{3}{4}J_{AB} - \frac{1}{2}J_{AX} + D_5$	$(\cos \theta_5 - \sqrt{2} \sin \theta_5)^2$
B transitions relative to $v_0(1 - \sigma_B)$	
$\frac{1}{2}v_0(\sigma_A - \sigma_B) - \frac{1}{2}J_{BX} - \frac{3}{4}J_{AB} - \frac{1}{2}J_{AX} - D_6$	$[\sqrt{2} \cos \theta_6 - \sin \theta_6]^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) - \frac{3}{4}J_{AB} - D_4$	$2[\sqrt{2} \cos \theta_4 - \sin \theta_4]^2$
$v_0(\sigma_A - \sigma_B) - J_{BX} + D_6 - D_5$	$[-\sin \theta_5 \cos \theta_6 + \sqrt{2} \cos(\theta_5 - \theta_6)]^2$
$v_0(\sigma_A - \sigma_B) + D_4 - D_3$	$2[-\sin \theta_3 \cos \theta_4 + \sqrt{2} \cos(\theta_3 - \theta_4)]^2$
$v_0(\sigma_A - \sigma_B) + J_{BX} + D_2 - D_1$	$[-\sin \theta_1 \cos \theta_2 + \sqrt{2} \cos(\theta_1 - \theta_2)]^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) + \frac{1}{2}J_{BX} - \frac{3}{4}J_{AB} + \frac{1}{2}J_{AX} - D_3$	$[\sqrt{2} \cos \theta_2 - \sin \theta_2]^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) - \frac{1}{2}J_{BX} + \frac{3}{4}J_{AB} - \frac{1}{2}J_{AX} - D_5$	$[\sin \theta_5 + \sqrt{2} \cos \theta_5]^2$
$v_0(\sigma_A - \sigma_B) - J_{BX} + D_5 - D_6$	$[\cos \theta_5 \sin \theta_6 + \sqrt{2} \cos(\theta_5 - \theta_6)]^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) + \frac{3}{4}J_{AB} - D_3$	$2[\sin \theta_3 + \sqrt{2} \cos \theta_3]^2$
$v_0(\sigma_A - \sigma_B) + D_3 - D_4$	$2[\cos \theta_3 \sin \theta_4 + \sqrt{2} \cos(\theta_3 - \theta_4)]^2$
$v_0(\sigma_A - \sigma_B) + J_{BX} + D_1 - D_2$	$[\cos \theta_1 \sin \theta_2 + \sqrt{2} \cos(\theta_1 - \theta_2)]^2$
$\frac{1}{2}v_0(\sigma_A - \sigma_B) + \frac{1}{2}J_{BX} + \frac{3}{4}J_{AB} + \frac{1}{2}J_{AX} - D_1$	$[\sin \theta_1 + \sqrt{2} \cos \theta_1]^2$
Combination transitions	
$v_0(\sigma_A - \sigma_B) - J_{BX} - D_5 - D_6$	$[\sqrt{2} \sin(\theta_6 - \theta_6) + \sin \theta_5 \sin \theta_6]^2$
$v_0(\sigma_A - \sigma_B) - D_3 - D_4$	$2[\sqrt{2} \sin(\theta_3 - \theta_4) + \sin \theta_3 \sin \theta_4]^2$
$v_0(\sigma_A - \sigma_B) + J_{BX} - D_1 - D_2$	$[\sqrt{2} \sin(\theta_1 - \theta_2) + \sin \theta_1 \sin \theta_2]^2$

and has a magnitude less than that of J_{AX} . With these definitions the angles θ_1 and θ_2 are negative, while the remaining four angles are positive with $0 < |\theta_i| < \pi/2$.

By standard formulæ it is now possible to derive the expressions listed in Tables 1 and 2 for the A, B, and X transition energies and relative intensities. It must be emphasised that the quantities D_i defined above are field-dependent because ν_0 and hence $\nu_0(\sigma_B - \sigma_A)$ are proportional to the strength of the applied magnetic field.

The observed and calculated 12 Mc. phosphorus, 40 Mc. fluorine, and 12 Mc. fluorine spectra are shown in Figs. 2, 3, and 4. It may be seen that in the 12 Mc. fluorine spectrum

FIG. 2. *Observed and calculated phosphorus resonance spectrum of $P_3N_3Cl_4F_2$ at 12 Mc.*

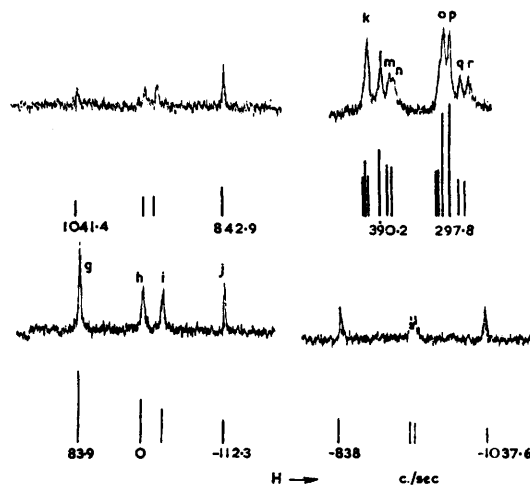


FIG. 3. *Observed and calculated fluorine resonance spectrum of $P_3N_3Cl_4F_2$ at 40 Mc.*

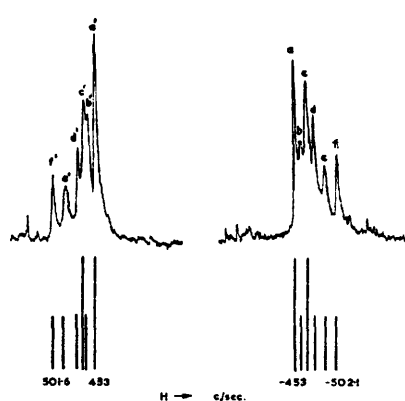


FIG. 4. *Observed and calculated fluorine resonance spectrum of $P_3N_3Cl_4F_2$ at 12 Mc.*

there is a marked difference between the high- and the low-field multiplet systems; there is also evidence of a series of low-intensity combination lines.

Analysis and Assignment of the Spectra.—It may be seen from the form of the expressions in Table 1 and the definitions of the quantities D_i that the fluorine transition energies are not very sensitive to small changes in the values of the phosphorus parameters $\nu_0(\sigma_A - \sigma_B)$ (the phosphorus chemical shift) and J_{AB} (the phosphorus-phosphorus spin-coupling constant). By taking account of the known pattern for the system AB_2 , it was possible to obtain estimates of the two phosphorus parameters from the phosphorus spectrum obtained at 12 Mc. (7000 gauss). These approximate values were sufficient for use in the calculation of the 40 Mc. (10,000 gauss) fluorine transition energies. In

calculating this fluorine spectrum allowance must be made for the fact that the field-dependent phosphorus chemical shift was determined with a field of 7000 gauss.

From the fluorine transition energies and relative intensities listed in Table 1, it is clear that there are four strong transitions in the fluorine doublet system having intensities approximately twice those of the remaining eight lines. Furthermore, these four transition energies are simply related to the constants J_{AX} and J_{BX} . These strong lines may be readily identified with the lines a, c, a', and c' in Fig. 2. This means that the separation ac or a'c' gives the value of J_{BX} . It is not immediately obvious whether aa' or cc' corresponds to the separation $|J_{AX}|$ because the two coupling constants J_{AX} and J_{BX} may have the same or opposite signs. To decide between these two cases use was made of the fluorine spectrum obtained at 12 Mc. (3000 gauss). Although the two fluorine multiplets are almost symmetrical in the 40 Mc. spectrum (they are not quite symmetrical, the separations bc and b'c' are not the same) the multiplets are quite obviously different in the 12 Mc. spectrum. The reason for this is that the value of the phosphorus chemical shift at this field (3000 gauss) is of the same magnitude as the coupling constant J_{AB} (see below).

The fluorine spectra at both 40 Mc. and 12 Mc. were calculated by using the approximate values of the phosphorus parameters (corrected for changes in the applied field), the observed value of $|J_{BX}|$, and the two alternative values for $|J_{AX}|$. It was possible to account for the fluorine spectra at the two different applied fields only if the signs of J_{AX} and J_{BX} were opposite and further if the sign J_{AB} was opposite to that of J_{AX} . It follows that in the 40 Mc. fluorine spectrum the separation of cc' gives the value of $|J_{AX}|$, so that either

$$J_{AX} = 934 \text{ c./sec. and } J_{BX} = -14 \text{ c./sec.}$$

or

$$J_{AX} = -934 \text{ c./sec. and } J_{BX} = 14 \text{ c./sec.}$$

By using these exact values of J_{AX} and J_{BX} it was then possible to return to the 12 Mc. phosphorus spectrum and to deduce exact values of $\nu_0(\sigma_A - \sigma_B)$ and $|J_{AB}|$ from the explicit expressions in Table 2. By taking the experimental frequencies for the transitions marked i, j, l, and p the following relations may be derived, with J_{AX} assumed positive and J_{BX} negative:

$$\frac{1}{2}\nu_0(\sigma_A - \sigma_B) + \frac{3}{4}J_{AB} + D_3 = -113 \text{ c./sec.}$$

$$\nu_0(\sigma_A - \sigma_B) + D_3 + D_4 = -28 \text{ c./sec.}$$

$$\nu_0(\sigma_A - \sigma_B) + D_3 - D_4 = 298 \text{ c./sec.}$$

$$\nu_0(\sigma_A - \sigma_B) + D_4 - D_3 = 390 \text{ c./sec.}$$

These equations, after elimination of D_3 and D_4 , lead to the values $\nu_0(\sigma_A - \sigma_B) = 344 \text{ c./sec.}$; $J_{AB} = -100 \text{ c./sec.}$ If the signs of J_{AX} and J_{BX} were changed simultaneously it would be deduced that $J_{AB} = +100 \text{ c./sec.}$

Thus to account completely for both sets of fluorine spectra and the phosphorus spectrum it was necessary to assume that the relative signs of the three coupling constants are such that if J_{AX} is of positive sign then both J_{BX} and J_{AB} are of negative sign. It is unusual to be able to determine the relative signs of all spin-coupling constants; the reason why this is possible in the present case may be seen from the explicit expressions in Tables 1 and 2. If the sign of J_{AB} relative to J_{AX} (and hence J_{BX}) be changed it can be seen from Table 2 that the predicted phosphorus spectrum is completely unchanged. This uncertainty in determining the sign of J_{AB} is a property of an AB_2 system.² However, the fluorine spectrum will be changed. Consider the six low-field components of the fluorine spectrum, that is, the first six transitions in Table 1. If J_{AB} is replaced by $-J_{AB}$ in the equations defining D_i and θ_i the following relabelling takes place:

$$D_1 \rightarrow D_2; \theta_1 \rightarrow -\theta_2$$

$$D_3 \rightarrow D_4; \theta_3 \rightarrow -\theta_4$$

$$D_5 \rightarrow D_6; \theta_5 \rightarrow -\theta_6$$

with corresponding changes in the reverse direction, *i.e.*, $D_2 \rightarrow D_1$, $\theta_2 \rightarrow -\theta_1$. This means that the six components now have the following forms for their transition energies and relative intensities:

$$\begin{array}{ll}
 -\frac{1}{2}J_{\text{BX}} + D_1 - D_3 & 2 \cos^2 (\theta_1 - \theta_3) \\
 \frac{1}{2}J_{\text{BX}} + D_2 - D_4 & 2 \cos^2 (\theta_2 - \theta_4) \\
 -\frac{1}{2}J_{\text{BX}} + D_3 - D_5 & 2 \cos^2 (\theta_3 - \theta_5) \\
 \frac{1}{2}J_{\text{AX}} & 4 \\
 \frac{1}{2}J_{\text{BX}} + D_4 - D_6 & 2 \cos^2 (\theta_4 - \theta_6) \\
 \frac{1}{2}J_{\text{AX}} + J_{\text{BX}} & 4
 \end{array}$$

These are not the same expressions as listed in Table 1 (although they are the *negative* of expressions listed in the six high-field components) and they will only give the same predicted fluorine spectrum if $D_1 - D_3$ is equal to $D_2 - D_4$ and $D_4 - D_6$ is equal to $D_3 - D_5$. Similar restrictions would have to be placed on $\theta_1 - \theta_3$ and $\theta_2 - \theta_4$. In fact it is found that at 40 Mc. these conditions are almost met, but at 12 Mc. the quantities $D_1 - D_3$ and $D_2 - D_4$ are significantly different. The values of these quantities, in c./sec., are:

	40 Mc.	12 Mc.
$D_1 - D_3 =$	495.1	501.4
$D_2 - D_4 =$	494.6	514.9
$D_3 - D_5 =$	467.9	455.6
$D_4 - D_6 =$	466.6	441.8

Thus it may be seen that the fluorine spectrum is not independent of the relative signs of J_{AB} and J_{AX} . It is the unsymmetrical nature of the fluorine multiplets, particularly at low fields, that enables one to distinguish between various sign combinations.

By similar reasoning it may be shown that the predicted spectra will be completely unchanged if all three of the coupling constants have their signs changed simultaneously. It is, therefore, possible to obtain only the relative signs of the constants; however, it appears reasonable to assume that the large constant J_{AX} , involving two nuclei directly connected by a single bond, has a positive sign so that the other two constants must be negative.

In the case of an ABX system it has been shown,^{2,3} that it is only possible to determine the relative signs of J_{AX} and J_{BX} . However, for an ABC system it is possible to determine the relative signs of all three spin interactions.⁴ It is because the X_2 spectrum of an AB_2X_2 system is more complicated than the X spectrum of an ABX system that it is possible to determine the relative signs of all the spin-coupling constants for the former system. For a five-spin system in which the chemical shift $\nu_B - \nu_A$ is much greater than the coupling constant J_{AB} (such a system would not, of course, be classified as an AB_2X_2 system) it would not be possible to determine the relative signs of all the coupling constants.

It has been suggested that the negative sign of coupling constants may be associated with multiple bonding or aromatic character.⁵ In this connection it is interesting that the two constants J_{AB} and J_{BX} , which may be negative, involve long-range coupling through the electronic structure of the phosphorus-nitrogen ring system which is currently believed to possess aromatic character.⁶

The final values obtained for the transition energies and relative intensities are listed in Table 3 for the fluorine spectra (at 40 and 12 Mc.) and the phosphorus (12 Mc.) spectrum. These quantities are also shown in Figs. 2-4, from which it may be seen that the agreement between the predicted and the observed spectra is satisfactory. The coupling

³ Anderson, *Phys. Rev.*, 1956, **102**, 151; Williams and Gutowsky, *J. Chem. Phys.*, 1956, **25**, 1288.

⁴ Alexander, *J. Chem. Phys.*, 1958, **28**, 358.

⁵ McConnell, *J. Chem. Phys.*, 1959, **30**, 126.

⁶ Craig and Paddock, *Nature*, 1958, **181**, 1052.

TABLE 3. Calculated and observed lines for $P_3N_3Cl_4F_2$ (energies in c./sec.).

Calc. energy	Obs. energy	Relative intensity	Calc. energy	Obs. energy	Relative intensity
F resonance at 40 Mc.			F resonance at 12 Mc.		
501.6	501	1.83	521.9	522	1.42
488.1	487	1.83	494.4	495	1.69
473.6	474	1.98	467	467	4.00
467	467	4.00	453	} 453	4.00
460.9	ca. 463	1.98	448.8		1.67
453	453	4.00	448.6	} 453	1.88
-453	-453	4.00	-434.8		-433
-459.6	-461	1.98	-453	-453	4.00
-467	-467	4.00	-462.6	-463	1.88
-474.9	-477	1.98	-467	-467	4.00
-487.0	-489	1.83	-507.9	} 507	1.42
-502.1	-502	1.83	-508.4		1.69
Combination lines					
1022.1	—	0.02	692	—	0.12
938.6	—	0.02	620.8	—	0.33
59.1	—	0.17	349.9	—	0.58
36.6	—	0.17	251	—	0.31
-22.6	—	0.17	-265	—	0.31
-73.1	—	0.17	-335.9	—	0.58
-924.6	—	0.02	-606.8	—	0.33
-1036.1	—	0.02	-706	—	0.12
A transitions			B transitions		
1041.4	1040	0.71	412	} ca. 413	1.84
950.3	948	0.92	410.1		2.67
934	934	1	407.6		1.86
842.9	841	1.37	390.2		390
83.9	84	3.33	378.5	378	2.37
0	0	2	372.6	372	2.29
-28.4	-28	1.57			
-112.3	-113	1.11	311.6	} ca. 308	2.15
-838	-837	1.16	308.4		2.16
-934	-935	1	306.3		4.89
-941.6	-941	0.98	297.8		298
-1037.6	-1039	0.86	281.5	282	1.71
			271.5	271	1.64
Combination lines					
1657	0.001				
716	ca. 0.003				
-290	0.001				

constants derived for triphosphonitric 1,1-difluoride 3,3,5,5-tetrachloride may be of use in accounting for some of the features of the more complex spectra of the 1,1,3-trifluoride 3,5,5-trichloride and 1,1,3,3-tetrafluoride 5,5-dichloride.¹

Experimental.—The nuclear magnetic resonance spectra were obtained with a Varian V 4300B high-resolution spectrometer operating at 40 Mc. (approx. 10,000 gauss) and 12 Mc. (approx. 3000 gauss) for fluorine and at 12 Mc. (approx. 7000 gauss) for phosphorus. The pure liquid compound was contained in a 5-mm. sample tube sealed to prevent reaction with atmospheric moisture. The spectra were referenced by the side-band technique.

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