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Citation: [The Journal of Chemical Physics](#) **2**, 867 (1934); doi: 10.1063/1.1749410

View online: <http://dx.doi.org/10.1063/1.1749410>

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A Study of the Methods of Interpretation of Electron-Diffraction Photographs of Gas Molecules, with Results for Benzene and Carbon Tetrachloride

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(Received September 17, 1934)

The reliability and accuracy of the visual method of interpreting electron-diffraction photographs, consisting in the correlation of values of $(4\pi \sin \vartheta/2)/\lambda$ obtained by visual measurement of rings of apparent maximum and minimum intensity with x values from a simplified theoretical curve (Eq. (7) or (8)), have been tested in the following ways: (a) The measurement and interpretation of "artificial electron-diffraction photographs" of bromine; (b) the comparison of electron-diffraction and band-spectral values of interatomic distances for bromine, chlorine and iodine chloride; (c) the study of micro-photometer records for benzene, and comparison of results

with those of the visual method; (d) the study of micro-photometer records for carbon tetrachloride, and comparison with the visual method. It is concluded that the visual method when carefully applied leads to values of interatomic distances accurate to about 1 percent (probable error), or to $\frac{1}{2}$ percent in favorable cases. The regular plane hexagon model of the benzene molecule is verified, the carbon-carbon distance in the ring being determined as $1.390 \pm 0.005\text{\AA}$. The carbon-chlorine distance in the carbon tetrachloride molecule is determined as $1.760 \pm 0.005\text{\AA}$. A brief discussion of the methods and results of other investigators is given.

THE investigation of the structure of gas molecules by the diffraction of electron waves was begun by Mark and Wierl¹ soon after the pioneer work of Debye² and co-workers on the diffraction of x-rays by gas molecules. The method has shown itself to be very useful, especially because the large scattering powers of atoms for electrons permit the use of very small exposure times (of a fraction of a second), and several groups of investigators (in the main with chemical interests) have entered the field. The recently discovered correlations of interatomic distances with electronic structure³ and with force constants of bonds⁴ have increased the interest in interatomic-distance measurements, and various other considerations, such as those regarding the angles between bonds, have emphasized the importance of determining accurately the configurations of many molecules. It is consequently desirable that the assumptions involved in the usual methods of interpretation of electron-diffraction photographs of gas molecules be critically examined, especially since these methods have received much unfavorable comment. We have carried out such an examination, using several independent and (we believe)

objective checks on the usual method. Our results, described in this paper, show that a simple method of interpretation (involving the visual measurement of diameters of rings of apparent maximum and minimum intensity and the comparison with simplified theoretical curves) leads, when carefully carried out, to the determination of molecular configurations with a probable error of about $\frac{1}{2}$ or 1 percent in the interatomic distances.

The general character of the following discussion of the theory and the correlated method of interpreting electron-diffraction photographs is determined by the nature of our interests. We are primarily concerned with developing a reliable method of determining interatomic distances which is simple enough to make practicable its application to a large number of compounds. The discussion of the theory in the next section indicates in part the arguments used by us in fixing on a particular procedure; it is not intended to be complete or rigorous. An attempt to establish the complete validity of the theoretical formulas for electron scattering would necessarily include the treatment of the incoherent scattering of electrons as well as the standardization of the photographic emulsions for electrons over a wide range of intensities, and the quantitative estimate of that part of the background intensity which is due to multiple scattering, to x-rays, and especially

¹ (a) H. Mark and R. Wierl, *Naturwiss.* **18**, 205, 778 (1930); (b) R. Wierl, *Ann. d. Physik* **8**, 521 (1931); (c) **13**, 453 (1932).

² P. Debye, *Phys. Zeits.* **30**, 524 (1929); **31**, 142, 348, 419 (1930); etc.

³ L. Pauling, *Proc. Nat. Acad. Sci.* **18**, 293 (1932).

⁴ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934).

to electrons scattered by gas in the diffraction chamber at points other than the intersection of the electron and gas beams. With this treatment quantitative agreement between calculated and observed intensities might be obtained. It would still be necessary, however, to resort to empirical tests in order to determine the sensitivity of the procedure as a method of finding interatomic distances.

We have chosen the visual treatment (for reasons given in the latter part of this paper) from among the various simplified procedures which are available. In view of the results reported below we believe that simplicity can be combined with accuracy in the use of electron diffraction as a method of determining interatomic distances.

A. DISCUSSION OF THE VISUAL METHOD OF INTERPRETATION

Electron-diffraction photographs of gas molecules, obtained by the usual experimental methods,⁵ show well-defined rings, making it appear that as the scattering angle increases the intensity of the scattered beam of electrons and the blackening of the photographic film pass through successive maximum and minimum values. This can be seen from the reproductions of Fig. 1, and much more clearly still on the original negatives, which may show as many as ten well-defined and measurable apparent maxima. The maxima and minima are not real, however, as was first pointed out by Wierl. Microphotometer records of three photographs are shown in Figs. 2 and 3. It is seen that the blackening of the film falls off monotonically from the center, the apparent maxima and minima on the photographs corresponding to fluctuations in the density about a rapidly falling background. It is a psychological or physiological phenomenon which causes the photographs to appear to show maxima and minima.

The character of the diffraction pattern as shown by the microphotometer records is in agreement with theoretical considerations. Debye⁶ and Wierl¹ have shown that the intensity

⁵ Such as described by Wierl.

⁶ P. Debye, *Ann. d. Physik* **46**, 809 (1915).

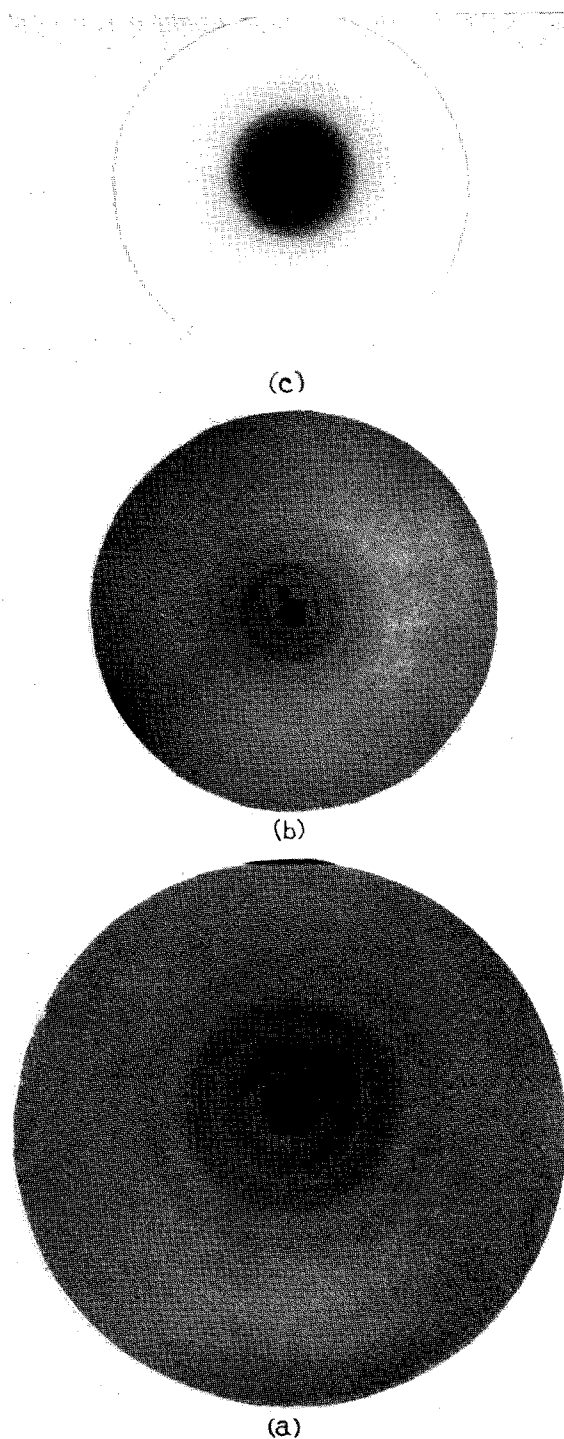


FIG. 1. Contact prints of electron-diffraction photographs. (a) Carbon tetrachloride at 28.7 cm. (b) Carbon tetrachloride at 12.19 cm. (The small spot to one side of the central image is due to visible light from the filament.) (c) Benzene at 12.19 cm.

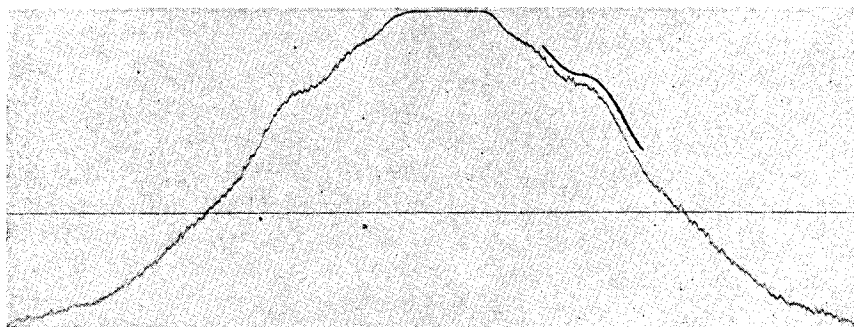


FIG. 2. Microphotometer record of a benzene photograph.

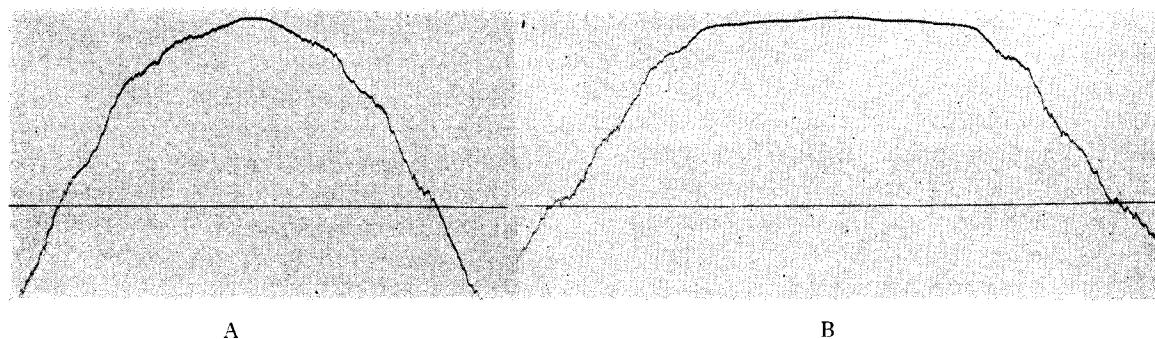


FIG. 3. Microphotometer records of carbon tetrachloride photographs, (A) showing the first, second, and third apparent maxima, (B) showing the first five apparent maxima.

of the coherent electron scattering at the angle ϑ is given by the expression

$$I = k \cdot \sum_i \sum_j \psi_i \psi_j (\sin x_{ij}) / x_{ij}, \quad (1)$$

in which k is a constant, and

$$x_{ij} = 4\pi l_{ij} ((\sin \vartheta/2)/\lambda), \quad (2)$$

with l_{ij} the distance between atoms i and j in the molecule and λ the wave-length of the electrons. The quantity ψ_i is the scattering function of the i 'th atom for electrons. It is approximated closely by the expression⁷

$$\psi_i = \frac{Z_i - f_i}{((\sin \vartheta/2)/\lambda)^2}, \quad (3)$$

in which Z_i represents the atomic number of the i 'th atom and f_i its scattering factor for x-rays, which is essentially a function of $(\sin \vartheta/2)/\lambda$.

⁷ H. Bethe, Ann. d. Physik **87**, 55 (1928); **5**, 325 (1930); N. F. Mott, Proc. Cambridge Phil. Soc. **25**, 304 (1929).

Reasonably accurate values of f_i are known for all atoms; in our discussion we have used Pauling-Sherman f -values.⁸ Now for convenience let us rewrite Eq. (1) as

$$I = I_{\text{atomic}} + I_{\text{molecular}}, \quad (4)$$

with

$$I_{\text{atomic}} = k \sum_i \psi_i^2 \quad (5)$$

and

$$I_{\text{molecular}} = k \sum_i \sum_j' \psi_i \psi_j (\sin x_{ij}) / x_{ij}. \quad (6)$$

The summations in Eqs. (5) and (6) include all the atoms in a molecule, except that in 6 the terms $i=j$ are omitted, as indicated by the prime.

The nature of the scattering functions ψ_i is such that I_{atomic} decreases very rapidly with increase in scattering angle ϑ , the increase in $Z-f$ not being sufficient to overbalance that in $\sin^2 \vartheta/2$. Consequently the photographs are ex-

⁸ L. Pauling and J. Sherman, Z. Krist. **81**, 1 (1932).

pected to show a very rapidly falling background, with fluctuations in the blackening about this background in accordance with the $\frac{\sin x}{x}$ functions of $I_{\text{molecular}}$.

Hence the correlation of theoretical intensity curves and observed blackening of the films cannot be made by any such simple objective method as comparing maxima and minima on the theoretical curves with those on the microphotometer records; to interpret the microphotometer records some more laborious procedure must be adopted, such as quantitative comparison over a wide angular range. In order to avoid any such time-consuming method of treatment as this, Wierl devised a simple expedient whereby the theoretical curves are so altered as to reproduce approximately the visual appearance of the photographs, with which they are then compared. This consisted in replacing the scattering function ψ_i by the atomic number Z_i , ignoring the term f_i and the factor $1/(\sin^2 \theta/2)$. The resultant curve then shows maxima and minima, which Wierl (and succeeding investigators) identified with the apparent maxima and minima in order to determine the structure of the molecule and to evaluate the interatomic distances.

This drastic simplification, which was given by Wierl without justification, other than the remark that the eye corrects for the effect of the factor $\csc^4 \theta/2$, can be made to appear reasonable by the following argument.

It is known that the sensitivity of the eye to change in stimulus is determined by the magnitude of the total stimulus, a change by a constant fraction of the total being detectable over a wide range of magnitudes of the total stimulus (Weber-Fechner law). It is accordingly not unreasonable for us to make the postulate that on the electron-diffraction photographs the eye detects fluctuations about a background to an extent determined by the ratio of the fluctuations to the background. Moreover, we assume for these considerations that the background is the function I_{atomic} , which falls off smoothly with increasing scattering angle. The apparent intensity of scattering we may then express as

$$I_{\text{apparent}} = \frac{I_{\text{molecular}}}{I_{\text{atomic}}} = \frac{\sum_i \sum_j \psi_i \psi_j (\sin x_{ij}) / x_{ij}}{\sum_i \psi_i^2}. \quad (7)$$

A curve showing this function for carbon tetrachloride is given in Fig. 4. It is seen on comparison with the photographs that this curve reproduces closely the appearance of the rings. For example, the second, fifth, seventh and tenth rings appear on the photographs to be as strong as the immediately preceding rings, or even somewhat stronger, in agreement with the calculated function (this phenomenon arising from the reinforcement of the carbon-chlorine and chlorine-chlorine terms). The function of Eq. (7) does not fall off in value with increasing angle quite as rapidly as is indicated by the appearance of the photographs, and it might be desirable to introduce a factor reducing the intensity at the rate of twenty or thirty percent for each maximum relative to the preceding one. We have not done this, however, because of the arbitrary character of such a correction; moreover, the quantitative comparison of maxima and minima would not be changed appreciably by this procedure (within about one-tenth of one percent).

We may emphasize the fact that the postulate underlying Eq. (7) is more definite than is necessary for the visual interpretation of the photographs in a satisfactory manner. The simple assumption that the eye observes the fluctua-

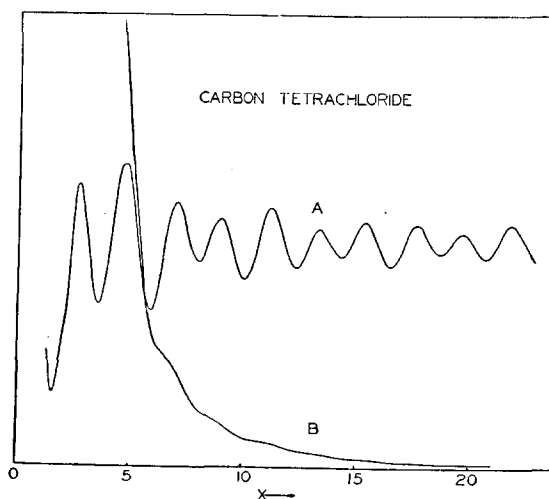


FIG. 4. The complete theoretical curve for carbon tetrachloride (B) and the simplified theoretical curve (A).

tions about the smooth background I_{atomic} with an apparent intensity lying somewhere between the actual intensity of the fluctuations (as given by Eq. (6) for $I_{\text{molecular}}$) and the intensity relative to the background (as in Eq. (7)) fixes the positions of the maxima and minima to within about 0.2 percent, after the first two maxima, for which the error is somewhat larger. This constancy in position of the maxima and minima, despite the fact that the magnitude of the fluctuations as given by Eq. (6) falls off from the first to the tenth maximum to one-thousandth of the value given by Eq. (7), results from the fixed position of the zeros of these two limiting curves and of all intermediate curves.

A further simplification in the calculation, leading to Wierl's treatment, can usually be made. If the molecule contains atoms of only one kind (Br_2 , P_4 , etc.) the terms $Z_i - f_i$ in numerator and denominator of Eq. (7) cancel, so that the expression is exactly the same as Wierl's expression

$$I_{\text{apparent}} = \sum_i \sum_j Z_i Z_j (\sin x_{ij}) / x_{ij}, \quad (8)$$

except for a constant factor and an additive constant, both of which are unimportant in the simplified procedure. Moreover, Eq. (7) reduces to 8 whenever the ratios $(Z_i - f_i) / Z_i$ are constant for all atoms in the molecule. These ratios are found to be roughly constant for most atoms. For example, for $(\sin \vartheta/2) / \lambda = 0.4$ the ratio has the values 0.87 for H, 0.61 to 0.69 for B to F, 0.46 to 0.51 for Al to Cl, and 0.39 to 0.42 for Ga to Br. Hence Eq. (8) can be safely used whenever the molecule contains only atoms from one row of the periodic table. Indeed, the error involved in even the most extreme cases is negligible in comparison with the limits of error inherent in the method at present, the positions of the maxima and minima never being shifted by more than a fraction of one percent, so that the simple expression (8) can almost always be used.

B. TESTS OF THE VISUAL METHOD OF INTERPRETATION

In order to obtain information as to the accuracy and reliability of the visual method

of interpretation of electron-diffraction photographs, involving the evaluation of interatomic distances through the quantitative identification of maxima and minima of the functions of Eq. (7) or (8) with the apparent maxima and minima on the photographs, we have carried out an extensive series of tests of various kinds. The nature of these and the results obtained are discussed in the following paragraphs.

A detailed description of our standard procedure is given in Section C.

I. The measurement of artificial photographs of Br_2

To test the fundamental postulate underlying the visual method of interpretation (Eq. (7)), we first prepared and measured "artificial electron-diffraction photographs." (This was done at the suggestion of Professor R. M. Badger, to whom we wish to express our thanks.) The complete intensity curve (neglecting incoherent scattering) was calculated for the bromine molecule, Br_2 , with the Br-Br distance 2.280 Å, using Eqs. (1) and (3) and Pauling-Sherman f -values. The portion of this curve including the region from the first maximum to the fourth minimum of the $(\sin x)/x$ function was then plotted on a large scale in polar coordinates (25 cm radius) in such a way that the intensity was represented by the length of the arc at the radius determined by the value of $(\sin \vartheta/2) / \lambda$, this portion of the arc being blackened. This drawing was then photographed on a process plate, to produce a mask. By passing light through this mask onto a photographic film rotating about its center, the film was subjected to the action of light of integrated intensity (at different distances from the center) represented by the original theoretical intensity curve for the bromine molecule, and the blackening of the film would correspond to this function except for the correction due to the characteristics of the emulsion for visible light. The resultant artificial electron-diffraction photograph was about 6 cm in diameter, corresponding to a gas-stream-to-film distance of about 30 cm for electron wave-length 0.06 Å. The photograph showed two well-defined minima and two maxima (the second and third of each), and closely resembled real electron-diffraction photographs of bromine.

At the time these photographs were prepared we were interested in the possibility of the existence of apparent maxima and minima (on visual examination) on photographs in which the density falls off monotonically from the center. This decrease would remain monotonic for any monotonic relation between photographic density and intensity of incident light, and so it was not necessary for us to correct the mask for the characteristics of the emulsion. The density of the photographs consequently did not reproduce exactly the calculated intensity curve. It is of interest, however, that measurements of the diameters of these apparent maxima and minima (which were reproducible to within one percent) led on comparison with the simple $(\sin x)/x$ curve (of Eqs. (7) and (8)) to the value Br-Br = 2.30Å. This value, which is one percent larger than the assumed value 2.28Å, lends support to the method of interpretation.

II. The comparison of electron-diffraction and band-spectral determinations of interatomic distances

A straightforward test of the accuracy of the electron-diffraction method can be made by comparing interatomic distances determined in this way with the values found from the rotational fine structure of band spectra. We have carried out this comparison for bromine in detail, and have made a similar but less thorough study of chlorine and iodine chloride.

The Br-Br internuclear separation in Br₂ is known⁹ to have the value 2.281Å (the average for the zeroth vibrational state). We found bromine vapor to produce satisfactory electron-diffraction photographs, on which (as a rule) five well-defined rings appeared. The calibration of the apparatus was carried out with gold foil, for which the value $a_0 = 4.070\text{Å}$ for the edge of the unit of structure was adopted. Measured values of $(4\pi \sin \vartheta/2)/\lambda$ for four apparent minima and five apparent maxima on one such bromine photograph are given in Table I. Each value is the average of three measurements, which with few exceptions lay within one-half

TABLE I. Measurement of photograph 375 of Br₂.

Maximum	Minimum	x	$\frac{4\pi \sin \vartheta/2}{\lambda}$	Br-Br
			observed	
1		7.725	3.48	(2.22Å)
	2	10.904	4.82	(2.264)
2		14.066	6.18	2.279
	3	17.221	7.56	2.278
3		20.371	8.89	2.292
	4	23.520	10.32	2.279
4		26.666	11.67	2.287
	5	29.81	12.96	2.302
5		32.96	14.48	2.278
			Average of seven	2.285Å

percent of their mean. The first minimum could not be measured with any accuracy. By comparing these with the values of x for which the function $(\sin x)/x$ shows its maxima and minima, the values given for the Br-Br distance were calculated. It is seen that except for the first one these values do not differ individually from their average by more than 0.02Å or one percent. We have found through experience that the measurements of the innermost rings are not very reproducible and are unreliable, the interatomic distances calculated for them from measurements made under standard conditions adopted by us showing deviations of several percent from the values given by the outer rings. For this reason we ordinarily discard measurements of the first maximum and second minimum. This has been done in taking the average in Table I.

In Table II there are given the averaged results for seven photographs, the last three of

TABLE II. Results of seven Br₂ photographs.

Photo-graph No.	Number of rings measured	Average Br-Br	Photo-graph No.	Number of rings measured	Average Br-Br
375	7	2.285Å	394	6	2.285Å
376	7	2.284	393	5	2.299
377	7	2.293	378	5	2.295
392	7	2.290	Average of measurements		2.289Å

which were somewhat less distinct than the others, permitting a smaller number of measurements. It is seen that the seven average values lie within a total range of 0.7 percent. The average of all the values is 2.289Å, the least-squares probable error being 0.0015Å. The actual

⁹ W. G. Brown, Phys. Rev. **29**, 777 (1932). Brown reported r_0 as 2.28Å; the value 2.281Å is calculated from his more accurately reported moments of inertia.

error, accepting the band-spectral value 2.281Å as correct, is 0.008Å.

Somewhat less satisfactory photographs have been obtained for chlorine and for iodine chloride. For chlorine four photographs, each showing four apparent maxima, were measured, the average value of the Cl-Cl distance provided by them being 2.009Å, with an average deviation of 0.015Å. This value is one percent larger than the band-spectral value¹⁰ 1.988Å. Three rather poor photographs of iodine chloride gave for the I-Cl distance the average value 2.301Å, with an average deviation of 0.010Å. This is slightly smaller than the band-spectral value¹¹ 2.315Å. We intend to continue the study of these compounds.

The electron-diffraction photographs used in this treatment of the three substances are of about average quality. The actual errors in the interatomic distances found from them (accepting the band-spectral values as accurate) are +0.4, +1.1 and -0.6 percent. From these results we draw the conclusion that the probable error of interatomic distances determined in this way from electron-diffraction photographs is of the order of magnitude of one percent.

III. The study of microphotometer records for benzene

The electron-diffraction photographs of benzene show several apparent maxima and minima, of which one (the second maximum) is very prominent. It appears on the microphotometer records (Fig. 2) as a well-defined shoulder, the slope nearly reaching zero. The microphotometer record shows, however, no single feature which can be quantitatively identified with confidence with a corresponding feature on the theoretical intensity curve. In order to obtain a value for the size of the molecule from the microphotometer records we have adopted the following procedure. The microphotometer was first calibrated for x-radiation, using time of exposure as a measure of integrated incident intensity. We

have assumed that the behavior of the film towards fast electrons is sufficiently closely similar to that towards x-rays to permit this calibration to be used for electron-diffraction photographs also. On comparison of the benzene photographs with the theoretical intensity expression, it was found that the photographs showed additional blackening; that is, there is present, aside from the diffraction pattern, a background, which probably is due to incoherently-scattered electrons, to electrons scattered by gas molecules in the body of the apparatus, to multiple scattering, and to other causes. Inside of the shoulder the background is unimportant (amounting to less than half the total intensity at the left end of the segment of curve drawn in Fig. 2), whereas outside of the shoulder the background is stronger than the diffraction pattern (amounting to three-quarters of the total intensity at the right end of the segment).

It was found that by adding a constant background intensity of suitable magnitude to the intensity expression of Eqs. (1) and (3) and by making use of the calibration of the microphotometer, a theoretical microphotometer curve for benzene could be calculated which could be closely fitted to the observed curves over a considerable region including the pronounced shoulder. One such curve is shown in Fig. 2. In calculating these curves the intensity expression including the atomic scattering factors ψ_i was used, with Pauling-Sherman f -values. The regular plane hexagonal model of benzene was assumed, the ratio of the C-H to C-C distances being taken as 1.06 to 1.38 (a small change in this ratio would not change the curves appreciably). The curves were plotted on a scale corresponding to a C-C distance of about 1.38-1.40Å. On superimposing such a curve on a microphotometer record, it was found in general that a satisfactory fit was obtained only by moving the curve towards or away from the center. The amount of this translation (for both branches of the curve) was measured, and from it there was calculated a new value for the carbon-carbon distance, the proper corrections being applied (for shrinkage of the print of the microphotometer record, etc.).

¹⁰ Recalculated by Professor R. M. Badger from the data of A. Elliott, *Proc. Roy. Soc. A* **123**, 629 (1929); **A127**, 638 (1930).

¹¹ W. E. Curtis and J. Patkowski, *Phil. Trans. Roy. Soc. A* **232**, 395 (1933). The smaller value 2.306Å was given by these authors in an earlier note (*Nature* **127**, 707 (1931)) which is not mentioned by them in their later paper.

In order to study the reliability of this procedure, various assumptions regarding the nature of the background were tried out. It was found that the background could be assumed to be constant, or to fall off linearly from the center, or to change in accordance with some other simple relation not deviating greatly from a constant value. When the theoretical curve for incoherent scattering was tried as the background no satisfactory fit of the theoretical microphotometer curve and the observed records could be obtained, the incoherent scattering falling off too rapidly from the center. This shows that the other background effects mentioned above are too important to be neglected in a quantitative comparison of theoretical and observed intensities. Whenever a satisfactory fit of the theoretical curve with the observed records could be obtained, the same size (to within about $\frac{1}{2}$ percent) was calculated for the molecule.

The results of the application of this procedure are given in Table III. It is seen that from the

TABLE III. Results of study of microphotometer records for benzene.

Film and plate	Number of curves used	Number of measurements	Average C-C distance	Average deviation
263 P17	5	14	1.395A	0.005A
264 P 6	6	10	1.388	.003
264 P20	5	17	1.386	.005
269 P 8	5	10	1.391	.002
269 P21	4	14	1.385	.005
Average of 65 measurements			1.389A	

consistency of measurements made with different background expressions, different films, and different microphotometer records the average value 1.389A for the carbon-carbon distance should be considered as very accurate, the least-squares probable error being only about $\pm 0.001A$ for each film and plate and also for the average of the five entries in the table.

IV. The visual interpretation of benzene photographs

The visual treatment of the photographs was made in the usual way. The theoretical curve for apparent intensity as given by Eq. (7) is shown in Fig. 5, calculated for the distances C-H=1.06A and C-C=1.380A. (The simple

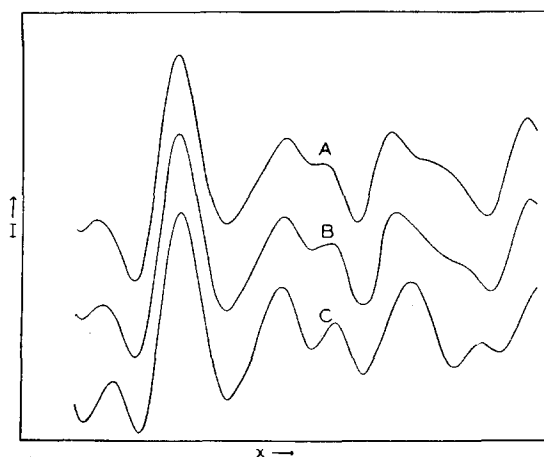


FIG. 5. The simplified theoretical curves for benzene. A, Plane hexagon model. B, Carbon atoms staggered to 0.1A above and below the original plane. C, Carbon atoms staggered to 0.2A.

curve of Eq. (8) is almost indistinguishable from this.) The qualitative agreement of the photographs and the curve is good. The films show a weak first maximum and a strong second maximum. These are followed by a poorly-defined third minimum and a broad third maximum showing a shelf on its outer edge. Then come a very narrow and distinct fourth minimum and a sharp fourth maximum. On some films a fifth minimum and maximum can also be seen.

Results of the measurement of one photograph are given in Table IV. Each observed value of

TABLE IV. Visual measurements of photograph 264 for benzene. $\lambda = 0.0599A$.

		$\frac{4\pi \sin \theta/2}{\lambda}$		C-C
Maximum	Minimum	observed	x for 1.380A	
1	2	3.35	2.84	1.17A
		4.39	4.23	1.33
2	3	5.805	5.86	1.392
		7.56	7.66	1.398
3	4	9.55	9.96	1.439
		12.61	12.60	1.379
4		13.83	13.91	1.388

$(4\pi \sin \theta/2)/\lambda$ is the mean of from three to five measurements, which in most cases lie within a total range of one percent. The first maximum and second minimum, as usual, lead to low values for the size of the molecule. The third minimum and third maximum were

poorly defined, and we consider them unsuited for quantitative use. The fourth minimum and maximum were very easily and reproducibly measured. We consider that they and the second maximum should be used for the determination of the size of the molecule.

The results of measurements on ten photographs of benzene are given in Table V. It is

TABLE V. *Results of visual measurement of benzene photographs.*

Photograph	λ	Carbon-carbon distance from		
		Second maximum	Fourth minimum	Fourth maximum
264	0.0599A	1.392A	1.379A	1.388A
269	.0602	1.391	1.372	1.380
263	.0599	1.387	1.387	1.402
265	.0632	1.403	1.375	1.406
268	.0602	1.400	1.389	1.383
315	.0614	1.388	1.368	1.395
316	.0614	1.403	1.389	1.400
317	.0614	1.403	1.387	1.399
318	.0614	1.392	1.369	1.395
319	.0614	1.408	1.390	1.406
Average		1.397A	1.381A	1.395A
Average of all values			1.391A	

seen that the results from the various photographs are concordant, the average deviation of the thirty values from the mean being 0.009A. There is evidently a constant error in opposite directions for the minimum and the two maxima (probably due to a small St. John effect), causing a difference of one percent in the averages calculated. If we accept the result of the microphotometer treatment, the error affects each to about one-half percent.

The average carbon-carbon distance given by the thirty measurements is 1.391A. This agrees excellently with the value 1.389A obtained from the much more objective discussion of the microphotometer records. We believe that the value 1.390A can be accepted for the carbon-carbon distance in the benzene molecule, with a probable error of about 0.005A.

V. The study of microphotometer records for carbon tetrachloride

When the attempt was made to treat the microphotometer records of carbon tetrachloride in the same way as those of benzene, it was found that the small amplitudes of the undulations prevented the procedure from being carried out with the desired accuracy of one or two

percent. In consequence another treatment was used. This treatment, which depends for its success on the regularity of the undulations corresponding to the successive apparent maxima and minima, consists in drawing three smooth curves, two of which just touch the microphotometer curve at the extreme points of the undulations, the third being midway between them. It is then assumed that the middle curve represents the intensity aside from the $(\sin x)/x$ terms of Eq. (6), and that the points of intersection of this curve with the microphotometer curve are the points at which the function of Eq. (6) passes through the value zero. The results of this identification are given in Table VIA, each

TABLE VI. *Measurements of microphotometer record 281 P26 of carbon tetrachloride.*

A. Measurement of midpoints of undulations			
$\frac{4\pi \sin \vartheta/2}{\lambda}$			
Midpoint	measured	x for 1.80A	C-Cl distance
6	6.59	6.50	1.775A
7	7.68	7.66	1.795
8	8.71	8.49	1.755
9	9.78	9.45	1.740
10	10.87	10.65	1.765
11	12.14	11.85	1.757
12	13.40	13.00	1.747
Average			1.762A
B. Measurement of extreme points of undulations			
$\frac{4\pi \sin \vartheta/2}{\lambda}$			
Maximum	Minimum	measured	C-Cl distance
3		7.21	1.747A
	3	8.27	1.735
4		9.37	1.731
	4	10.18	1.776
5		11.50	1.750
	5	12.66	1.757
6		13.66	1.754
Average			1.750A

value reported for $(4\pi \sin \vartheta/2)/\lambda$ being the average from two independent constructions. It was also assumed that the points of contact of the other two curves and the microphotometer curve correspond to the maxima and minima of the function of Eq. (6). The results for these curves are given in Table VIB.

The values C-Cl=1.762A and 1.750A from this treatment we estimate to be reliable to about $\pm 0.02A$, the average deviation from the mean in the two cases being 0.014A and 0.011A. The agreement with the visual treatment is

satisfactory, the visual measurements of this photograph (discussed in the next section) yielding the value $C-Cl=1.750\text{\AA}$ (average of ten maxima and minima with an average deviation of 0.009\AA), and the average for all photographs being 1.760\AA .

VI. The visual interpretation of carbon tetrachloride photographs

We have obtained very good electron-diffraction photographs of carbon tetrachloride, on some of which twenty apparent minima and maxima could be seen and measured. As mentioned before, the qualitative appearance of these photographs is in excellent concordance with the curve of Fig. 4 calculated from Eq. (7). The diameters of the rings of apparent maximum and minimum intensity were measured on nineteen photographs taken at the film distance 12.19 cm and with various electron wavelengths. In accordance with our standard practice, three series of measurements of ring diameters were made for each photograph, and the results averaged to give the observed value of $(4\pi \sin \vartheta/2)/\lambda$.

The results of this treatment for one photograph (No. 282) are given in Table VII. The

TABLE VII. Results of visual treatment of photograph 282 of carbon tetrachloride. $\lambda=0.0609\text{\AA}$.

Maximum	Minimum	$4\pi \sin \vartheta/2$		C-Cl distance
		λ observed	x for 1.800\AA	
1		2.93	2.67	(1.64A)
	2	3.83	3.57	(1.68)
2		4.91	4.71	(1.728)
	3	6.00	5.90	1.770
3		7.13	7.00	1.767
	4	8.14	8.04	1.777
4		9.23	9.01	1.757
	5	10.28	10.05	1.761
5		11.34	11.22	1.780
	6	12.53	12.35	1.773
6		13.54	13.39	1.780
	7	14.61	14.39	1.771
7		15.79	15.42	1.759
	8	16.81	16.55	1.771
8		17.82	17.70	1.788
	9	18.90	18.77	1.787
9		19.98	19.73	1.777
	10	21.22	20.70	1.756
10		22.34	21.86	1.762
Average				1.771A

individual ring-diameter measurements usually lay within one-half percent of their mean; for

example, for this photograph the readings in centimeters for some rings are: fourth maximum, 2.187, 2.192, 2.177; fifth minimum, 2.437, 2.438, 2.438; fifth maximum, 2.694, 2.690, 2.690; sixth minimum, 2.969, 2.970, 2.983; etc. The values of x corresponding to the maxima and minima on the curve calculated for an assumed $C-Cl$ distance of 1.800\AA are given in Table VII. From these and the observed $(4\pi \sin \vartheta/2)/\lambda$ values there are calculated the values of the $C-Cl$ distance given in the last column.

We have found that on the 12.19 cm photographs the inner rings are not reliable, the interatomic distances calculated from them being usually too small. This is illustrated by the first three values of Table VII, which we discard. The following sixteen values are satisfactorily constant, showing a maximum deviation of only one percent from their mean. The average of the sixteen values is 1.771\AA , with an average deviation from this of 0.009\AA and a least-squares probable error of 0.0017\AA .

The results of a similar treatment of all nineteen photographs are contained in Table VIII. In each case the value given is the average

TABLE VIII. Results of visual treatment of nineteen carbon tetrachloride photographs.

Photograph number	λ	Number of rings	Average C-Cl distance
243	0.0609A	6	1.748A
244	.0609	9	1.754
245	.0609	6	1.747
271	.0611	10	1.768
274	.0611	6	1.728
279	.0609	11	1.770
280	.0609	15	1.756
281	.0609	10	1.750
282	.0609	16	1.771
347	.0619	12	1.737
348	.0619	11	1.731
356	.0619	14	1.781
357	.0619	8	1.769
P.1	.0609	8	1.800
365	.0604	8	1.759
366	.0604	8	1.753
367	.0604	10	1.757
368	.0604	8	1.769
369	.0617	8	1.777
Weighted average*			1.760A

* Weighted with the numbers in the third column.

for a series of rings (each measured in triplicate) beginning at about the third minimum and ending at the place where the photograph became indistinct. The values are reasonably consistent,

though not so consistent as those from the various rings of a single photograph. We think it probable that there is some error in the wavelength values resulting from uncertainty as to the accelerating potential at the instant of exposure.

The average for the 184 measured rings is 1.760Å. The average for the nineteen photographs is 1.759Å, with an average deviation of 0.014Å and a least-squares probable error of 0.0026Å. The average for the nine most distinct photographs, those with ten or more useful rings, is 1.758Å, with an average deviation of 0.013Å. In view of these results, and those of the previous section, we write for the carbon-chlorine distance C-Cl=1.760Å, with a probable error of about 0.005Å.

C. CONCLUSIONS REGARDING THE VISUAL METHOD OF INTERPRETATION

From the results of the various tests described in the preceding sections we conclude that the visual method of interpretation of electron-diffraction photographs, when carefully carried out, can be relied on to lead to values of interatomic distances which in many cases are accurate to within about one-half percent as probable error.

In our standardized procedure the photographs are usually prepared with electron wavelength about 0.06Å and the distance from gas stream to film equal to about 12 cm (or in some cases 20 cm or 30 cm). The diameters of rings of apparent maximum and minimum intensity are then measured on a specially designed comparator, consisting of an illuminated opal glass plate on which the negative is mounted and of two pointers which are moved independently by micrometer screws. The ring diameters are read directly on a vernier and scale mounted on the carriages which support the pointers. The average of several readings of each diameter is used for the calculation of the value of $(4\pi \sin \theta/2)/\lambda$. In the interpretation of the photographs our first step is to attempt to decide among various reasonable models by the qualitative comparison of the simplified theoretical curves calculated for them and the visual appearance of the photographs. This qualitative comparison is some-

times more effective in the selection of the correct model than the quantitative comparison. The interatomic distances for the selected model are then found by the comparison of the values of $(4\pi \sin \theta/2)/\lambda$ and of x , the choice among alternatives sometimes being made by the consideration of the mutual consistency of these values.

We have found that on short-distance photographs of some substances rings close to the central image (that is, about 1 cm in diameter) have apparent diameters corresponding to too small values of the interatomic distances. The effect is not observed, however, when the first ring lies farther out, as in the case of photographs of molecules of small dimensions (for example, carbon tetrafluoride, silicon tetrafluoride), and also in the case of photographs of most other substances taken at greater camera distances. This is probably a contrast effect of the dense central image on visual measurements made close to it.

In the application of the visual method consideration must also be given the fact that the measured diameters for unsymmetrical apparent maxima and minima do not correspond exactly to the maxima and minima of the simplified theoretical curve, as a result of the St. John effect. This effect causes the two components of a double maximum to be read with too large a separation. An apparent maximum with an outer shelf gives a small measured ring diameter, corresponding to too large an interatomic distance, and an apparent maximum with an inner shelf shows an error in the opposite direction. We propose to make a thorough study of this phenomenon, with the view of formulating a method of correction. At the present time the procedure which we recommend is to ignore interatomic-distance values given by very unsymmetric apparent maxima and minima in calculating the averaged interatomic distances for a molecule, and to include the values for the less unsymmetric ones, with the hope that the errors will to some extent cancel in the averaging.

The photographs of benzene show this phenomenon in a pronounced form. The broad third maximum shows an outer shelf, as a result of which the ring diameter as measured is

three or four percent too small. (In other cases this error may be as great as ten percent.) The fourth minimum and fourth maximum seem also to show a very small St. John effect, amounting to about one-half percent, as mentioned before.

It is our belief that the most reliable method of obtaining molecular sizes from electron-diffraction photographs at present is the objective method we have applied to benzene, consisting in matching over a considerable range a theoretical microphotometer curve and an actual microphotometer record. This method can be applied, however, only when the microphotometer record shows very pronounced reverse curves, as for benzene. We consider that whenever the photographs show several well-shaped apparent maxima and minima the visual method is reliable for the determination of interatomic distances, as mentioned above, and that, moreover, the qualitative and quantitative application of the visual method provides by far the most satisfactory basis of choice among several models for a molecule. An important advantage of the visual method is that it permits use to be made of a larger angular range of the diffraction pattern (for the qualitative comparison) and of a larger number of measured ring diameters (for the quantitative comparison) than the methods based on microphotometer records.

In our opinion the various hybrid methods of interpretation, such as, for example, the correlation of single points on a microphotometer record with points on a theoretical curve as applied by us to carbon tetrachloride in Section V, are less reliable than the visual method. Other examples of such methods are mentioned in the last section of this paper. Until these methods have been shown to lead to consistent and correct results, we feel that they are unreliable.

THE STRUCTURE OF THE BENZENE MOLECULE

In the foregoing discussion we have assumed, in view of various experimental and theoretical arguments, that the equilibrium positions of the six carbon atoms of the benzene molecule are at the corners of a regular plane hexagon. The qualitative agreement of the electron-diffraction

photographs with the theoretical curve for this model (curve *A* of Fig. 5) supports this assumption. In order to find the extent of this support, we have calculated similar curves for a puckered hexagonal model; namely, curve *B* for a displacement of 0.1Å above and below the original plane (corresponding to a bond angle of 118°), and curve *C* for a displacement of 0.2Å (corresponding to a bond angle of 112°). Curve *C* is in definite disagreement with the appearance of the photographs, and curve *B* is somewhat less satisfactory than *A*. The principal feature of comparison is the third observed apparent maximum, which on the photographs shows an outer shelf, but does not appear as a double ring. Consequently we conclude that the electron-diffraction photographs require the benzene ring to show no puckering greater than corresponding to curve *B*.

Our value for the carbon-carbon distance, $1.390 \pm 0.005\text{Å}$, agrees with the less accurate value of Wierl, given by him as $1.39 \pm 0.03\text{Å}$ ^{1b} or $1.40 \pm 0.03\text{Å}$.^{1c} So far as we know, no value from x-ray diffraction by gas molecules has been reported, though the investigation of benzene has been mentioned by workers in this field.¹²

It is probable that the carbon-carbon distance in the benzene ring retains the value 1.390Å (to within about 0.01Å) in benzene derivatives. It has been customary in recent years to quote the value 1.42Å (as in graphite), on the basis of the x-ray investigation of crystals of hexamethylbenzene¹³ and durenene¹⁴ (sym. tetramethylbenzene). The values found for these substances, $1.42 \pm 0.03\text{Å}$ and 1.41Å, are probably in agreement with our lower value to within their experimental error. In aromatic molecules with condensed benzene rings we expect the carbon-carbon distance to lie between the benzene value and the graphite value, as is true of the values reported for naphthalene,^{15a} anthracene,^{15b} and chrysene,¹⁶ which are 1.40–1.41Å, 1.41Å, and 1.41Å, respectively.

¹² L. Bewilogua, *Phys. Zeits.* **32**, 114 (1931); **33**, 688 (1932).

¹³ K. Lonsdale, *Proc. Roy. Soc.* **A123**, 494 (1929).

¹⁴ J. M. Robertson, *Proc. Roy. Soc.* **A141**, 594 (1933); **A142**, 659 (1933).

^{15a} J. M. Robertson, *Proc. Roy. Soc.* **A142**, 674 (1933); **A140**, 79 (1933).

¹⁶ J. Iball, *Proc. Roy. Soc.* **A146**, 140 (1934).

THE STRUCTURE OF CARBON TETRACHLORIDE

Our photographs are in complete agreement with the regular tetrahedral model of the carbon tetrachloride molecule.

The chlorine-chlorine distance in carbon tetrachloride was reported by Debye and his collaborators to have the value 3.3Å,¹⁷ 3.1Å,^{18a} and finally $2.99 \pm 0.03\text{Å}$,^{18b} the last of these corresponding to a carbon-chlorine distance of $1.83 \pm 0.02\text{Å}$. In regard to the 4 percent discrepancy between this value and ours, it is of interest that Bewilogua, after claiming in the first of the papers of reference 12 that the x-ray diffraction method is in principle a more accurate method of measuring the dimensions of gas molecules than the electron-diffraction method, retracts the statement in the second paper, which ends with the remarks that x-ray methods are the more satisfactory for the determination of electron distribution, and that electron-diffraction methods are to be preferred for the measurement of interatomic distances. Bewilogua refers to the excellent agreement between observed and calculated intensities of scattering of x-rays by chlorine molecules obtained in the investigation carried out by Richter.¹⁹ Richter, however, assumed the band-spectral value of the interatomic distance (2.0Å) to be correct, and stated only that a change of ± 5 percent in this distance was not compatible with his observations.

The same value $1.83 \pm 0.02\text{Å}$ was also reported by Wierl¹ from electron-diffraction experiments, and has since been said to have been substantiated by several groups of investigators using the electron-diffraction method.^{20, 21, 22} Others found the distance to be smaller. In our early work,²³ using a film distance of 30 cm, we obtained values between 1.73 and 1.79Å, the two photographs given in Table I of that paper

(showing five maxima) leading to 1.788Å and 1.761Å, respectively. We did not have confidence in these values, and thought, in view of the work of Debye and Wierl, that the value should be larger, suggesting 1.80Å as not unreasonable. Braune and Knoke²⁴ also obtained a smaller value, 1.78Å.

In the earlier investigations only a few rings were measured (not over five), and the methods of interpretation (discussed in the following section) were often arbitrary. We feel that the value $1.760 \pm 0.005\text{Å}$ obtained in the present investigation from photographs showing as many as ten apparent maxima and ten apparent minima is reliable to the degree given by the probable error. This value is supported by the value $1.754 \pm 0.02\text{Å}$ reported in a preliminary communication by Cosslett and de Laszlo,²⁵ on the basis of their measurement of seven apparent maxima.

It is of interest that the value C-Cl = 1.760Å is just the sum of the covalent radii for carbon and chlorine,²⁶ and is thus equal (to within 0.005Å) to the average of the carbon-carbon distance in diamond, 1.542Å, and the chlorine-chlorine distance in Cl₂, 1.988Å.

DISCUSSION OF THE METHODS AND RESULTS OF OTHER INVESTIGATORS

Our experience has shown that in order that interatomic distances determined by electron-diffraction methods may be relied on to within 0.01 or 0.02Å (the values then being useful in considerations regarding the electronic structure of molecules) a standardized and tested procedure for measuring and interpreting the photographs must be used. We recommend two such procedures. One of these consists in matching theoretical and observed microphotometer records over a considerable range of scattering angle, as described in Section III of this paper. The second (and more generally applicable) method is the visual method of measurement and

¹⁷ P. Debye, L. Bewilogua and F. Ehrhardt, *Phys. Zeits.* **30**, 84 (1929).

^{18a} P. Debye, *Phys. Zeits.* **30**, 524 (1929); etc.

^{18b} P. Debye, *Phys. Zeits.* **31**, 419 (1930); L. Bewilogua, *Phys. Zeits.* **32**, 270 (1931); etc.

¹⁹ H. Richter, *Phys. Zeits.* **33**, 587 (1932).

²⁰ J. Hengstenberg and L. Brú, *Anales Soc. Espan. Fis. y Quim.* **30**, 341, 483 (1932); **31**, 115 (1933).

²¹ S. B. Hendricks, L. R. Maxwell, V. L. Mosley and M. E. Jefferson, *J. Chem. Phys.* **1**, 549 (1933).

²² R. W. Dorn, *J. Chem. Phys.* **1**, 566 (1933).

²³ L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.* **19**, 68 (1933).

²⁴ H. Braune and S. Knoke, *Zeits. f. physik. Chemie* **B21**, 297 (1933).

²⁵ V. E. Cosslett and H. G. de Laszlo, *Nature* **134**, 63 (1934).

²⁶ L. Pauling, *Proc. Nat. Acad. Sci.* **18**, 293 (1932).

interpretation with the use of a simplified theoretical curve.

Other investigators have used various methods without testing their accuracy and reliability. Wierl¹ obtained values of $(\sin \vartheta/2)/\lambda$ from his photographs by visual measurement. (For one substance, carbon tetrachloride, he also applied an undescribed procedure in interpreting microphotometer records.) He obtained x values either by taking the points on the complete theoretical curve lying farthest above a rather arbitrarily chosen background curve, or by using the simplified theoretical expression given in Eq. (8) of this paper. In some cases he made arbitrary changes in the x values found by these methods. We believe that in general the interatomic distances reported by Wierl as determined in the course of his important and extensive investigations are reliable to about 3 percent; for some substances (benzene, certain halogen compounds²⁷) results from this laboratory agree with Wierl's to within 1 or 2 percent, for others (carbon tetrachloride, cyanogen,²⁸ etc.) the discrepancies are larger.²⁹

Hengstenberg and Brú²⁰ applied methods closely similar to those of Wierl in studying acetone, formic acid, formaldehyde, methyl ether, ethyl ether, and ethyl chloride, bromide and iodide. Their results are presumably reliable to within a few percent, considerable uncertainty arising from arbitrary corrections applied to the x values.³⁰

²⁷ L. O. Brockway and F. T. Wall, *J. Am. Chem. Soc.* **56**, November (1934).

²⁸ L. O. Brockway, *Proc. Nat. Acad. Sci.* **19**, 868 (1933).

²⁹ Some of Wierl's results are uncertain because of variation in his procedure. For many substances he compared visually measured ring diameters directly with x values from the simplified theoretical curve. In other cases (such as bromine) he compared visually measured ring diameters with x values from the complete theoretical curve, differing by about 5 percent with those from the simplified curve. In still other cases (ethane, ethylene, allene, acetylene) he used x values taken from the simplified curve and then corrected by an arbitrary amount. These variations in procedure indicate the necessity of formulating a standard method of interpretation and testing its accuracy.

It may be mentioned that the St. John effect, which appears clearly in our measurements and in those of Braune and Knoke for certain substances, is not indicated in Wierl's $(\sin \vartheta/2)/\lambda$ values.

³⁰ We have reinvestigated formic acid (*Proc. Nat. Acad. Sci.* **20**, 336 (1934)), finding a structure different from that of Hengstenberg and Brú.

Braune and Knoke^{24, 31} correlated visual measurements made by laying a scale graduated in half-millimeters on the illuminated negatives with x values obtained from the complete theoretical curve by some undescribed procedure. Although their treatment was not justified by any tests, it seems to lead to consistent results, the interatomic distances reported by them for the tetrachlorides of carbon and silicon and the hexafluorides of sulfur, selenium and tellurium agreeing with ours^{23, 27} to within 2 percent.

Hendricks and co-workers^{21, 32} seem to have obtained x values by a procedure similar to that used by Wierl, consisting in drawing a more or less arbitrary background curve for a complete theoretical curve (including in some cases the incoherent scattering) and selecting the points on the complete curve lying farthest above the background. (There is some uncertainty as to their exact procedure; the authors themselves make the obviously incorrect statement that they use the points of inflection of the theoretical curve.) These x values are correlated with $(\sin \vartheta/2)/\lambda$ values obtained from a similar treatment of densitometer records of the photographs. Until the accuracy of this treatment has been thoroughly tested, there is no way of estimating it except by use of the fact that it was reported by the authors²¹ to lead to the value 2.98 Å for the Cl-Cl distance in carbon tetrachloride, a value 4 percent larger than that $2.87 \pm$ found by us,³³ and also to lead to values for the I-I distances in iodine molecules and in 1,3 and 1,4-diiodo-benzene in approximate

³¹ H. Braune and S. Knoke, *Naturwiss.* **21**, 349 (1933); *Zeits. f. physik. Chemie* **B23**, 163 (1933).

³² L. R. Maxwell, V. M. Mosley and L. S. Deming, *J. Chem. Phys.* **2**, 331 (1934).

³³ This discrepancy between our preliminary measurements on carbon tetrachloride and those of others, including themselves, was pointed out by Hendricks and co-workers. The results of this paper (and of Coslett and de Laszlo) show that our early measurements were not in error.

It may be mentioned that these investigators³² make the fact that their photographs of nitrogen dioxide show no rings the basis of choice among several molecular models. Our experience has shown that when the proper experimental precautions (such as the effective condensation of the introduced gas) are not observed a substance capable of producing a photograph with well-defined apparent maxima and minima may produce photographs not showing these features. We accordingly feel that the absence of rings cannot be safely used for the determination of molecular configuration and size.

agreement with those obtained by other methods.

Dornte^{22, 34} has reversed the procedure of Braune and Knoke, using the simplified theoretical curves for determining the x values and correlating them with experimental values taken by some undescribed procedure from microphotometer records. As mentioned above, Dornte's interatomic-distance value for carbon tetrachloride is 4 percent too high. We have repeated Dornte's work on carbonyl compounds, with the help of Mr. J. Y. Beach, and shall soon publish the results of the investigation.

³⁴ R. W. Dornte, *J. Chem. Phys.* **1**, 630 (1933); *J. Am. Chem. Soc.* **55**, 4126 (1933).

Cosslett and de Laszlo²⁵ in their short note on carbon tetrachloride do not describe their method in detail. They find, as we do, that the first two rings on a short-distance photograph have apparent diameters corresponding to too small values of the interatomic distances.

A preliminary note on carbon suboxide has been published by Boersch.³⁵

³⁵ H. Boersch, *Naturwiss.* **22**, 172 (1934). Boersch reports a structure for carbon suboxide different from that found by us (*Proc. Nat. Acad. Sci.* **19**, 860 (1933)). We have calculated the theoretical curve based on his model and find pronounced disagreement with our photographs. A more complete comparison of results will be made after his detailed publication has appeared.

DECEMBER, 1934

JOURNAL OF CHEMICAL PHYSICS

VOLUME 2

Raman Effect of Acetylenes. I. Methyl-, Dimethyl- and Vinyl-Acetylene

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(Received September 27, 1934)

An improved helical discharge tube containing neon and mercury with a saturated solution of sodium nitrite as filter served as a monochromatic source of radiation (4358 Hg). A mechanical filter avoided overexposure of the exciting radiation. The vibration frequencies were studied on the basis of the symmetry properties of the molecules and the usual assignments have been made.

Faint rotation lines were found accompanying the C : C vibration in liquid dimethyl-acetylene. They are interpreted as rotation of the six hydrogen atoms around the figure axis of the molecule. The moment of inertia is $I = 10^{-39} \text{ g} \times \text{cm}^2$. The three compounds were studied in the liquid state.

INTRODUCTION

SEVERAL new features of experimental technique have been developed and thoroughly tried and since the resulting spectrograms are of excellent quality, it seems worth while to describe them.

NE-Hg DISCHARGE TUBE

The ordinary mercury arc is quite an expensive piece of apparatus and it is usually inconvenient to run it for long periods; if there are voltage variations it is liable to be extinguished. Further-

more, the arc runs hot and it is not possible to place it very near a Raman tube containing a liquefied gas. For these reasons a helical discharge tube on the principle of the usual "neon-sign" was developed and has been used in this laboratory for several years.² The design can best be seen from Fig. 1 (A, C and D). The helix is made of quartz, corex-D or Pyrex glass. The electrodes are made of copper or iron and are large in area so that at 6600 volts 300 milliamperes pass the tube. It contains a drop of liquid mercury and several mm of neon gas. The tube runs quite cool. One can just hold one's hand on the surface. As

¹ This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by H. M. Davis in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. For a preliminary note on methyl-acetylene see *Phys. Rev.* **41**, 370 (1932).

² R. W. Wood (*J. Frank. Inst.* **208**, 617 (1929)) has used a helical discharge tube containing helium. The Hanovia Chem. & Mfg. Co., manufactures lamps similar to the one discussed here. However, the tubes used in this laboratory carry a much greater current than any others described so far.