inappreciable, inasmuch as the number of layers in a crystal (other than an extremely small crystal) is very small compared with the number of atoms.

In this connection it might be mentioned that there exists the possibility that ice may crystallize with such an alternating layer structure. The oxygen-atom arrangement assigned to ice corresponds to superimposing double oxygen layers in the sequence ABAB—(A at 00, B at $^1/_3\,^2/_3$, C at $^2/_3\,^1/_3$ of a hexagonal net). The sequence ABCABCABC— would also lead to an arrangement (diamond) such that each oxygen atom is surrounded by four others arranged tetrahedrally, which is indeed, so far as I can see, just as satisfactory as the reported arrangement. There is no good evidence that such a cubic modification of ice has been observed. However, the arbitrariness of orientation which we have found to exist for the water molecules in ice suggests that there may also be an arbitrariness in the sequence of double oxygen layers, with configurations such as ABABABCBCB— occurring. Such an alternating layer structure would have hexagonal symmetry, might develop faces at angles corresponding to the axial ratio $c/a = 1.63$, and would not be distinguishable so far as residual entropy is concerned from a crystal with fixed oxygen atom arrangement. The x-ray data show that the sequence of layers is not completely random, the structure being essentially ABABAB—; it is possible, however, that a change in the sequence, corresponding to twinning on the basal plane, occurs occasionally.

I am indebted to Professor W. F. Giauque for discussing the question of the structure and entropy of ice, as well as related questions, with me.

Summary

It is suggested that ice consists of water molecules arranged so that each is surrounded by four others, each molecule being oriented in such a way as to direct its two hydrogen atoms toward two of the four neighbors, forming hydrogen bonds. The orientations are further restricted by the requirement that only one hydrogen atom lie near each O–O axis. There are $(^3/_2)^N$ such configurations for N molecules, leading to a residual entropy of $R \ln {}^3/_2 = 0.805$ E. U., in good agreement with the experimental value 0.87 E. U.

The structure and entropy of other crystals showing randomness of atom arrangement are discussed.

PASADENA, CALIF. RECEIVED SEPTEMBER 24, 1935

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 507]

The Radial Distribution Method of Interpretation of Electron Diffraction Photographs of Gas Molecules

BY LINUS PAULING AND L. O. BROCKWAY

Introduction

The only method of interpretation of electron diffraction photographs of gas molecules which has been used to any great extent is the so-called *visual method*, involving the correlation of apparent maxima and minima on the photographs with maxima and minima on simplified theoretical curves calculated for various models of the molecule under consideration. This method of interpretation, originally developed by Wierl,[1] has been thoroughly tested by Pauling and Brockway[2] who have shown it to yield values of interatomic distances accurate to within about 1% (estimated probable error). The main disadvantage of the method is that it does not involve a straightforward process of determining the structure of a molecule from the analysis of experimental results, but consists instead in the testing (and rejection or acceptance) of any structures which may be formulated, a tedious calculation being required for each structure.

We have developed a new method of interpretation of the photographs which does not suffer from this disadvantage. This *radial distribution method*, which is closely related to the method of interpretation of x-ray diffraction data developed by Zernike and Prins[3] for the study of the structure of liquids and applied by Warren and Gingrich[4] to crystals, consists in the calculation (from

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

[2] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[3] F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927); see also P. Debye and H. Menke, *Ergeb. Tech. Röntgenkunde*, Akad. Verlagsges., Leipzig, Vol. II, 1931.

[4] B. E. Warren and N. S. Gingrich, *Phys. Rev.*, **46**, 368 (1934).

data provided by the electron diffraction photograph) of a distribution function for scattering power, representing the product of the scattering powers in volume elements the distance l apart as a function of l. Since the scattering power of an atom for fast electrons is large only in the neighborhood of the nucleus, a maximum in this distribution function indicates that the internuclear distance for two atoms in the molecule is given by the corresponding value of l. The radial distribution method thus leads directly to values of the internuclear distances and hence to the structure of the molecule.

Because of the difficulty of obtaining satisfactory photometer records of electron diffraction photographs of gas molecules, we have adapted and extended the visual method to the calculation of radial distribution curves, by making use of the values of $(4\pi \sin \vartheta/2)/\lambda$ obtained by the measurement of ring diameters (as in the usual visual method) in conjunction with visually estimated intensities of the rings, as described below. Various tests of the method indicate that the important interatomic distances can be determined in this way to within 1 or 2% (probable error).

The radial distribution method, while thus not completely independent of the usual visual method, is sufficiently different from it to lead in some cases to somewhat different values for interatomic distances. We feel that these values carry some weight, and we have accordingly discussed by the new method a number of molecules whose structures as determined by the usual visual method have been reported in earlier publications, and have then combined the results of the two methods in presenting a revised set of values of interatomic distances for these molecules.

The radial distribution method is especially satisfying in that it leads directly to the values of the principal interatomic distances, and so immediately rules out all structures for the molecule except those compatible with these values. Moreover, the method can be applied unchanged to those molecules for which the investigator is unable to formulate a reasonable structure (such as S_2Cl_2, in which the rotation about the S–S bond may be restricted to some extent, leading to difficultly predictable variation in the Cl–Cl distance), yielding a distribution curve which reveals the information provided by the photograph regarding the structure of the molecule.

We are greatly indebted to Dr. S. Weinbaum, Dr. J. Sherman, and Mr. J. Y. Beach for assistance in the preparation of this paper.

Description of the Method

The intensity of the coherent electron scattering at the angle ϑ by gas molecules is usually represented by the expression

$$I(\vartheta) = K \sum_i \sum_j \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}} \tag{1}$$

in which K is a constant, and

$$x_{ij} = \frac{4\pi \sin \vartheta/2}{\lambda} l_{ij} \tag{2}$$

with l_{ij} the distance between atoms i and j in the molecule, λ the wave length of the electrons, and ψ_i the scattering function for the ith atom. A more general expression is

$$s^4 I(s) = K' \int_0^\infty l^2\, D(l)\, \frac{\sin sl}{sl}\, \mathrm{d}l \tag{3}$$

in which we have introduced the new angle variable

$$s = (4\pi \sin \vartheta/2)/\lambda \tag{4}$$

and have replaced the double sum by an integral, writing in place of the product of atomic scattering powers $\psi_i\psi_j$ the function $l^2\, D(l)/s^4$, representing, aside from the factor $1/s^4$ (the scattering factor for electrons by a unit charge), the product of scattering powers in all volume elements the distance l apart. This expression is a Fourier integral for $s^5 I(s)$, the coefficients of the Fourier terms being $lD(l)$. On inverting the Fourier integral we obtain the following expression for $D(l)$ in terms of $I(s)$

$$D(l) = K'' \int_0^\infty s^6\, I(s)\, \frac{\sin sl}{sl}\, \mathrm{d}s \tag{5}$$

Instead of attempting to apply the expression in this form, we simplify it radically in a way suggested by the appearance of the electron diffraction photographs, which to the eye show a succession of rings; namely, by replacing the integral by a finite sum of terms, including one term for each ring. We accordingly write, ignoring the constant K''

$$D\,(l) = \sum_{k=1}^{n} I_k \frac{\sin s_k l}{s_k l} \tag{6}$$

in which

$$s_k = (4\pi \sin \vartheta_k/2)/\lambda$$

ϑ_k being the scattering angle for the kth ring as measured in the usual way,[2] and I_k an estimated value[5] for the integrated intensity of the kth ring

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(5) It is our experience that the intensities as estimated visually (the change from ring to ring being small, as seen in the tables) are satisfactory, despite neglect of the factor s^6. This may be due in part to the comparison by the eye of each ring with the adjacent background, which falls off in intensity approximately with $1/s^4$.

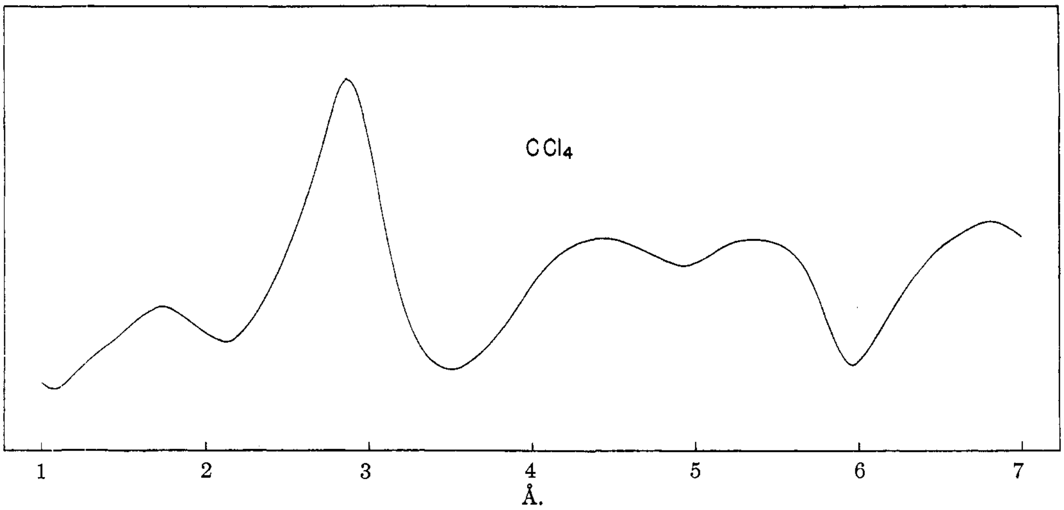

Fig. 1.—Radial distribution function for carbon tetrachloride. The part of the curve beyond 4 Å. is without significance.

(the factor s^6 being included in I_k). This simplification, which at first seems extreme, is seen on analysis not to be unreasonable; each section of the integral, corresponding to the range of angles between successive apparent minima, is replaced by a single Fourier term, whose frequency is in the middle of the frequencies for the range replaced, the coefficient of the single term being an integrated coefficient over the range. For values of l in the region of importance (corresponding to interatomic distances in the molecule) this simplification will not change the form of $D(l)$ very much; at smaller and larger values of l, however, it will introduce false maxima, instead of falling asymptotically to zero.

It is seen that the calculation of a radial distribution curve is closely similar to the calculation of a simplified theoretical intensity curve for the usual visual method, the summation being over the rings seen on the photograph instead of over the interatomic distances in the assumed model; but whereas in the usual treatment the calculation may need to be repeated for many models, a single curve only is required for the new method.

In the usual treatment the apparent intensities of the rings play only a minor part, in that some use is made of them in the decision among models by qualitative comparison of photograph and curves. Numerical values of estimated intensities are needed for the new method; it is found empirically, however, that the positions of the principal maxima are not very sensitive to changes in the estimated intensities, as long as the rings are kept in correct qualitative relation to one another. It is sometimes necessary to introduce a term in the series to represent a shelf on one side of a ring, or some similar feature of the photograph.(6)

In the calculations reported in this paper the curves were evaluated at intervals of 0.1 Å. except in the neighborhood of the principal maxima, where smaller intervals (usually 0.02 Å.) were used. The values of $(\sin sl)/sl$ were obtained from tables prepared by Dr. P. C. Cross with the aid of Sherman's $(\sin x)/x$ tables.(7)

Tests of the Method

Carbon Tetrachloride.—By the usual visual method and by other methods involving microphotometer records, we have assigned(8) to the carbon tetrachloride molecule the value 1.760 ± 0.005 Å. for the C–Cl distance, a value supported by other recent work.(9) The radial distribution function for this molecule calculated by Equation 6, using the ten terms for which data are given in Table I, is shown in Fig. 1.

It is seen that the six Cl–Cl terms are shown by a very sharp peak, the four C–Cl terms appearing

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(6) Dr. Simon Bauer has suggested that it may sometimes be convenient to introduce terms corresponding to the apparent minima between rings, using negative coefficients.

(7) J. Sherman, *Z. Krist.*, **85**, 404 (1933). The tables prepared by Dr. Cross give values of $(\sin sl)/sl$ for $0.80 \leqslant s \leqslant 4.00$ at intervals of 0.01, for values of l up to 40, and $4.02 \leqslant s \leqslant 8.00$ at intervals of 0.02, for values of l up to 20, the intervals for l being 0.2.

(8) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(9) V. E. Cosslett and H. de Laszlo [*Nature*, **134**, 63 (1934)] report 1.754 ± 0.02 Å. and V. E. Cosslett [*Trans. Faraday Soc.*, **30**, 981 (1934)] reports 1.74 ± 0.02 Å. C. Degard, J. Pierard and W. van der Grinten give the values 1.75 ± 0.02 Å. (electron diffraction) and 1.74 ± 0.02 Å. (x-ray diffraction) in a letter to *Nature*, **136**, 142 (1935).

TABLE I

CARBON TETRACHLORIDE

k	I_k	s_k
1	20	2.93
2	30	4.91
3	15	7.13
4	10	9.23
5	10	11.34
6	5	13.54
7	4	15.79
8	2	17.82
9	1	19.98
10	1	22.34

as a small peak at a smaller value of l; in addition some broad peaks occur at larger values of l. The complete Fourier integral representing the radial distribution would, of course, fall asymptotically to zero after the Cl–Cl maximum. Because of the crudity of our approximation to the integral by a series of ten terms we can expect our function to continue to vary appreciably in this region, the maxima there having no significance.

The l value given by the small C–Cl peak, about 1.74 Å., is unreliable, inasmuch as it is rather sensitive to change in the number of rings considered. That given by the Cl–Cl hump, however, is reliable. It is Cl–Cl = 2.856 Å., which corresponds to C–Cl = 1.749 Å., in good agreement with the earlier value, the deviation being in the direction of the values of Cosslett and de Laszlo.

The effect of including successive rings is shown in Fig. 2, the first curve including only one term (ring 1), the second two (rings 1 and 2), and so on. It is seen that the principal peak assumes its position and shape very quickly, the Cl–Cl distance being given to within 2% (2.81 Å.) by two terms alone, and quickly rising to a constant value (2.85 Å. for five terms, 2.86 Å. for six and more terms). The small C–Cl peak, on the other hand, fluctuates considerably, the l value varying between 1.72 and 1.78 Å. for curves 5 to 10.

Bromine and Chlorine.—Accurate values of the internuclear distances in the molecules Br_2 and Cl_2 are known from band spectral studies, namely, Br–Br = 2.281 Å. and Cl–Cl = 1.988 Å. The visual method led to results (2.289 Å. and 2.009 Å., respectively) in satisfactory agreement with these.[8] Radial distribution curves for these substances are shown in Fig. 3, the data used being given in Tables II and III. For bromine, with seven rings, three different estimates of intensities lead to the same Br–Br distance, 2.270 Å., less than 0.5% from the band spectral value. The Cl–Cl distance, given by the curve, 1.995 Å., is still closer to that found from band spectra. The agreement for these two molecules indicates that there is no large error inherent in the radial distribution method.

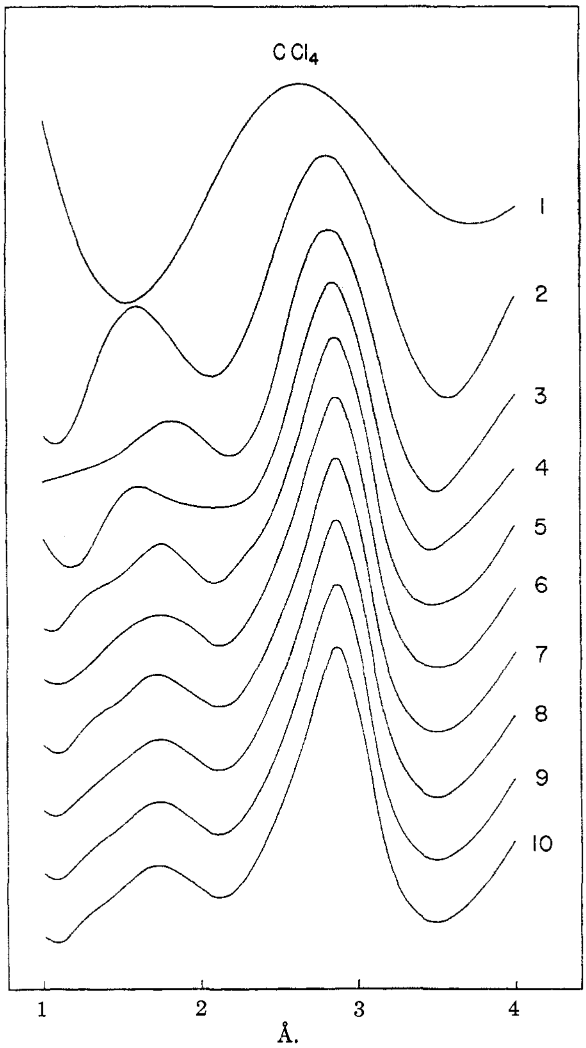

Fig. 2.—Radial distribution curves for carbon tetrachloride, calculated with one term (1), two terms (2) and so on.

Benzene.—A careful study of photographs of benzene both by the visual method and by the analysis of microphotometer records[8] has led to the value C–C = 1.390 ± 0.005 Å. for the edge of the plane hexagon formed by the carbon atoms, in agreement with the values 1.39 ± 0.03 Å. and 1.40 ± 0.03 Å. reported by Wierl.[1] The accuracy of this determination and the fact that the various carbon–carbon distances are geometrically related

TABLE II

BROMINE

k	I_k A	B	C	s_k
1	6	32	16	3.50
2	5	16	12	6.17
3	4	8	8	8.90
4	3	4	4	11.67
5	2	2	2	14.44
6	1	1	1	17.19

TABLE III

CHLORINE

k	I_k	s_k
1	10	3.94
2	5	6.99
3	2	10.08
4	1	13.30

make benzene a suitable substance for testing the new method.

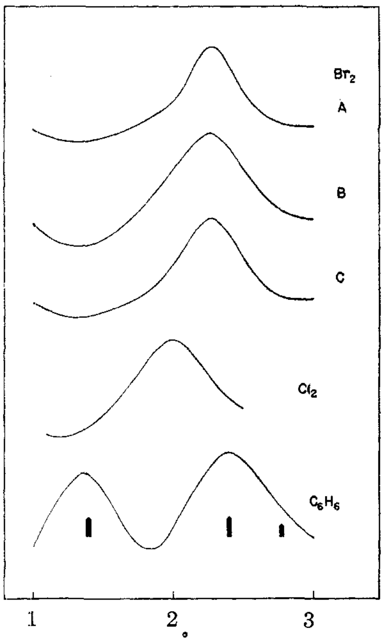

Fig. 3.—Radial distribution curves for bromine, chlorine and benzene.

The radial distribution curve calculated with the inclusion of seven terms, for which data are given in Table IV (the fourth and sixth terms corresponding to apparent shelves rather than well-defined rings), is shown in Fig. 3.

Only the two principal distances, corresponding to the six ortho C–C interactions and the six meta C–C interactions, are represented by maxima, the three para C–C interactions (which should yield a hump about one-half as pronounced as the others at the position indicated by the smallest arrow) and the various C–H interactions not being indicated on the curve. This is in agreement with our experience in general with the radial distribution method, which usually can be relied on (in the form in which we are using it) to provide information regarding only the two or three most important interactions, the peaks for which must also be separated by at least about 0.5 Å. in order to be resolved.

TABLE IV

BENZENE

k	I_k	s_k
1	50	3.35
2	160	5.805
3	20	9.55
4	5	11.50
5	15	13.83
6	3	16.23
7	8	18.66

The two maxima occur at the distances 1.381 and 2.390 Å., their ratio being 1:1.731. The close approximation of this ratio to the value $1:\sqrt{3}$ required by the hexagonal configuration of the molecule provides an interesting check on the method.

The value 1.381 Å. is 0.009 Å. less than that found in the earlier treatment. We believe that in this case the earlier treatment, involving the analysis of microphotometer records as well as the application of the usual visual method, is the more reliable, and we prefer not to change from the value 1.390 ± 0.005 Å. Indeed, we think that the usual visual method is itself somewhat more reliable than the radial distribution method in the case of benzene, inasmuch as the photographs show some precisely measurable features (very sharp fourth minimum and fourth maximum) as well as some rather diffuse rings which can be measured only with less precision; in the usual visual method great weight can be given to the results calculated from the precisely measured features, whereas in the radial distribution method the weighting is determined by the intensities of the rings, the result being dependent on the diffuse as well as the sharp ones.

Tetrahedral Molecules.—The tetrahedral molecules MX_4 permit an interesting test of the radial distribution method in that the ratio of the two distances X–X and M–X should be $2\sqrt{2}/\sqrt{3} = 1.633$. We have seen that in carbon tetrachloride this ratio is given by the curve to within about 1%. The compounds CF_4, SiF_4,

$SiCl_4$, $GeCl_4$ and $SnCl_4$ provide better tests, inasmuch as the two maxima arise from more nearly equal interactions. The curves for these five molecules, calculated for the constants[10] given in Table V, are shown in Fig. 4. It is seen that each curve shows two well-defined peaks, that for X–X being stronger than that for M–X in CF_4 and $SiCl_4$, and weaker in the other three. The lack of symmetry of the peaks (particularly pronounced for $GeCl_4$) could presumably be remedied by changing the estimated values of I_k; though such a procedure might be justified, we have not adopted it, retaining instead the original estimates in every case.

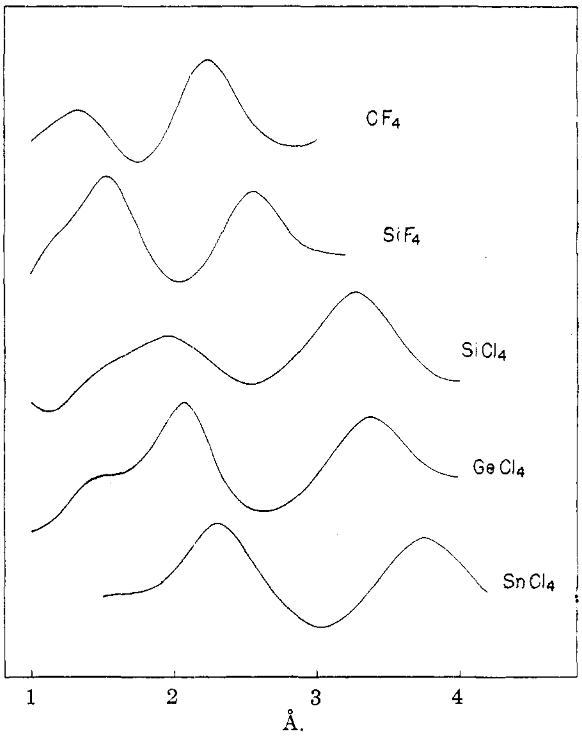

Fig. 4.—Radial distribution curves for carbon and silicon tetrafluorides and silicon, germanium and tin tetrachloride.

The values of l for the X–X and M–X peaks are given in Table VI, together with their ratios. It is seen that the ratio is in every case slightly higher than the correct value 1.633. The deviations of 0.3 to 2.7% provide some indication as to the reliability of the method; there seems to be some tendency for the maxima of the two peaks to be displaced away from one another.

TABLE V

TETRAHALIDES

	CF_4		SiF_4		$SiCl_4$		$GeCl_4$		$SnCl_4$	
k	I_k	s_k	I_k	s_k	I_k	s_k	I_k	s_k	I_k	s_k
1	10	3.56	40	5.41	15	2.55	3	2.29	60	3.67
2	25	6.18	20	8.27	40	4.25	30	4.09	60	5.62
3	10	9.28	5	9.97	15	6.29	20	6.27	20	6.70
4	3	12.06	10	13.02	5	8.04	8	7.22	16	8.78
5	3	14.49	3	17.27	8	9.90	15	9.75	8	11.67
6			1	21.34	1	11.89	6	12.75	4	14.23
7					3	13.85	3	15.46	2	16.79
8					1	15.93	2	18.51		

TABLE VI

DISTANCES IN TETRAHALIDE MOLECULES

Compound	CF_4	SiF_4	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$
X–X, Å.	2.235	2.555	2.870	3.274	3.385	3.760
M–X, Å.	1.335	1.527	1.74	1.963	2.070	2.295
Ratio	1.674	1.673	1.649	1.668	1.635	1.638

Carbon Disulfide and Carbon Oxysulfide.—Radial distribution curves for carbon disulfide and carbon oxysulfide (treated by the usual method by Cross and Brockway[11]) are shown in Fig. 5. For carbon disulfide the maxima of the two peaks occur at 1.60 and 3.07 Å. In this symmetrical linear molecule the C–S distance is just one-half the S–S distance; the values found deviate from this ratio by 4%. Similarly in carbon oxysulfide the sum of two interatomic distances equals the third. The values C–S = 1.60 Å. and O–S = 2.70 Å. given by the two maxima differ by 1.10 Å. The C–O distance is not given by the curve (being indicated only by a hump at the point indicated by the arrow); there is little doubt that the value 1.16 ± 0.02 Å. found by Cross and Brockway is

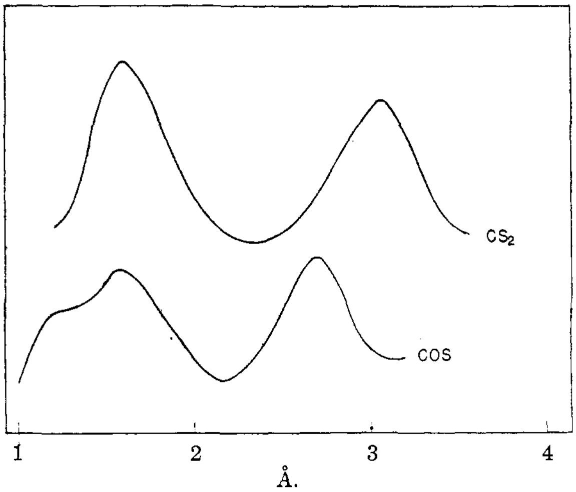

Fig. 5.—Radial distribution curves for carbon disulfide and carbon oxysulfide.

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[10] The s_k values are in the main taken from (a) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934), and (b) L. O. Brockway, *ibid.*, **57**, 958 (1935), with values for shelves (not given in these papers) obtained by measurement of the original photographs.

[11] P. C. Cross and L. O. Brockway, *J. Chem. Phys.*, **3**, December (1935).

reliable, however, showing that there is an error of about 3% in the values given by the maxima. It is interesting to note that the two peaks for these curves are displaced toward one another, rather than away from one another as for the tetrahalides.

The comparison with the interatomic distance values reported by Cross and Brockway, C–S = 1.54 ± 0.03 Å. and S–S = 3.08 ± 0.06 Å. in CS_2, C–O = 1.16 ± 0.02 Å., C–S = 1.56 ± 0.03 Å., and O–S = 2.72 ± 0.05 Å. in COS, indicates that of the two peaks of these radial distribution curves the outer one is somewhat more reliable than the inner one.

TABLE VII

CARBON DISULFIDE AND CARBONYL SULFIDE

	CS_2		COS	
Ring	*I*	*s*	*I*	*s*
1	50	4.713	15	5.23
2	12	6.312	10	7.67
3	16	8.698	4	9.82
4	4	10.63	6	12.20
5	8	12.65	2	14.04
6	2	14.58	3	16.65
7	4	16.81		
8	1	18.7		
9	2	21.0		

Discussion of the Method

From the examples given we see that the radial distribution method in the simplified form which we have developed for the treatment of electron diffraction photographs of gas molecules is reasonably reliable and accurate, usually providing values of the two or three most important interatomic distances in the molecule (that is, those which contribute most to the diffraction pattern) with an accuracy of 1 or 2%. Probably the principal advantage of the method is that its application is straightforward; no previous information or hypothesis regarding the structure of the molecule (or, in fact, regarding even the chemical composition of the scattering gas) is needed. The information provided by a radial distribution curve usually eliminates all models of the molecule under consideration except those defined by a narrow range of values of the structural parameters; these models can then be considered in detail by the usual method, this consideration usually leading to a further restriction in the parameter values. The calculation of a radial distribution curve is thus the logical first step in the analysis of an electron diffraction photograph. Examples showing the use of these curves are included in the following paper.

We recommend that in general values of interatomic distances given by the two methods be averaged, with about equal weights unless it is felt that in a special case one method is more satisfactory than the other. The usual visual method is superior to the radial distribution method under circumstances such as the following: (1) when there are geometrical relations among interatomic distances (CS_2, C_3O_2, benzene, etc.); (2) when the photographs show some especially precisely measurable features, such as some very sharp rings (benzene); (3) when knowledge regarding certain structural parameters is available and it is desired to vary only the others; (4) when the molecule contains two or more important interatomic distances with values so close to one another that the corresponding peaks are not resolved on the radial distribution curves. On the other hand, the radial distribution method is superior in cases such as the following: (1) when the molecule contains rotating groups or some other structural feature making the detailed formulation of a model difficult (S_2Cl_2, etc.); (2) when the decision as to the model depends on quantitative intensity estimates and small changes in ring diameters (ClO_2, SO_2, etc.).

Revised Values of Structural Parameters of Molecules

On calculating radial distribution curves for molecules for which structures have been previously reported from this Laboratory on the basis of the usual method of interpretation, we have in some cases obtained interatomic distance values agreeing exactly with the earlier values and in some cases values which deviate by a small amount (rarely more than 3%). For a few molecules the new method has provided information (bond angles in ClO_2 and SO_2) not before available. We feel that it is worth while to present a table of revised values of structural parameters for these molecules, giving weight to the results of both methods. The revision includes most of the substances which have been studied in this Laboratory; some (methyl azide, diacetylene, carbon suboxide, dioxane, etc.) are omitted because of the small number of rings shown on the photographs or the unsuitability of the radial distribution method (for reasons such as those mentioned above).

Benzene.—We recommend no change in the value C–C = 1.390 ± 0.005 Å. in benzene.

Tetrahalides.—Values of M–X and (X–X)/1.633 given by the maxima on the radial distribution curves (Figs. 1 and 4) for six tetrahalides are shown in the second and third columns of Table XI, with the values obtained by the usual visual method[10a] in the fourth column. In averaging these we have assigned weights to the two radial distribution peaks as indicated by their prominence, and have given the two distinct methods about equal weight. It is seen that in no case is the change made greater than 1%.

Trihalides of Phosphorus and Arsenic.—Radial distribution curves for PF_3, AsF_3, PCl_3 and $AsCl_3$, calculated with the data given in Table VIII, are shown in Fig. 6. Each curve shows two peaks, corresponding to M–X and X–X; values for their maxima (except for X–X in AsF_3, this peak being so broad as to make its maximum unreliable) are given in Table XII, together with the values obtained by the usual visual method in an earlier investigation.[10a] The weighted averages for M–X, X–X and the X–M–X angle are given in the last three columns.

TABLE VIII

TRIHALIDE MOLECULES

	PF_3		AsF_3		PCl_3		$AsCl_3$	
Ring	*I*	*s*	*I*	*s*	*I*	*s*	*I*	*s*
1	4	5.74	10	4.73	5	2.76	2	2.33
2	2	8.82	5	8.09	15	4.54	20	3.944
3	1	13.45	2	11.77	10	6.66	10	6.234
4			1	15.26	1	8.75	3	9.55
5					4	10.38	2	12.13
6					3	12.58		

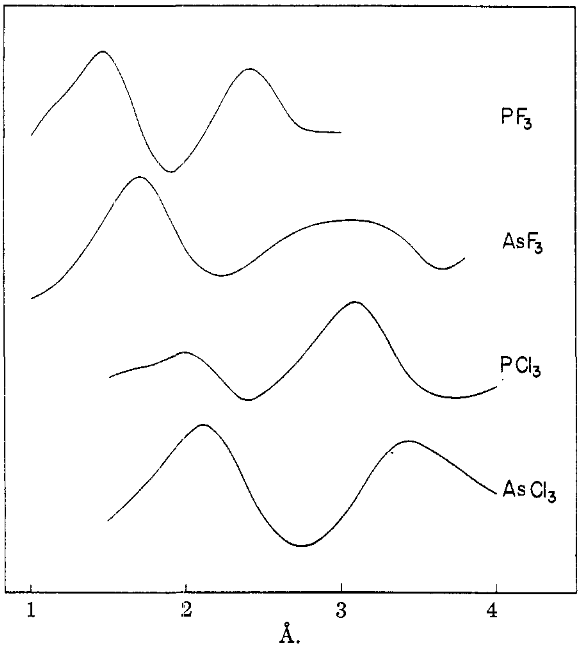

Fig. 6.—Radial distribution curves for triflourides and trichlorides of phosphorus and arsenic.

Methylene Chloride and Chloroform.—Curves for CH_3Cl, CH_2Cl_2 and $CHCl_3$ (Table IX) are shown in Fig. 7. The maximum for methyl chloride lies at 1.80 Å.; we do not consider this value sufficiently reliable to warrant a change from the value C–Cl = 1.77 ± 0.02 Å. previously reported.[12] The M–X and X–X values given by the maxima for methylene chloride and chloroform (Table XII) are in excellent agreement with those found by the usual method.

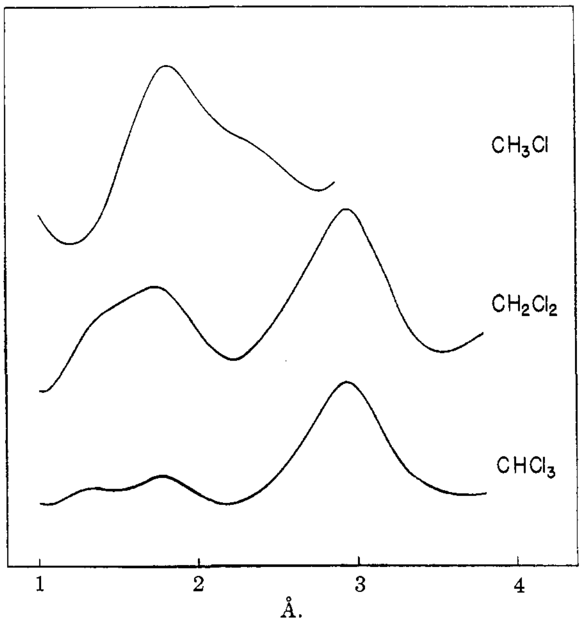

Fig. 7.—Radial distribution curves for methyl chloride, methylene chloride and chloroform.

TABLE IX

	CH_3Cl		CH_2Cl_2		$CHCl_3$	
Ring	*I*	*s*	*I*	*s*	*I*	*s*
1	15	4.07	15	2.81	25	2.74
2	8	8.12	40	4.81	40	4.78
3	3	11.24	15	7.00	20	6.99
4	1	14.49	8	8.84	10	9.04
5			10	11.01	15	11.16
6			3	13.28	3	13.32
7			5	15.41	3	15.32
8			1	17.94	1	17.47

Chlorine Monoxide, Dimethyl Ether, Chlorine Dioxide and Sulfur Dioxide.—The radial distribution curves for Cl_2O, $(CH_3)_2O$, ClO_2 and SO_2 (Fig. 8) show two peaks, the positions of the

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(12) Sutton and Brockway, THIS JOURNAL, **57**, 473 (1935).

maxima being recorded in Table XII. For chlorine monoxide we have averaged the results of the two methods with equal weights (the agreement being less satisfactory than usual). In the case of dimethyl ether smaller weight is given to the results of the radial distribution method because of the lack of symmetry of the first peak, which may cause the maximum to be displaced. It is interesting to note that the radial distribution method provides values of the angles in ClO_2 and SO_2, whereas the usual method of interpretation failed in this respect, presumably because the qualitative comparisons must be supplemented by quantitative considerations in order to obtain this information.

TABLE X

	ClO_2		$(CH_3)_2O$		ClO_2		SO_2	
Ring	*I*	*s*	*I*	*s*	*I*	*s*	*I*	*s*
1	5	2.801	10	6.024	5	4.98	10	5.625
2	15	4.835	4	9.744	2	9.25	6	9.66
3	3	7.328	2	13.63	1	13.68	2	13.76
4	1	9.14	1	17.78			1	18.15
5	1	11.45						

TABLE XI

M–X DISTANCES IN TETRAHALIDE MOLECULES

	Radial distribution		Visual	
	M–X	X–X/1.633	method	Final values of M–X
CF_4	1.335 Å.	1.369 Å.	1.360 Å.	1.36 ± 0.02 Å.
SiF_4	1.527	1.565	1.544	1.54 ± 0.02
CCl_4	(1.74)	1.749	1.760	1.755 ± 0.005
$SiCl_4$	1.963	2.005	2.016	2.00 ± 0.02
$GeCl_4$	2.070	2.073	2.103	2.08 ± 0.C2
$SnCl_4$	2.295	2.303	2.289	2.30 ± 0.02

Summary

It is shown by empirical tests that the radial distribution function given by a sum of Fourier terms corresponding to the rings observed on an electron diffraction photograph of gas molecules (using visually measured ring diameters and estimated intensities) provides values of the important interatomic distances accurate to one or two per cent. (probable error). The substances used in the tests include carbon tetrachloride and other tetrahalides, bromine, chlorine, benzene, carbon disulfide and carbon oxysulfide.

The radial distribution method of interpretation is applied to a number of molecules previously investigated, and revised values of interatomic distances and bond angles, obtained by considering the results of this method as well as of the usual visual method, are presented (Tables XI and XII).

It is pointed out that the radial distribution method is particularly satisfying in that it leads directly to the values of the important interatomic distances in the molecule, thus eliminating many possible models and usually limiting the molecule to the structures represented by small ranges of values of the structural parameters.

TABLE XII

INTERATOMIC DISTANCES IN MOLECULES MX_2 AND MX_3

	Radial distribution			Visual method			Final values		
	M–X	X–X	Angle	M–X	X–X	Angle	M–X	X–X	Angle
PF_3	1.47 Å.	2.41 Å.	110°	1.56 Å.	2.37 Å.	99°	1.52 ± 0.04 Å.	2.39 ± 0.03 Å.	104 ± 4°
AsF_3	1.70	...	...	1.73	...	...	1.72 ± .02	... ...	... ..
PCl_3	1.98	3.08	102	2.02	3.09	100	2.00 ± .02	3.09 ± 0.02	101 ± 2
$AsCl_3$	2.13	3.43	107	2.18	3.36	101	2.16 ± .03	3.39 ± .04	103 ± 3
CH_2Cl_2	(1.73)	2.935	...	1.77	2.92	111	1.77 ± .02	2.93 ± .02	112 ± 2
$CHCl_3$	(1.77)	2.931	...	1.78	2.93	111	1.77 ± .02	2.93 ± .02	112 ± 2
Cl_2O	1.65	2.86	120	1.71	2.82	111	1.68 ± .03	2.84 ± .03	115 ± 4
$(CH_3)_2O$	1.38	2.28	111	1.44	2.39	111	1.42 ± .03	2.35 ± .05	111 ± 4
ClO_2	1.53	2.85	137	1.53	...	...	1.53 ± .02	2.85 ± .15	137 ± 15
SO_2	1.43	2.56	127	1.46	...	...	1.45 ± .02	2.56 ± .15	124 ± 15

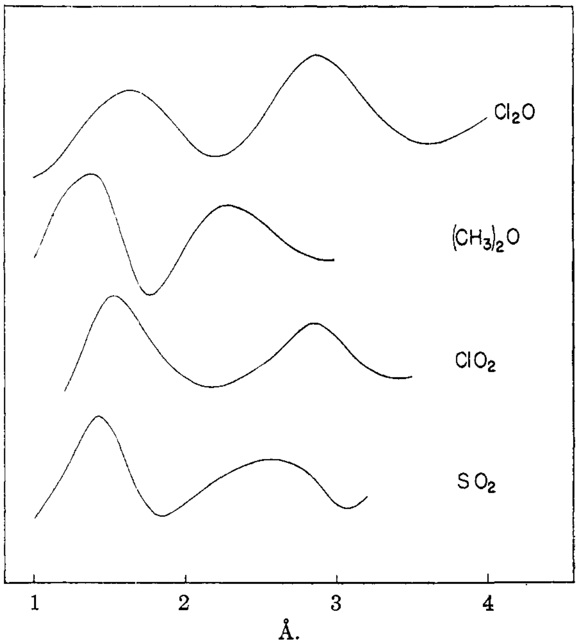

Fig. 8.—Radial distribution curves for chlorine monoxide, dimethyl ether, chlorine dioxide and sulfur dioxide.

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