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In conclusion, the author wishes to acknowledge the valuable collaboration he has had with Professor T. F. Young and Dr. B. Rice in the work on aluminum borohydride. He is also greatly indebted to Drs. R. D. Cowan and H. C. Longuet-Higgins for much helpful criticism and for permission to quote unpublished data, to members of Professor H. I. Schlesinger's group for providing the materials, and to Professor R. S. Mulliken for his active interest in the spectra of boron compounds,

and also to Professor E. Teller. Thanks are due to the ONR for sponsoring the work.

Note added in proof.—It should not be inferred from the comparison of the spectra of *gaseous* beryllium and aluminum borohydride with those of *crystalline* lithium and sodium borohydride that, if the binding in the former were completely ionic, their BH frequencies should approximate those of the latter. The terminal and internal BH frequencies should still fall into two fairly distinct groups in "ionic" beryllium and aluminum borohydrides in the gas phase. These two groups are of course equivalent in sodium borohydride where the $(\text{BH}_4)^-$ is surrounded by Na^+ ions.

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Internal Motion and Molecular Structure Studies by Electron Diffraction*

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A procedure has been developed for the determination of molecular structure by electron diffraction which yields accurate intensity data and obviates the necessity for visual examination of the diffraction photographs. The theory for computing radial distribution curves has been extended to permit accurate curves to be obtained from scattering data covering only a restricted range of angle. From this method, it is possible to obtain not only equilibrium distances but also the probability distributions for the vibrational motion between pairs of atoms in a molecule. The procedure has been applied to CCl_4 and CO_2 and when comparisons may be made with spectroscopic results, satisfactory agreement is obtained.

THE study of molecular structures using electron diffraction by gases has usually involved the visual examination of the diffraction pattern¹ which consists of small oscillations about a steeply falling background. The positions of the apparent maxima and minima are measured, their relative intensities are estimated visually, and some estimate is made of the shape of those features which appear to be neither maxima nor minima. The observed curve is used as the basis for evaluating the equilibrium distances in the molecule being studied. This is accomplished by calculating a radial distribution curve which is used as a guide for selecting various models to represent the structure of the molecule. From these models intensity curves are computed and compared to the visually observed curve. The model chosen to represent the structure of the molecule depends upon the agreement between the computed and observed curves. Some differences are found in the form of the functions used by various investigators to compute the radial distribution and intensity curves.

The uncertainties in the visual examination of the diffraction patterns and in the mathematical analysis, make it very desirable to establish a quantitative procedure which uses an unambiguous theory and eliminates the visual study of the photographs. A procedure to eliminate this visual study has been developed by the Norwegian school and they have used it to study

the structures of a large number of molecules.² Their procedure involves the use of a rotating sector³ in order to accentuate the oscillating features of the pattern and the photographs are scanned with a microphotometer. The main difference between their procedure and the one to be outlined concerns the method of analyzing the scattering data. By our method accurate values of the equilibrium distances can be expected and, in addition, it is possible to evaluate the magnitude of the vibrational motion between pairs of atoms in a molecule.

THEORY

When free molecules are struck by a beam of fast electrons, part of the scattering of the primary beam arises from the spacings between the atoms in individual molecules and can be represented by the formula

$$I_m(s) = \sum_{i=1}^n \sum_{j=1}^n c_i c_j A_{ij} \quad (i \neq j) \quad (1)$$

The rest of the scattering does not depend upon the molecular structure and forms a steeply falling background upon which the molecular scattering, Eq. (1), is superimposed. The upper limit n in the summation is

² (a) Chr. Finbak, *Avhandl. Norske Vid.-Akad. Oslo, I Mat.-Naturv. Kl.*, No. 7 (1941). (b) Chr. Finbak and O. Hassel, *Archiv. f. Mat. o. Naturvid.* B45, No. 3 (1941). (c) H. Viervoll, *Acta Chem. Scand.* 1, 120 (1947). (d) O. Hassel and H. Viervoll, *Acta Chem. Scand.* 1, 149 (1947).

³ (a) C. Finbak, *Avhandl. Norske Vid.-Akad. Oslo, Mat.-Naturv. Kl.*, No. 13 (1937). (b) P. P. Debye, *Physik. Zeits.* 40, 66, 404 (1939).

* Presented at the meeting of the American Society for X-Ray and Electron Diffraction, Columbus, Ohio, December 16, 1948.

¹ L. O. Brockway, *Rev. Mod. Phys.* 8, 231 (1936).

equal to the total number of atoms in the molecule. The coefficients c_{ij} are characteristic of the i th and j th atoms and in the subsequent analysis are assumed to be constant. In practice, this is a good approximation, except for very small scattering angles, if the molecular scattering is obtained by dividing the total scattering by the background scattering. If a molecule is absolutely rigid, then the interference function A_{ij} is equal to $\sin sr_{ij}/sr_{ij}$ where r_{ij} is the distance between the nuclei of the i th and j th atoms and $s = (4\pi \sin\theta/2)/\lambda$ where θ is the scattering angle and λ is the wave-length of the electron beam. Since there is some motion of the nuclei in all molecules, the interference function A_{ij} assumes the form

$$A_{ij} = \int_0^\infty P_{ij}(\rho) (\sin s\rho/s\rho) d\rho, \quad (2)$$

where $P_{ij}(\rho)d\rho$ is the probability that the distance between the i th and j th atoms has a value between ρ and $\rho + d\rho$.

A Fourier transformation may be made on the molecular scattering function,

$$I_m(s) = \sum_{i=1}^n \sum_{j=1}^n c_{ij} \int_0^\infty P_{ij}(\rho) (\sin s\rho/s\rho) d\rho, \quad (i \neq j) \quad (3)$$

by multiplying it by $s \sin sr$ and integrating with respect to s . The result of such a procedure is a function of the variable r which represents the radial distribution curve, $D(r)$;⁴

$$D(r) = \int_0^\infty s I_m(s) \sin sr ds \quad (4)$$

$$= \sum_{i=1}^n \sum_{j=1}^n c_{ij} \int_0^\infty \sin sr ds \int_0^\infty \frac{P_{ij}(\rho)}{\rho} \sin s\rho d\rho \quad (4a)$$

$$= \frac{\pi}{2} \sum_{i=1}^n \sum_{j=1}^n c_{ij} \frac{P_{ij}(r)}{r}. \quad (4b)$$

The ordinates of the radial distribution curve essentially represent the probability of the occurrence of the internuclear distances, r , in the molecule. It has been found in our experiments that in the vicinity of an equilibrium distance, r_{ij} , which is not very close in value to other ones in the molecule, the function $D(r)$ can usually be represented by

$$D(r) = c_{ij} (\pi h_{ij})^{\frac{1}{2}} \exp[-h_{ij}(r-r_{ij})^2]/2r_{ij}, \quad (5)$$

where $(2h_{ij})^{-\frac{1}{2}}$ is a measure of the average deviation from the equilibrium position and is equal to $(\bar{l}_{ij}^2)^{\frac{1}{2}}$ where l_{ij} is the displacement from equilibrium. The quantity r in the denominator in Eq. (4b) may be replaced by r_{ij} when h_{ij} is sufficiently large.

⁴ The derivation follows the treatment by P. Debye, J. Chem. Phys. 9, 55 (1941).

In order to evaluate the integral in Eq. (4), the molecular scattering data must be known to values of s equal to infinity. In practice, only a limited amount of data are available. Nevertheless, this limited data uniquely determines the structure of a molecule. The procedure used is to compute the following modified function,⁵

$$f(r) = \int_0^{s_{\max}} s I_m(s) \exp(-as^2) \sin sr ds, \quad (6)$$

where s_{\max} bounds the range of scattering data and a can be so chosen that the integrand of Eq. (6) makes no essential contribution beyond s_{\max} . The computed $f(r)$ curve, therefore, is the same as that which would have been obtained if s_{\max} approached infinity. It is possible then to obtain the desired function, $D(r)$, from $f(r)$ by making use of the relationship⁶

$$f(r) = \frac{1}{2(\pi a)^{\frac{1}{2}}} \int_{-\infty}^{\infty} D(\rho) \exp[-(r-\rho)^2/4a] d\rho, \quad (7)$$

where a is the same as that used in Eq. (6). The introduction of $D(r)$ as defined in Eq. (5) leads to an evaluation of the integral in Eq. (7), giving for $f(r)$ the expression

$$f(r) = c_{ij} (\pi h_{ij})^{\frac{1}{2}} \times \exp[-h_{ij}(r-r_{ij})^2/(4ah_{ij}+1)]/2r_{ij}(4ah_{ij}+1)^{\frac{1}{2}}. \quad (8)$$

In practice, the bell-shaped peaks which result from the computation of Eq. (6) are curve fitted by the function, $B_{ij} \exp[-H_{ij}(r-r_{ij})^2]$, where $H_{ij} = h_{ij}/(4ah_{ij}+1)$ (see the exponent in Eq. (8)). Since a is the value used in computing Eq. (6), h_{ij} can be readily obtained. The values of h_{ij} so determined, as pointed out, are the measure of the magnitude of the vibrational motion between pairs of atoms in a molecule.

Equation (8) may be used to illustrate the unique determination of the function, $D(r)$, from a limited amount of data. By this we mean in a mathematical sense that the data may be extended uniquely beyond its experimentally determined range. There is, of course, always some uncertainty in experimental data. In a practical sense, then, it is possible to extend a function on the basis of a uniqueness property in a definite fashion beyond its known experimental range, but the uncertainties in the experiment will introduce some uncertainty into the extension. There is a unique relation between the function in Eq. (8) whose parameters may be determined from experiment and the desired function in Eq. (5). If h_{ij} and r_{ij} are evaluated by applying Eq. (8) to a computed curve, then $D(r)$ is a known numerical function of r . From one rather re-

⁵ The damping factor $\exp(-as^2)$ was introduced by Degard in order to improve radial distribution calculations. See C. Degard, Bull. Soc. Roy. Sci. Liege 12, 383 (1937). The effect of this and other damping factors on radial distribution curves has been studied by J. Waser, Thesis, California Institute of Technology.

⁶ E. C. Titchmarsh, *Introduction to the Theory of the Fourier Integral* (Clarendon Press, Oxford, 1937), p. 51.

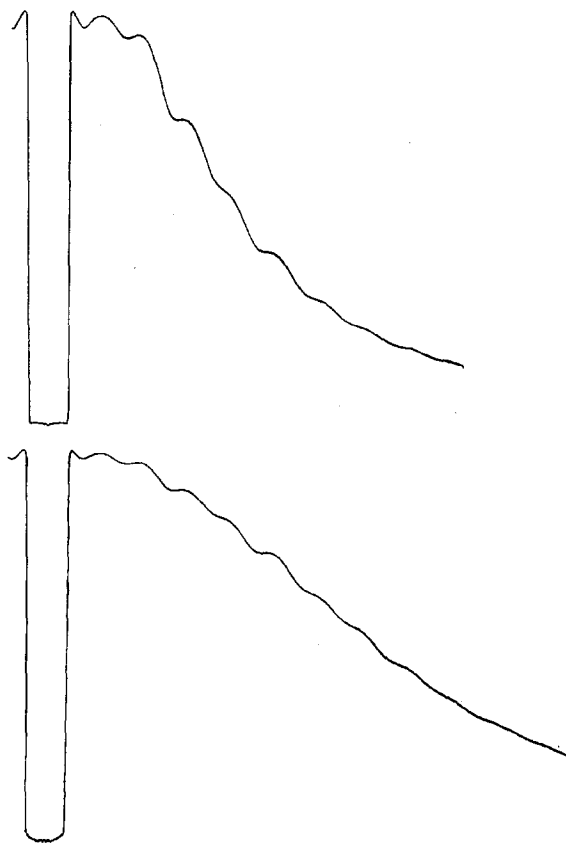


Fig. 1. Typical microphotometer traces of a light and medium exposure of CCl_4 . The vertical scales are not the same.

stricted, but simple, point of view, this uniqueness can be based upon the theoretical result⁷ that the computed radial distribution curve can be represented by the sum of Gaussian distributions. From another point of view, the study of the mathematics of positive Fourier integrals shows that the scattering function, $I(s)$, known only in a restricted range of angle is related within narrow bounds to only one positive distribution function. This idea has been used in our laboratory to improve the accuracy of determining electron distributions^{8(a)} about atoms. The restrictiveness of positive functions has also been found useful for small angle scattering and in the evaluation of the phases of the Fourier coefficients in the determination of crystal structure.^{8(b)}

In the case of gas molecules, though, it is not necessary to resort to powerful mathematical arguments to obtain accurate information from a restricted amount of data. If the experimental curve, $f(r)$, is merely fit well by a function in the vicinity of r_{ij} (though the function may even become negative at some larger distance), a good evaluation of the desired $D(r)$ in the vicinity of r_{ij} can be obtained. This may be seen from Eq. (7) which

shows that for values of a usually used (0.005–0.010), the exponential function is practically a delta-function so that $f(r)$ is merely a smeared or broadened version of $D(r)$. The main contribution of the integrand of Eq. (7) is in the vicinity of $\rho = r$.

The radial distribution curve yields three kinds of information; the equilibrium interatomic distances, an evaluation of the vibrational motion between pairs of atoms, and the coefficients for the molecular scattering expression which are related to the areas under the peaks. The structures of many molecules can be completely determined from radial distribution calculations alone. If several interatomic distances in a molecule fall close together, however, the information obtainable from a radial distribution curve is restricted and should be supplemented by additional data which can be obtained from computed intensity curves. The formula to be used is

$$I_m(s) = \sum_{i=1}^n \sum_{j=1}^n c_{ij} \exp(-s^2/4h_{ij}) \sin sr_{ij}/sr_{ij} \quad (i \neq j), \quad (9)$$

where the values of c_{ij} , h_{ij} , and r_{ij} for various models are chosen to be consistent with the data available from the radial distribution curve. Equation (9) has been obtained by James⁷ by integrating Eq. (3), using a probability distribution function which is derived on the basis of Hooke's law forces.

PROCEDURE

The diffraction photographs were taken with an electron diffraction camera which has been constructed recently in our laboratory. The accelerating voltage usually used is about 40,000 volts and is regulated to about one volt in 10,000. The voltage can be read continuously on a Type *K* potentiometer. The voltage obtained from the measurement of diffraction rings on a gold photograph agrees to within 0.1 percent with that read on the potentiometer. The electron beam is focused by a focusing grid and two magnetic lenses. The beam passes through a defining aperture of 0.1 mm diameter and is essentially parallel between the aperture and the photographic plate.

A rotating sector is incorporated in the specimen chamber. The sector is attached to a ball-bearing race six inches in diameter which is rotated by a synchronous motor using a friction drive. The motor is in the specimen chamber and its operation does not affect the vacuum nor the electron beam. When the sector reaches a speed of 1300–1400 r.p.m., the motor is turned off and pulled away from the race. The speed decreases to about 800 r.p.m. in five seconds during which time an exposure is made. An s^2 sector which is cut to operate between s values of one and 35 has been used so far. The portion between s values of zero to one acts as a beam stop. In order to facilitate the centering of the sector with respect to the electron beam, a speck of fluorescent material is placed in a 0.1-mm diameter

⁷ R. W. James, *Physik. Zeits.* **33**, 737 (1932).

⁸ (a) H. Hauptman and J. Karle, submitted to *Phys. Rev.*

(b) J. Karle and H. Hauptman, submitted to *Acta Cryst.*

hole bored in the center of the sector. Photographs of the beam using this arrangement show that there is no correction for fogging required for the exposure times ordinarily used.

The diffraction patterns obtained on contrast lantern slides are traced on a Leeds and Northrup microphotometer. During the tracing they are rotated rapidly⁹ in order to average out any irregularities caused by graininess. Care is taken to set the zero of the microphotometer on an unexposed portion of the plate. Traces obtained by this procedure are shown in Fig. 1. The microphotometer readings are calibrated to read electron intensities by taking several series of transmission photographs of evaporated gold on Formvar for various exposure times. The results of such a procedure are easily interpreted since the reciprocity law holds for fast elections,¹⁰ that is, the exposure is equal to the product of the intensity and the time. The gold photographs are taken using the rotating sector and are rotated during the tracing in order to duplicate as closely as possible the procedure used with the gas photographs. A typical calibration curve is illustrated in Fig. 2.

The microphotometer readings are converted to intensity readings which are plotted against the variable s and a smooth background is drawn through the oscillations.¹¹ It usually is easier to draw the background line beyond s values of 5 or 6 if the experimental intensity curve is multiplied by s or s^2 to accentuate the oscillations about the background. In this respect

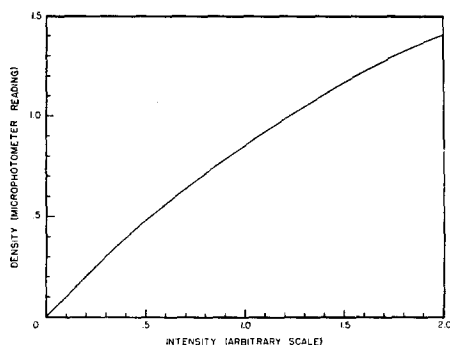


FIG. 2. Typical calibration curve for converting microphotometer readings to electron intensities.

⁹ Karle, Hooper, and Karle, *J. Chem. Phys.* **15**, 765 (1947).

¹⁰ (a) A. Becker and E. Kipphan, *Ann. d. Physik* (5) **10**, 15 (1931). (b) W. Bothe, *Zeits. f. Physik* **8**, 243 (1922).

¹¹ Uncertainties in the position of the background line affect mainly the shapes but not the positions of the maxima in the radial distribution curve. Hence, fairly reliable equilibrium distances in a molecule can be obtained from the first computation of a radial distribution curve and an intensity curve based on these distances may be computed. The background line may then be corrected if necessary to correspond to the position of the zero axis in the intensity curve provided that no sudden changes occur in curvature of this line. This procedure may be repeated until it is evident that no additional improvement is possible. The improvement in the position of the background line should ordinarily be accompanied by a decrease in the magnitude of the negative portions of the radial distribution curve. Ideally, the radial distribution curve should be positive.

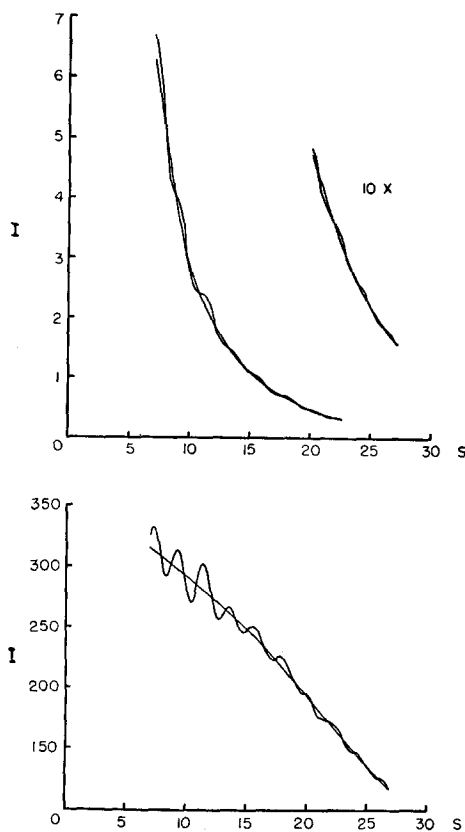


FIG. 3. The upper curve represents the intensity obtained from a fairly dark photograph of CCl_4 taken with an s^2 sector. The lower curve represents the intensity from the upper curve multiplied by s^2 . Background curves are drawn through the oscillations.

our experiments would probably have been aided by the use of a sector cut to a power of s higher than 2. Figure 3 illustrates how the background line was drawn for an intensity curve from a photograph of CCl_4 whose useful density range covers values from seven to 27. The molecular scattering is obtained by dividing the experimental intensity by the background curve. This procedure not only eliminates the background scattering but replaces by constants, except at low s values, the variable coefficients in the molecular scattering expression. It is possible to measure the intensity of molecular scattering to much higher accuracy than may be implied by the inaccuracies in determining the absolute intensity. The inaccuracy in absolute measurement may be greater than the magnitude of an oscillation at the larger scattering angles. However, molecular intensity measurements concern the magnitude of an oscillation relative to a background line. The accuracy is therefore determined by the amplitude of an oscillation rather than by the measurement of total photographic intensity. Five photographs ranging from light to heavy exposures were used to obtain the molecular scattering curves. The uppermost curves in Figs. 4 and 5 are the experimental molecular scattering curves for CCl_4 and CO_2 . The upper curve in Fig. 5 shows the

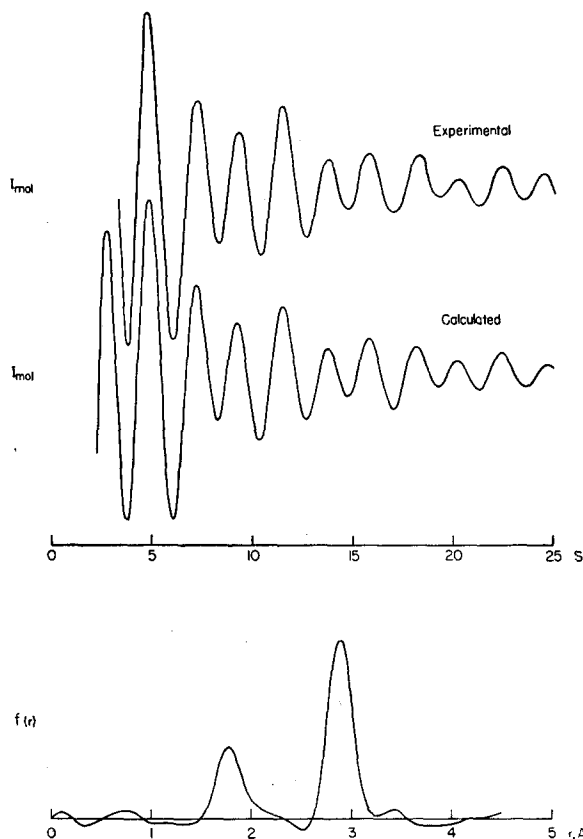


FIG. 4. The three curves represent the experimental molecular scattering, the calculated molecular scattering, and the radial distribution for CCl_4 . The vertical scales for the molecular scattering curves are the same.

spread of experimental points for CO_2 . The magnitudes of the maxima and minima in this experimental curve are known to within five percent. The characteristic asymmetry in the maxima and minima is well defined.

A radial distribution curve is calculated using the experimental data. The integral in Eq. (6) is replaced by a summation where the s interval is 0.2. For the CCl_4 and CO_2 computations, maximum s was 25 and a was chosen to be 0.0057. The calculations were performed with the aid of punched cards and I.B.M. machines.¹² In the experimental intensity curve there is no useful data below s values of two and the region below s values of three or four does not represent a molecular scattering curve with constant coefficients. Hence, the region between s values of zero to three or four is replaced by an intensity curve computed with constant coefficients from an assumed model. If this model is inconsistent with the results of the radial distribution calculation, the calculated portion of the intensity curve is adjusted and a new radial distribution curve is computed. With this method of successive approximations, relatively few calculations need be made. The radial distribution curve should consist of a series of

¹² Shaffer, Schomaker, and Pauling, J. Chem. Phys. 14, 659 (1946).

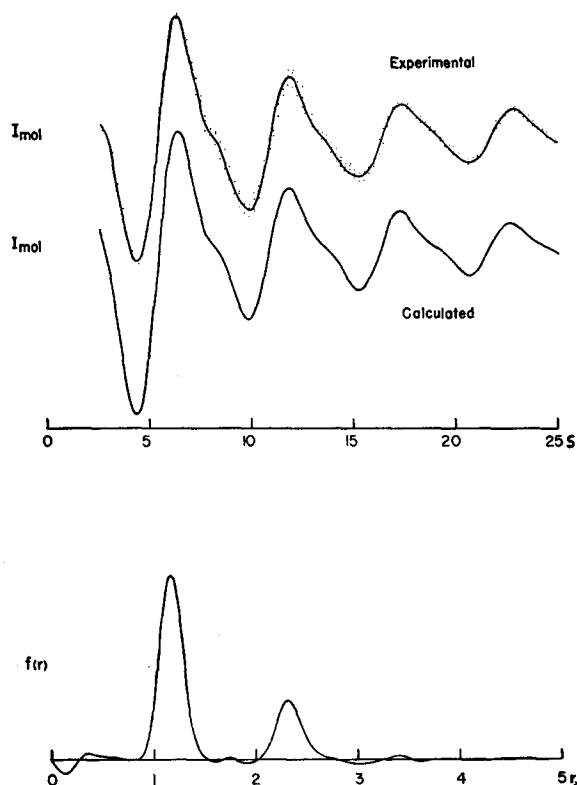


FIG. 5. The three curves represent the experimental molecular scattering, the calculated molecular scattering, and the radial distribution for CO_2 . The dots in the upper curve are the experimental points obtained in five independent experiments. Many of the points lie on the curve itself. The vertical scales for the molecular scattering curves are the same.

positive peaks, since the scattering from the electronic shells of the atoms has been eliminated. The radial distribution curves for CCl_4 and CO_2 are illustrated in Figs. 4 and 5.*

Each peak of the radial distribution curve is fitted with the function $B_{ij} \exp[-h_{ij}(r-r_{ij})^2/(4ah_{ij}+1)]$, Eq. (8), to obtain h_{ij} and r_{ij} values. Only the upper two-thirds of a peak is used in order to minimize the effect from small oscillations in the base line. Relative values of the coefficients c_{ij} which are used in the calculated intensity curves can be obtained in two ways; (a) each c_{ij} value is proportional to the area under its corresponding peak multiplied by the equilibrium distance associated with that peak, or (b) the maximum value of the peak, B_{ij} , is proportional to $c_{ij}(h_{ij})^{1/2}/r_{ij}(4ah_{ij}+1)^{1/2}$. Using the experimental h_{ij} , r_{ij} , and c_{ij} values, theoretical intensity curves were computed for CCl_4 and CO_2 .

* Note added in proof.—Recent investigations in our laboratory on more complicated molecules have demonstrated that extraneous oscillations such as those which appear in the $f(r)$ curves of Figs. 4 and 5 can be considerably reduced by readjusting the background line in the total intensity curves. It has also been found that a peak in the radial distribution curve formed from several interatomic distances may be decomposed into its components which yield directly the detailed structure of the molecule. Computed molecular intensity curves are used mainly to establish the range of uncertainty.

using Eq. (9). As expected, these were found to agree very well with the experimental curves (Figs. 4 and 5). In this instance, the calculated intensity curves merely illustrate the consistency of the procedure. On the other hand, when there are structural features that are not resolved in the radial distribution curve, more emphasis will have to be placed on theoretical intensity curves.

RESULTS

The experimental results are listed in Table I. For CO_2 , the C—O distance compares favorably with the spectroscopic result of 1.163 Å for the equilibrium value. The experimentally determined values for the O—O distance is not exactly double the value for the C—O distance. This deviation, however, falls within the experimental uncertainty. The average amplitude of the vibrations of the C—O bond was calculated from spectroscopic data using the expression⁴

$$l^2 = 1/2h = (\mu_1 + \mu_2)/2\alpha, \quad (10)$$

where α is the force constant between the C and O atoms and μ is the average energy of an oscillator given by Planck's expression, $\mu = h\nu/2 + h\nu/(\exp(h\nu/\beta T) - 1)$. The expression for the O—O distance is

$$l^2 = \mu_1/\alpha. \quad (11)$$

The numerical values used were $\alpha = 15.5 \times 10^5$ dynes cm^{-1} , $\nu_1 = 4.0 \times 10^{13}$ sec^{-1} , and $\nu_2 = 7.0 \times 10^{13}$ sec^{-1} .¹³ The electron diffraction value for $(l^2)^{1/2}$ for the C—O distance agrees well with the spectroscopic value. The difference between the electron diffraction and the spectroscopic values of $(l^2)^{1/2}$ for the O—O distance may be attributed mainly to the fact that the O—O peak in the radial distribution curve is small which makes the determination less accurate. In addition, it should be noted that the spectroscopic value is computed from a simplified theory (Eq. (11)).

There are no spectroscopic values for the interatomic distances in CCl_4 available for comparison. Our values may be compared with other electron diffraction determinations. Finbak and Hassel^{2(b)} obtained 1.770 Å and 2.876 Å for the C—Cl and Cl—Cl distances using their sector method. Pauling and Brockway¹⁴ obtained 1.76 Å and 2.87 Å for the C—Cl and Cl—Cl distances using the visual method. The spectroscopic values for the vibrational motion between the C—Cl and Cl—Cl pairs listed in Table I have been computed by James⁷ using the central force model. Rosenthal¹⁵ has shown that CH_4 is the only tetrahedral molecule to which the central force model is applicable. By applying a general force field to tetrahedral molecules, Rosenthal¹⁶ obtained a value of 3.6×10^5 dynes cm^{-1} for the C—Cl

TABLE I.

	$r_{ij}(\text{\AA})$	$(\bar{l}_{ij}^2)^{1/2}$ elec. diff.	$(\bar{l}_{ij}^2)^{1/2}$ spect.
CCl_4			
C—Cl	1.770 ± 0.010	0.041 ± 0.005	0.055
Cl—Cl	2.877 ± 0.020	0.054 ± 0.005	0.071
CO_2			
C—O	1.162 ± 0.010	0.034 ± 0.003	0.034
O—O	2.310 ± 0.020	0.040 ± 0.007	0.029

force constant in CCl_4 . This is larger than the value 2.0×10^5 dynes cm^{-1} used by James and implies that the amplitude for the vibrational motion obtained by James is too large. Better agreement between the electron diffraction and spectroscopic evaluations of the vibrational motion can be expected therefore from a recalculation of the spectroscopic values based on the more general force model for CCl_4 .

It should be mentioned that even very small vibrations like those found in CCl_4 and CO_2 damp the intensity of molecular scattering considerably. For CCl_4 the intensity at s equal to 25 is 60 percent less than it would be for a rigid structure while for CO_2 the intensity is 35 percent less.

The c_{ij} values were obtained from the radial distribution peaks using the methods given above. For CO_2 the value found for the ratio $c_{\text{C—O}}/c_{\text{O—O}}$ is 1.50 ± 0.02 . This value may be compared to the ratio $2Z_{\text{C}}Z_{\text{O}}/Z_{\text{O}}Z_{\text{O}}$ which also is equal to 1.50. Z_{C} and Z_{O} are the atomic numbers of carbon and oxygen. For CCl_4 the experimental values of the ratio $c_{\text{Cl—Cl}}/c_{\text{C—Cl}}$ is 4.22 ± 0.04 whereas the ratio $3Z_{\text{Cl}}Z_{\text{Cl}}/2Z_{\text{C}}Z_{\text{Cl}}$ equals 4.25. These figures indicate that the scattering factors of the atoms involved have about the same shape and that their variability with respect to the angle variable s can be eliminated by dividing the total scattering by the background scattering.

An approximation was made in Eq. (5) by replacing the variable r in the denominator by the equilibrium distance r_{ij} . The effect of this approximation on the determination of the equilibrium distances is very small. The correction is equal to $1/2h_{ij}r_{ij}$ and amounts to not more than 0.001 Å for the CO_2 and CCl_4 molecules. There is a negligible effect on the shape of the peak.

DISCUSSION

The results on CCl_4 and CO_2 indicate that accurate intensity data can be obtained from electron diffraction investigations of gases. This is borne out by the results in Table I and also by the fact that the radial distribution curves are essentially positive. Relatively little error in the experimental intensity can yield large negative fluctuations in the radial distribution curves. By the procedure described above the magnitude and shape of the various features of the diffraction pattern can be reliably determined, thus minimizing considerably the uncertainties which are bound to arise in the visual examination of the diffraction photographs. The

¹³ G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 173.

¹⁴ L. Pauling and L. O. Brockway, *J. Chem. Phys.* 2, 867 (1934).

¹⁵ J. Rosenthal, *Phys. Rev.* 46, 730 (1934).

¹⁶ J. Rosenthal, *Phys. Rev.* 49, 535 (1936).

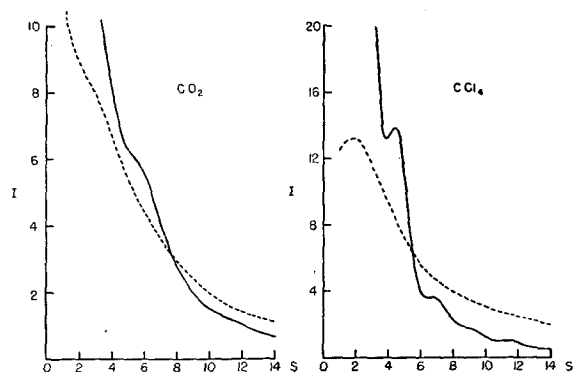


FIG. 6. The solid lines are the experimental scattering curves obtained with an s^2 sector for CCl_4 and CO_2 . The dotted lines represent the background scattering calculated from tabulated values and multiplied by s^2 .

visual method can be used with confidence to determine the equilibrium distances in a molecule if the diffraction pattern consists of well-defined maxima and minima and if the determination can be based mainly on the positions of these maxima and minima. When the determination of a molecular structure depends upon the relative intensities of the maxima and minima or upon special features such as shelves or asymmetries, the results from the visual method may be considerably less reliable.

There is sufficient difference between the procedure developed by the Norwegian school and the one presented here to merit some comment. In their analysis of the diffraction data, the molecular scattering curve is obtained using the expression^{2(a)}

$$I_m(s) = K \left[\frac{P_t(s)}{P_a(s)} - 1 \right] \left[\frac{\sum_i (Z_i - F_i)^2 + \sum_i S_i}{s^4} \right], \quad (12)$$

where $P_t(s)$ is the density reading on a microphotometer trace of a diffraction photograph, $P_a(s)$ is the background curve drawn on this trace to represent the atomic scattering, and $[\sum_i (Z_i - F_i)^2 + \sum_i S_i]/s^4$ is the coherent plus incoherent atomic scattering where Z_i is the atomic number, F_i is the atomic scattering factor for x -rays, and S_i is the incoherent scattering function tabulated by Bewilogua.¹⁷ Our procedure differs in that the molecular scattering function with constant coefficients is obtained from the expression

$$I_m(s) = K \left[\frac{I_t(s)}{I_a(s)} - 1 \right], \quad (13)$$

¹⁷ L. Bewilogua, *Physik. Zeits.* **32**, 740 (1931).

where the photographic density readings have been converted to intensity readings. In addition, we do not reintroduce the variable scattering factors once they have been eliminated by dividing by the background. The disadvantage of using Eq. (12) for the molecular scattering function is that a proper Fourier inversion cannot be made on an intensity function whose coefficients (corresponding to the c_{ij} in Eq. (4a)) are functions of s . The use of Eq. (12) in a Fourier transform affects the accuracy of determining the equilibrium distances in a molecule very little. However, it is not possible to use such a curve for the evaluation of the vibrational motion in a molecule.

The background scattering merits some discussion. It has always been considered that the background scattering in electron diffraction patterns of gases can be represented by

$$I_a(s) = (K/s^4) \left[\sum_i (Z_i - F_i)^2 + \sum_i S_i \right]. \quad (14)$$

The results of our experiments are shown in Fig. 6 where the dotted lines represent Eq. (14) calculated from tabulated values and multiplied by s^2 , and the solid line is the experimental scattering obtained with an s^2 sector for CCl_4 and CO_2 . Theoretically, the solid line should oscillate about the dotted line. The same type of discrepancy is apparent from the examination of published microphotometer traces by the Norwegian school¹² and by Yearian and Barss.¹⁸ Experiments on the scattering from free atoms have been performed and are being continued to establish with certainty that the shape of the background is not a result of some error in the technique of performing the diffraction experiment. The consistency obtained in our experiments to date indicates that the theory of the background scattering may be incorrect. It is obvious, however, from the procedure described in this paper that it is not necessary to have a theoretical expression for the background scattering for the determination of molecular structures.

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¹⁸ H. J. Yearian and W. M. Barss, *J. App. Phys.* **19**, 700 (1948).