[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 425]

The Electron Diffraction Investigation of Some Non-metallic Halides

BY L. O. BROCKWAY AND FREDERICK T. WALL

The most recently developed method of investigating the structure of molecules is that of electron diffraction. Since the pioneer work of Wierl[1] it has been described and used by a number of investigators working on a considerable variety of problems. We have applied the method in a study of the structures of the chlorides and fluorides of phosphorus, arsenic, carbon and silicon and the chloride of tin.

The present work is a part of an experimental investigation of the validity of Pauling's table of normal covalent radii.[2] We have been especially interested in testing the postulate of additivity. It should be mentioned that the tetrachlorides of carbon, silicon and tin and the trichloride of phosphorus have been investigated by Wierl, but it seemed desirable to repeat the work on these compounds.

The experimental procedure has been described previously.[3] The wave length, usually in the neighborhood of 0.06 Å., was calibrated with the aid of photographs of gold foil with the dimensions of the unit cube of gold taken as 4.070 Å. The gold photographs were taken on Eastman Process Plates and the gas photographs on x-ray film. The apparent maxima and minima on each photograph were measured on a specially designed comparator and these points were correlated with the maxima and minima in the approximate theoretical intensity curves given below. The results obtained by this method of interpretation have been justified by Pauling and Brockway[4] on the basis of a critical comparison of results of the visual treatment with those obtained from microphotometer records and from band spectra. The theoretical intensity curves were calculated from the formula for coherent scattering of electrons

$$I = k\,\Sigma_i\Sigma_j\,Z_iZ_j\,\frac{\sin x_{ij}}{x_{ij}},\ \text{with}\ x_{ij} = 4\pi l_{ij}\,\frac{\sin \theta/2}{\lambda}$$

in which the true atomic scattering factor $\psi_i = (Z_i - f_i)/(\sin^2 \theta/2/\lambda^2)$ has been replaced by the atomic number Z_i.

Tetrachlorides and Tetrafluorides.—The compounds of carbon, silicon and tin were assumed to have molecular structures based on a regular tetrahedron. The corresponding intensity curves are given in Figs. 1 and 2 in which the intensity of electron scattering is plotted as a function of x referred to the distance from the center to a corner of the tetrahedron. The increasing relative importance of the central atom scattering is shown by the progressive disappearance of the maxima which in carbon tetrachloride are the first, fourth and sixth. In carbon tetrachloride the chlorine–chlorine interference effects are most important and the curve is not very different from that for the simple $(\sin x)/x$ function; in tin tetrachloride, the other extreme, the curve again approximates that of the $(\sin x)/x$ function but here it is the term involving chlorine with the central atom which predominates. The curve for germanium tetrachloride is included here for the

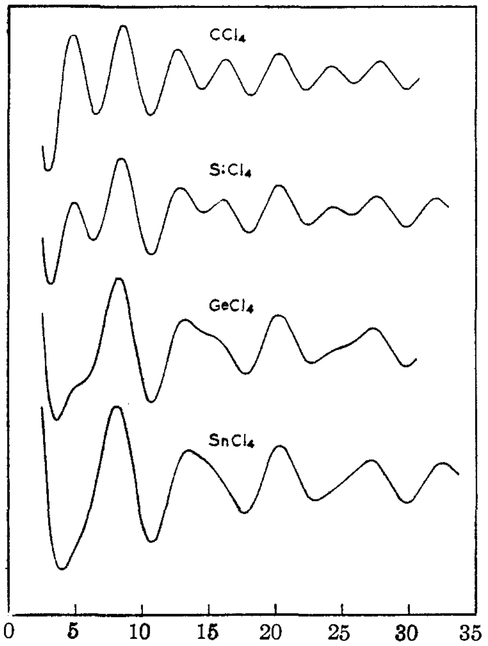


Fig. 1.—Simplified theoretical intensity curves for the tetrachlorides of carbon, silicon, germanium and tin, as a function of the variable $x = 4\pi\, l\, (\sin \vartheta/2/\lambda)$, in which l is the metal–chlorine distance.

---

(1) R. Wierl, *Ann. Physik*, **8**, 521 (1931); **13**, 453 (1932).

(2) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

(3) L. O. Brockway and L. Pauling, *ibid.*, **19**, 68 (1933).

(4) L. Pauling and L. O. Brockway, to be published in the *Journal of Chemical Physics*.

sake of comparison; the compound has not yet been available to us.[5] Wierl published curves for the tetrachlorides which presumably were calculated from the same formula; but after carefully checking our calculations we are unable to make our curves agree with his for germanium tetrachloride and tin tetrachloride. It seems likely that Wierl's curves were labeled incorrectly since his germanium tetrachloride curve is practically identical with his curve for titanium tetrachloride, the tin tetrachloride curve is identical with our curve for germanium tetrachloride, and he has no curve which compares with our tin tetrachloride curve.

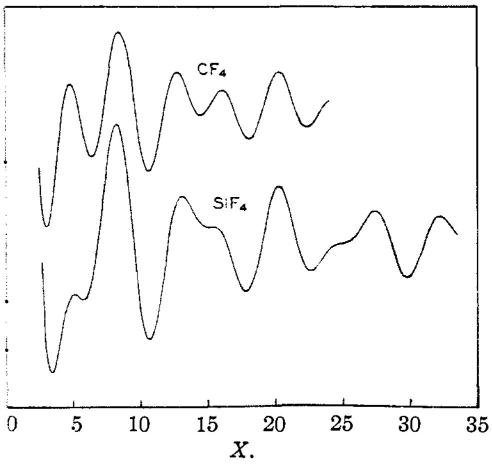


Fig. 2.—Theoretical intensity curves for carbon tetrafluoride and silicon tetrafluoride.

The electron-diffraction photographs are in excellent qualitative agreement with the curves. The carbon tetrachloride photographs show a regular series of rings in which the second, fifth and seventh appear to be stronger than the respective preceding ones. The photographs for silicon tetrachloride show the same effect in a considerably more pronounced way. In the case of tin tetrachloride the second maximum is broader than the first or third and shows a sharp maximum on the inside edge fading off rather gradually toward the outside. The fluorides of carbon and silicon similarly give electron diffraction photographs which reproduce the qualitative features of the curves.

The quantitative comparisons and results are given in Tables I–V. The individual values for the interatomic distance which were not included in obtaining the indicated averages are enclosed in parentheses. They have been eliminated because of the St. John effect. In comparing the results of visual and photometric measurements of spectral photographs St. John and Ware[6] found

TABLE I

CARBON TETRACHLORIDE[a]

Camera distance = 12.19 cm. λ = 0.0604 to 0.0619 Å.

No. of photos	Max.	Min.	x	$4\pi (\sin \theta/2)/\lambda$	a = C–Cl
13	1		4.81	2.870	(1.675)
19		2	6.43	3.789	(1.697)
19	2		8.48	4.912	(1.727)
19		3	10.62	6.064	1.752
19	3		12.60	7.144	1.764
19		4	14.47	8.224	1.759
19	4		16.22	9.263	1.751
19		5	18.09	10.33	1.752
19	5		20.20	11.44	1.766
16		6	22.23	12.58	1.767
16	6		24.10	13.65	1.765
10		7	25.90	14.71	1.761
10	7		27.76	15.81	1.756
4		8	29.79	16.89	1.764
4	8		31.86	18.02	1.768
2		9	33.79	19.07	1.771
2	9		35.51	20.14	1.763
1		10	37.26	21.22	1.756
1	10		39.35	22.34	1.762
				Weighted average	1.760

C–Cl = 1.760 ± 0.005 Å.
Wierl—1.83 ± 0.02 Å.
(x-ray—1.83 ± 0.02 Å.)

[a] A more complete presentation of the results of our study of carbon tetrachloride will be found in Reference 4.

TABLE II

SILICON TETRACHLORIDE

Three photographs. Camera distance = 12.19 cm. λ = 0.0606 Å.

Max.	Min.	x	$4\pi (\sin \theta/2)/\lambda$	a = Si–Cl
1		4.83	2.545	(1.898)
	2	6.35	3.315	(1.915)
2		8.41	4.247	1.980
	3	10.65	5.360	1.987
3		12.81	6.285	2.037
	4	14.56	7.202	2.022
4		15.97	8.044	1.987
	5	18.01	8.996	2.002
5		20.22	9.895	2.043
	6	22.42	11.00	2.038
6		24.30	11.89	2.044
7		27.60	13.85	1.993
	8	29.82	14.88	2.004
8		32.00	15.93	2.008
			Average	2.016

Si–Cl = 2.02 ± 0.02 Å.
Wierl—2.02 ± 0.03 Å.
(x-ray[a]—2.17 Å.)

[a] R. W. James, *Physik. Z.*, **33**, 737 (1932).

---

(5) Since submitting this paper we have obtained a sample of germanium tetrachloride through the kindness of Professor L. M. Dennis of Cornell University. The results of our measurements on this compound will be reported in THIS JOURNAL very soon.

(6) C. E. St. John and L. W. Ware, *Astrophys. J.*, **44**, 35 (1916).

TABLE III

TIN TETRACHLORIDE

Three photographs. Camera distance = 12.19 cm. λ = 0.0604 Å.

Max.	Min.	x	$4\pi (\sin \theta/2)/\lambda$	a = Sn–Cl
1		8.11	3.670	(2.210)
	2	10.72	4.732	2.264
2		13.55	5.620	(2.410)
	3	17.68	7.78	2.273
3		20.32	8.78	2.313
	4	22.95	10.09	2.276
4		27.19	11.67	2.328
	5	29.82	13.05	2.286
5		32.45	14.23	2.280
			Average	2.289

Sn–Cl = 2.29 ± 0.02 Å.
Wierl—2.33 ± 0.05 Å.

TABLE IV

CARBON TETRAFLUORIDE

Two photographs. Camera distance = 12.19 cm. λ = 0.0624 Å.

Max.	Min.	x	$4\pi (\sin \theta/2)/\lambda$	a = C–F
1		4.83	3.560	1.356
	2	6.40	4.819	1.328
2		8.41	6.183	1.359
	3	10.62	7.908	1.344
3		12.76	9.276	1.376
	4	14.53	10.56	1.375
4		16.34	12.06	1.354
	5	18.08	13.36	1.353
5		20.21	14.49	1.395
			Average	1.360

C–F = 1.36 ± 0.02 Å.

TABLE V

SILICON TETRAFLUORIDE

Three photographs. Camera distance = 12.19 cm. λ = 0.0614 Å.

Max.	Min.	x	$4\pi (\sin \theta/2)/\lambda$	a = Si–F
1		8.30	5.406	1.535
	2	10.69	6.932	1.542
2		13.09	8.266	1.582
	3	17.82	11.59	1.539
3		20.25	13.02	1.555
	4	22.67	15.08	1.503
4		27.42	17.27	1.588
	5	29.80	19.32	1.542
5		32.20	21.34	1.508
			Average	1.544

Si–F = 1.54 ± 0.02 Å.

that in the visual treatment the apparent position of maximum density for an asymmetric line is always shifted toward the side of greater contrast; the effect on the measurement of a doublet is such that the apparent separation is greater than the true. The cause for this shift lies in the psychological effect of the difference in brightness of the background on the two sides of the line. This effect has been observed in the electron diffraction photographs of a number of compounds; and while the general appearance of the asymmetric characteristics of such a photograph is very useful in the qualitative comparison with theoretical curves, good quantitative agreement among all the rings is impossible. An allowance for the effect may be made by determining the interatomic distance only from the sharply defined single rings. It should be pointed out that in the photographs of the larger molecules taken at a distance of 12.19 cm. the contrast effect of the very dense central image causes the first one or two maxima to be read with too large diameters; thus, in Table I for carbon tetrachloride the first three points show progressively decreasing deviations from the average of the remaining sixteen points. In Table III for tin tetrachloride the second maximum gives a much larger a-value than any other maximum or minimum; the shape of this maximum on the theoretical curve indicates that this discrepancy is due to the St. John effect.

The value of the interatomic distance is given at the end of each table together with an estimated probable error. The corresponding values for the interatomic distances obtained by Wierl are also given.

Excellent photographs of Si_2Cl_6 have also been obtained, but since the structure involves four parameters (of which the one determining the relative rotation of the tri-chloro groups is probably not constant) a complete survey of possible parameter values has not been attempted. Curves based upon a model in which the Si–Cl bond at one end lies in a plane bisecting the angle between the two Si–Cl bonds at the other end are in much better agreement with the photographs than are the curves based upon the model in which two Si–Cl bonds at opposite ends of the molecule lie in the same plane.

Trichlorides and Trifluorides.—The phosphorus and arsenic chlorides and fluorides are given structural models corresponding to a trigonal pyramid. Figures 3–6 show the theoretical intensity curves. In each case a number of calculations have been made for different ratios of the length of the base to the slant height of the pyramid corresponding to a range of bond angles. The total range covered in the different cases depends upon how much the shape of the curve is affected by changes in bond angle. The curves for phosphorus trichloride are most sensitive, then phosphorus trifluoride, arsenic trichloride and arsenic trifluoride in decreasing order.

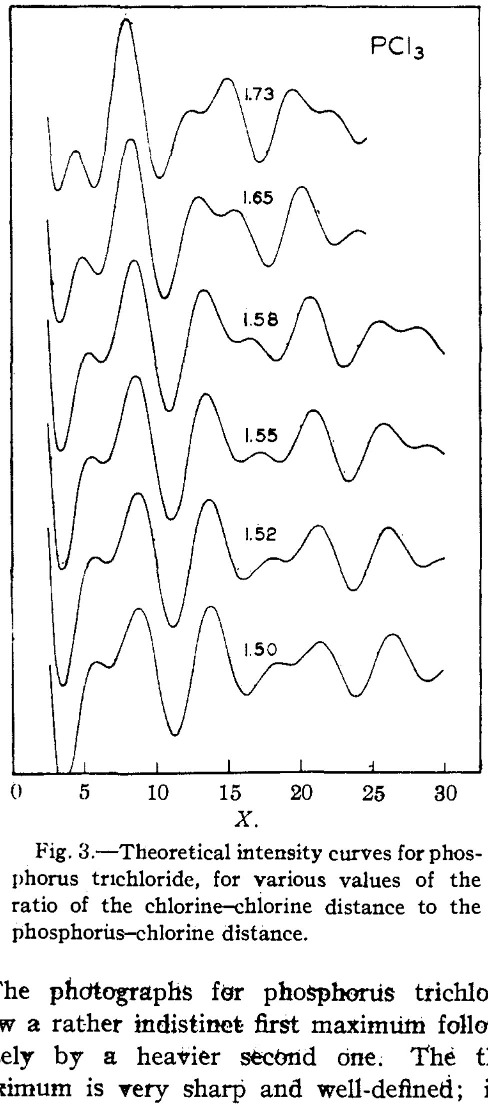


Fig. 3.—Theoretical intensity curves for phosphorus trichloride, for various values of the ratio of the chlorine–chlorine distance to the phosphorus–chlorine distance.

The photographs for phosphorus trichloride show a rather indistinct first maximum followed closely by a heavier second one. The third maximum is very sharp and well-defined; it is followed by a weak maximum which is less distinct than the two succeeding ones. The characteristic appearance of the third maximum eliminates the 1.73 and 1.65 models. Table VI gives the quantitative data on the other models. It will be noticed that the first three points show the St. John effect. The first maximum usually gives a much smaller interatomic distance than do the outer rings because of the contrast effect of the central image, but in this case the asymmetric character of the ring causes the resulting value of the interatomic distance to be larger than usual. The second minimum and maximum are read too far out and hence give interatomic distance values which are too small. The observed position of the fourth maximum relative to the third and fifth indicates that the most probable model lies between 1.55 and 1.52; and the final values for bond distance and angle correspond to a model halfway between.

In arsenic trichloride the increase in relative scattering power of the central atom has caused the scattering curve to lose many of the characteristic features observed in the case of phosphorus trichloride; and the photographs of arsenic trichloride show a series of fairly regular rings with only one striking feature—the third minimum is very wide. Comparison of the curves for various molecular models show that only the 1.55 model has this unusually broad third minimum.

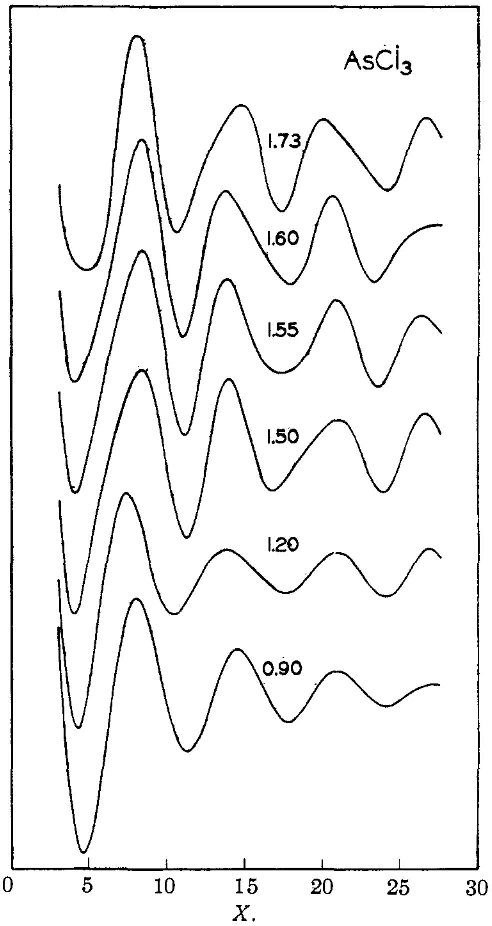


Fig. 4.—Theoretical intensity curves for arsenic trichloride.

In Table VII the qualitative comparison is given for all of the models discussed. The average deviations of the individual values for 1.73, 1.60 and 0.90, respectively, are too large. Of the remaining three the 1.20 model shows the smallest

TABLE VI

PHOSPHORUS TRICHLORIDE

Two photographs. Camera distance = 12.19 cm. λ = 0.0583 Å.

Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	$x_{1.58}$	$x_{1.55}$	$x_{1.52}$	$x_{1.50}$	$a_{1.58}$	$a_{1.55}$	$a_{1.52}$	$a_{1.50}$
1		2.757	5.35	5.55	5.80	5.83	(1.940)	(2.013)	(2.104)	(2.115)
	2	3.568	6.20	6.35	6.53	6.70	(1.739)	(1.781)	(1.831)	(1.878)
2		4.537	8.45	8.59	8.71	8.75	(1.863)	(1.894)	(1.920)	(1.930)
	3	5.634	10.90	11.05	11.18	11.25	1.935	1.961	1.985	1.997
3		6.660	13.31	13.45	13.65	13.75	2.000	2.020	2.050	2.064
	4									
4		8.746	16.45	17.20	17.97	18.48	1.880	1.966	2.054	2.111
	5									
5		10.38	20.69	20.95	21.20	21.37	1.991	2.018	2.042	2.058
	6	11.62	23.09	23.38	23.65	23.82	1.985	2.011	2.035	2.052
6		12.58	25.45	25.80	26.13	26.37	2.023	2.050	2.077	2.096
						Average	1.968	2.004	2.041	2.063
						Average deviation	0.041	0.027	0.020	0.027

P–Cl = 2.02 ± 0.02 Å. $\alpha = 100 \pm 2°$.
Wierl—2.04 ± 0.06 Å. 102°.

TABLE VII

ARSENIC TRICHLORIDE

Four photographs. Camera distance = 21.49 cm. λ = 0.0574 Å.

Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	$x_{1.73}$	$x_{1.60}$	$x_{1.55}$	$x_{1.50}$	$x_{1.20}$	$x_{0.90}$	$a_{1.73}$	$a_{1.60}$	$a_{1.55}$	$a_{1.50}$	$a_{1.20}$	$a_{0.90}$
1		3.944	7.90	8.18	8.25	8.28	7.29	8.00	(2.003)	(2.075)	(2.092)	(2.100)	(1.849)	(2.029)
	2	5.279	10.45	10.85	11.00	11.18	10.35	11.30	(1.980)	(2.056)	(2.084)	(2.119)	(1.961)	(2.141)
2		6.232	14.60	13.58	13.68	13.87	13.70	14.40	2.343	2.180	2.196	2.225	2.199	2.311
	3	7.859	17.22	17.75	17.25	16.65	17.50	17.75	2.191	2.259	2.195	2.119	2.228	2.259
3		9.554	19.87	20.31	20.75	20.90	20.90	20.92	2.080	2.127	2.172	2.189	2.189	2.190
	4	11.00	23.90	23.12	23.30	23.75	24.00	24.10	2.172	2.103	2.119	2.159	2.182	2.191
4		12.13	26.50	27.12	26.14	26.42	26.78	27.09	2.185	2.237	2.155	2.179	2.208	2.232
								Average	2.194	2.181	2.167	2.174	2.201	2.236
								Average deviation	0.059	0.053	0.024	0.028	0.015	0.039

As–Cl = 2.18 ± 0.03 Å. $\alpha = 101 \pm 4°$.

average deviation although the other two are scarcely greater than the experimental error. Model 1.20, however, lacks the broad third minimum which is characteristic of the photographs; and we chose a model just below 1.55 as the most probable. The corresponding angle is 101° with an estimated probable error of ±4° based on the definite inferiority of models 1.60 and 1.50. The As–Cl distance, 2.18 Å., is obtained from the table by giving extra weight to the very sharp second maximum which gave extraordinarily consistent readings.

TABLE VIII

PHOSPHORUS TRIFLUORIDE

Three photographs. Camera distance = 28.70 cm.
λ = 0.0548 Å.

Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	$x_{1.55}$	$x_{1.50}$	$x_{1.45}$	$a_{1.55}$	$a_{1.50}$	$a_{1.45}$
1		5.74	8.30	8.37	8.25	(1.446)	(1.460)	(1.437)
	2	7.48	11.05	11.17	11.35	(1.478)	(1.494)	(1.517)
2		8.82	13.68	13.84	14.08	1.552	1.570	1.596
3		13.45	20.81	20.93	19.80	1.548	1.556	1.472
					Average	1.550	1.563	

P–F = 1.56 ± 0.02 Å. $\alpha = 99 \pm 4°$.

Phosphorus trifluoride was photographed only with the 29 cm. camera and the three rings observed covered the negative. The very sharp second maximum eliminates the models corresponding to the first two curves in Fig. 5. The quantitative comparison in Table VIII shows that the 1.45 model is unsatisfactory because of the poor agreement between the second and third maxima. The other two models are equally satisfactory and we believe the most probable model lies in between. The bond angle is nearly the same as in phosphorus trichloride with only slightly less certainty of the exact value.

The compound arsenic trifluoride gives theoretical scattering curves which are not much affected by changes in bond angle, since the As–F interference is so much stronger than that due to F–F. As in the case of chlorine dioxide,[7] the bond distance is nearly the same for all models and is scarcely affected by the uncertainty in angle. It seems probable that the angle is near 100° as in

---

(7) L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 303, 868 (1933).

TABLE IX

ARSENIC TRIFLUORIDE

Six photographs. Camera distance = 12.19 and 21.49 cm. λ = 0.0595 Å.

Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	$x_{1.73}$	$x_{1.55}$	$x_{1.35}$	$x_{1.00}$	$x_{0.70}$	$a_{1.73}$	$a_{1.55}$	$a_{1.35}$	$a_{1.00}$	$a_{0.70}$
1		Maximum too broad to allow consistent reading										
	2	6.712	10.70	10.95	11.12	10.87	10.87	(1.595)	(1.632)	(1.657)	(1.620)	(1.620)
2		8.085	14.30	13.83	14.31	14.10	13.77	1.769	1.710	1.770	1.744	1.704
	3	9.845	17.20	17.23	17.25	17.25	16.87	1.747	1.749	1.752	1.752	1.714
3		11.77	20.12	20.60	20.20	20.37	20.37	1.710	1.750	1.716	1.730	1.730
	4	13.87	23.75	23.47	23.25	23.50	23.70	1.713	1.691	1.675	1.695	1.708
4		15.26	26.60	26.36	26.62	26.65	26.93	1.743	1.726	1.744	1.746	1.765
							Average	1.737	1.725	1.731	1.734	1.724
							Average deviation	0.020	0.020	0.029	0.017	0.018

As–F = 1.73 ± 0.02 Å.

the other three compounds of this type but we have no direct evidence for this.

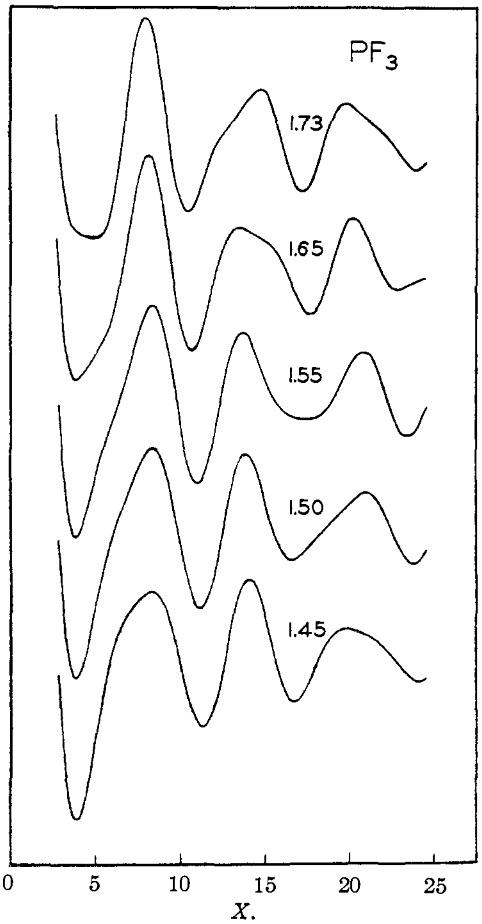


Fig. 5.—Theoretical intensity curves for phosphorus trifluoride.

The observed bond distances are compared with the respective sums of Pauling's normal covalent radii in Table X.[8] It will be noticed that in nearly every case the difference is considerably greater than the experimental error. An inspection of the observed distances shows that a set of constant radii which agrees with the experimental results cannot be devised. The explanation of this must be sought in some effect in bond formation which varies from one compound to another.

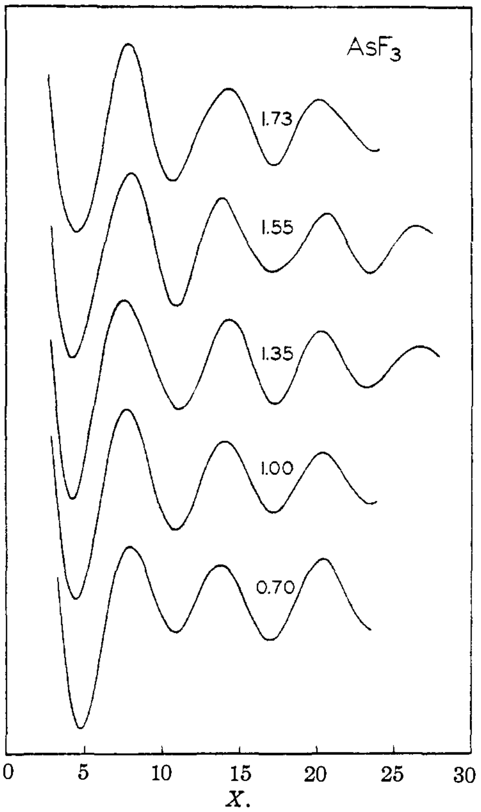


Fig. 6.—Theoretical intensity curves for arsenic trifluoride.

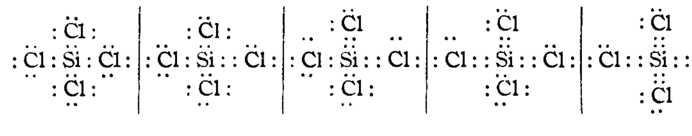
A consideration of the relative electronegativity of the elements involved especially in relation to

---

(8) Preliminary values for the As–F and As–Cl distances were given to Professor Yost before the completion of this investigation and were published by Yost and Sherborne, *J. Chem. Phys.*, **2**, 125 (1934).

the map prepared by Pauling[9] leads us to believe that the bonds under discussion have various degrees of ionic character. The differences in electronegativity are greater for the fluorides than for the corresponding chlorides. The differences between predicted and observed bond distances are also observed to be greater for the fluorides than the chlorides. This suggests that the shortening of the bond may be due in part to the ionic character; for example, in the C–F bond fluorine is more negative than carbon and the mutual attraction of their unlike charges strengthens the bond and brings the atoms closer together than they would be in a pure covalent bond in which the atoms have the same charge. The effect of the relative electronegativity of the central atom in the molecule agrees in general with the foregoing suggestion both for the fluorides and chlorides. The relation is much less certain for comparisons of a fluoride of one element with a chloride of another.

The large bond deviations for some of the compounds and the lack of universal applicability of the explanation based on ionic character leads to the consideration of the formation of double electron-pair bonds. Elements in the first row of the periodic table have only four bond-forming orbitals which do not lead to high-lying energy states so that in the normal valence compounds only single bonds can be formed. In the following rows this restriction no longer holds. Silicon, for example, in its lowest state has four electrons with total quantum number three and nine orbitals with the same total quantum number. The following electronic structures may contribute to the normal state of silicon tetrachloride



$$\begin{array}{c|c|c|c|c} \begin{array}{c}:\ddot{\mathrm{Cl}}:\\ :\ddot{\mathrm{Cl}}:\ddot{\mathrm{Si}}:\ddot{\mathrm{Cl}}:\\ :\ddot{\mathrm{Cl}}:\end{array} & \begin{array}{c}:\ddot{\mathrm{Cl}}:\\ :\ddot{\mathrm{Cl}}:\ddot{\mathrm{Si}}::\mathrm{Cl}:\\ :\ddot{\mathrm{Cl}}:\end{array} & \begin{array}{c}:\ddot{\mathrm{Cl}}\\ :\mathrm{Cl}:\ddot{\mathrm{Si}}::\mathrm{Cl}:\\ :\ddot{\mathrm{Cl}}:\end{array} & \begin{array}{c}:\ddot{\mathrm{Cl}}\\ :\mathrm{Cl}::\ddot{\mathrm{Si}}::\ddot{\mathrm{Cl}}:\\ :\ddot{\mathrm{Cl}}:\end{array} & \begin{array}{c}:\ddot{\mathrm{Cl}}\\ :\mathrm{Cl}::\ddot{\mathrm{Si}}::\ddot{\mathrm{Cl}}:\\ :\ddot{\mathrm{Cl}}\end{array} \end{array}$$

At the present time it is not possible to say how important these contributions are, but if any of the double-bond structures are involved the bond distance would be decreased in some degree. There are the same possibilities for elements of the fifth and sixth columns of the periodic table. The importance of this effect may be determined by studying the structure of compounds in which the double-bond formation is not possible, as in silicon tetramethyl. Any observed deviation then must be ascribed to ionic character. Such investigations are now under way in this Laboratory.

TABLE X

Bond	Observed distance	Radius sum	Difference	Angle	Ratio of fluoride to chloride
C–Cl	1.76	1.76	0.00		
					0 772
C–F	1 36	1.41	.05		
Si–Cl	2.02	2.16	.14		
					.762
Si–F	1.54	1.81	.27		
Sn–Cl	2.29	2.39	.10		
P–Cl	2.02	2.09	.07	100°	
					.772
P–F	1.56	1.74	.18	99°	
As–Cl	2.18	2.20	.02	101°	
					.794
As–F	1.73	1.85	.12		

The validity of the table of normal covalent radii is not affected by the foregoing discussion of ionic character and double-bond formation. The experimental basis of the table includes only compounds between like atoms and in which it is certain that no double bonds are formed; and the analysis of our present results shows that the table is not strictly applicable to them. While we do not believe that the table is infallible, we have no evidence yet for applying any corrections.

Professor Yost has pointed out that the ratio of the fluorine bond distance to the chlorine bond distance for each of a large number of elements is nearly constant. These ratios for the elements considered here are given in the last column of Table X.

We wish to express our appreciation to Professor D. M. Yost for making the compounds of carbon, silicon, phosphorus and arsenic available to us. The tin tetrachloride was prepared by Mr. C. F. Chatham. We are grateful to Professor Linus Pauling for encouragement and help during the investigation.

Summary

The molecular structures of the chlorides and fluorides of carbon, silicon, phosphorus and arsenic and the chloride of tin have been investigated by means of electron diffraction with the results indicated in Table X. The significance of deviations from additivity of the covalent radii has been discussed with respect to ionic character of the bonds and the formation of double electron pair bonds.

PASADENA, CALIF. RECEIVED AUGUST 22, 1934

---

[9] L. Pauling, THIS JOURNAL, 54, 3570 (1932).