Part 1

Electron Diffraction Investigations of Vanadium Tetrachloride, Dimethylketene Dimer, Tetrachloroethylene, and Trichloroethylene

Part 2

The Crystal Structure of Methylammonium Chloride

Part 3

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Thesis by

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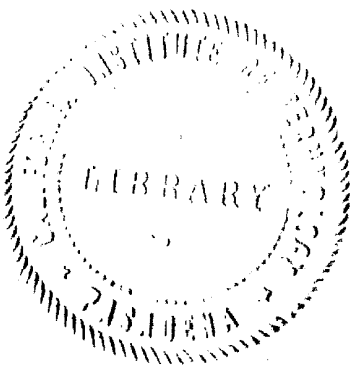

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Contents

Part 1

Electron Diffraction Investigations of Vanadium Tetrachloride, Dimethylketene Dimer, Tetrachloroethylene, and Trichloroethylene

Part I. Electron Diffraction Investigations of Gas Molecules

I. An Electron Diffraction Investigation of Vanadium Tetrachloride

A. Introduction

On the basis of vapor density measurements Roscoe (1) assigned the formula VCl_4 to vanadium tetrachloride in the gas phase. The physical and chemical properties of this interesting compound have recently been summarized by Simons and Powell (2).

Prompted mainly by the possibility that the unpaired electron in the monomer might play a steric role leading to a structure different from the common tetrahedral structure, we have undertaken an electron diffraction investigation of vanadium tetrachloride, with the results described below.

B. Experimental

Vanadium tetrachloride was prepared by the method described by Mertes (3). Dry chlorine was passed over ferrovanadium (containing about 50% of vanadium and 4% of silicon) in a glass combustion tube at 400°C. in an electric furnace. The crude product was purified by two successive fractionations through a 30-cm. all-glass column packed with glass spirals.

The final product was analyzed for quadrivalent vanadium by titration with standard permanganate solution. The results indicated 99.3% of vanadium tetrachloride; the impurities were probably chiefly silicon chlorides.

The electron diffraction investigation was carried out with the apparatus described by Brockway (4). Photographs were taken at camera distances of

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(1) H. E. Roscoe, Ann. Chem., Supplement VII, 70 (1870).
(2) J. H. Simons and M. G. Powell, J. Am. Chem. Soc., 67, 75 (1945).
(3) A. T. Mertes, J. Am. Chem. Soc., 35, 671 (1913); see also Reference (2).
(4) L. O Brockway, Rev. Mod. Phys., 8, 231 (1936).

10.91 cm. and 20.19 cm. with electrons of wavelength 0.0610 Å, as determined by standardization against zinc oxide (5). The photographs were taken with the sample at about 50°C.

C. Interpretation

The appearance of the photographs, which show measureable features out to s values of about twenty-five $s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$, is represented by curve V of Figure 1. Since the first feature (dotted portion of curve V), which cannot be read from the photographs is relatively insensitive to structure, it could be estimated satisfactorily from previous experience with the theoretical curves of other more or less similar molecules.

The radial distribution function (6) was calculated from the visual curve, V, by means of the equation

$$rD(r) = \sum_{s_1 = \frac{\pi}{10}}^{s_{max}} I(s_i)\, e^{-as_i^2} \sin(rs_i) \qquad (1)$$

where the summation was carried out in steps of $s = \frac{\pi}{10}$ and a was so chosen that $e^{-as_{max}^2} = 0.10$. The radial distribution curve thus obtained (curve RD, Figure 1) indicates two important distances, at $r = 2.04$ Å and $r = 3.30$ Å, whose ratio 1.618 agrees satisfactorily with the expected ratio for a tetrahedral molecule, $(8/3)^{\frac{1}{2}} = 1.633$. The other smaller peaks of the radial distribution curve are undoubtedly spurious; the only prominent ones, those at 1.57 Å and 4.58 Å, do not correspond to sensible interatomic distances for any configuration of this molecule. We assume that the scattering gas contained no significant amounts of molecules other than VCl_4.

(5) C. S. Lu and E. W. Malmberg, Rev. Sci. Instr., 14, 271 (1943).
(6) L. Pauling and L. O. Brockway, J. Am. Chem. Soc., 57, 2684 (1935); R. A. Spurr and V. Schomaker, ibid., 64, 2693 (1942).

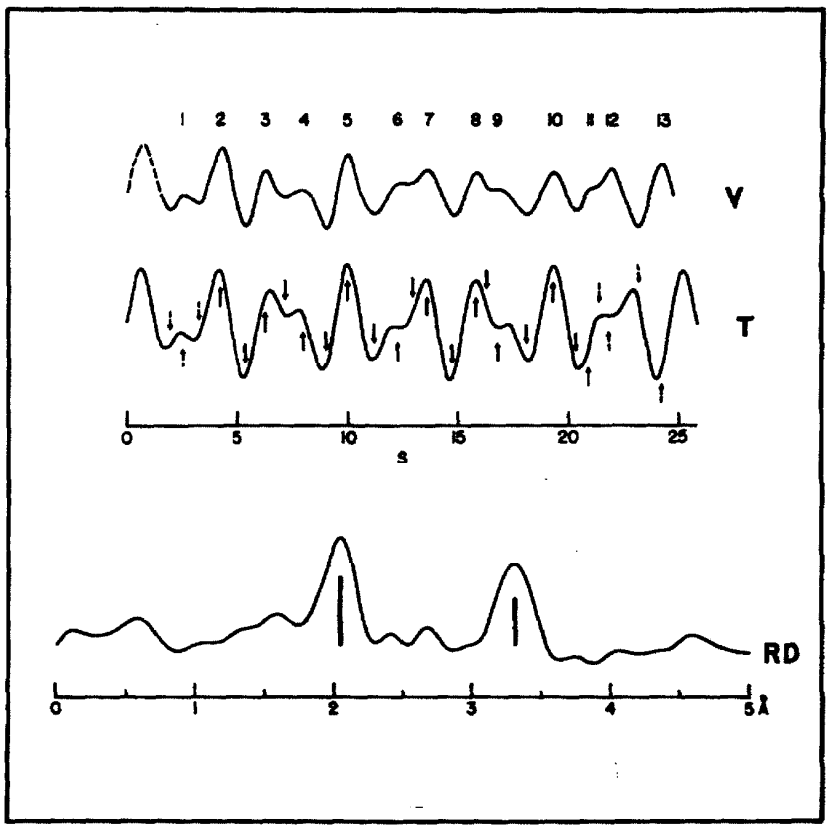

Figure 1.

Legend for Figure 1.

Electron diffraction curves for vanadium tetrachloride: visual curve V, theoretical intensity curve T, and radial distribution curve RD. The numbers above curve V and the arrows on curve T refer to the measured s values in Table I.

Hence the radial distribution method indicates that the molecule is tetrahedral.

The correlation method (7) was used to test the conclusion of the radial distribution treatment. The theoretical intensity curve T was calculated for a tetrahedral model with V-Cl = 2.04 Å and Cl-Cl = 3.33 Å, according to the formula

$$I(s) = \sum_{i,j} \frac{z_i z_j}{r_{ij}} \sin(r_{ij} s) \qquad (2)$$

The major features of this theoretical curve are in agreement with those of curve V. Although some slight discrepancies are apparent, for example with regard to the intensities of the 10th maximum and the 8th and 11th minima relative to neighboring features, reexamination of the photographs showed that their appearance is actually entirely consistent with the theoretical curve. In the radial distribution curve the spurious smaller peaks mentioned above are probably the result of these aspects of the visual curve which we now believe are quantitatively in considerable error, rather than of numerous more subtle errors in the drawing of the visual curve; however it did not seem worth while to verify this by recalculation of the radial distribution function.

The quantitative comparison of the measurements of the features with the theoretical curve for the tetrahedral model is shown in Table I. The values in parentheses were omitted from the averages because it is known that the corresponding measurements (of extreme outer and inner rings) are unreliable.

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

Table I

Min	Max	$s_{obs.}$	$s_{calc.}$	$s_{calc.}/s_{obs.}$
1		1.94	1.70	(0.877)
	1	2.51	2.40	(.956)
2		3.24	3.01	(.927)
	2	4.23	4.15	.980
3		5.32	5.26	.989
	3	6.21	6.45	{1.038}
4		7.12	7.14	{1.004}
	4	7.95	7.71	{0.970}
5		8.98	8.74	0.974
	5	9.92	9.94	1.002
6		11117	11.08	0.992
	6	12.27	12.03	{ .980}
7		12.92	12.42	{ .961}
	7	13.61	13.50	.992
8		14.76	14.61	.990
	8	15.82	15.85	1.002
9		16.25	16.85	{1.037}
	9	15.77	17.29	{1.031}
10		18.08	18.18	1.005
	10	19.28	19.31	1.001
11		20.35	20.39	1.002
	11	20.91	21.55	(1.031)
12		21.34	22.00	(1.031)
	12	21.86	22.88	(1.046)
13		23.11	23.97	(1.038)
	13	24.17	25.16	(1.041)
			Average[a]	0.996
			Average deviation[a]	.013

[a] In the calculation of the average and average deviation the values in parentheses were omitted and those in braces were given half weight.

Furthermore, the ratios enclosed in braces were given only half weight since the measurements of unsymmetrical rings on which they depend are distorted by what has been called a St. John effect (4). The quantitative comparison leads, in agreement with the radial distribution function, to the following structural parameters and probable limits of error: V-Cl = 2.03 ± 0.02 Å and Cl-Cl = 3.32 ± 0.03 Å.

An additional theoretical curve, which is not included in Figure 1, was calculated in which account was taken (8) of the actual ratio of the scattering powers of vanadium and chlorine, $(Z - F)_{Cl} / (Z - F)_{V}$. This curve was found to be substantially identical to the one given in Figure 1.

D. Discussion

The vanadium-chlorine distance of 2.03 Å in vanadium tetrachloride is shorter than that found by Palmer (9) in vanadium oxytrichloride (V-Cl = 2.12 Å). The bond distances in these molecules and those reported for the related compounds chromyl chloride (9), titanium tetrachloride (10), and titanium tetrabromide (10) can be brought together in a simple discussion based on values of the covalent radii for titanium, vanadium, and chromium, estimated as described below, and on the assumption that six of the nine available central atom orbitals ($3d^5\ 4s\ 4p^3$) are used, on the average, for bond formation by each of these atoms. This assumption is probably only approximately valid since these three elements will not have the same tendency to employ the available orbitals and since other mechanisms than the formation of multiple bonds may play a role in shortening the bonds.

(8) R. Spitzer, W. J. Howell, Jr., and V. Schomaker, J. Am. Chem. Soc., 64, 62 (1942).
(9) K. J. Palmer, J. Am. Chem. Soc., 60, 2360 (1938).
(10) M. W. Lister and L. E. Sutton, Trans. Faraday Soc., 37, 393 (1941).

Plausible values of single-bond covalent radii may be assigned to these three elements. A titanium radius of 1.28 Å is obtained (10) by multiplication of the octahedral radius of titanium (1.36 Å) by the value 0.943 found for the ratio of the tetrahedral and octahedral radii in tin and lead compounds. A chromium radius of 1.13 Å may be obtained by subtracting the chlorine radius 0.99 Å from the chromium-chlorine distance in chromyl chloride, 2.12 ± 0.02 Å. This radius, which is less than that (9) assumed by Palmer (1.15 Å), may well be slightly small if more than six orbitals (on the average) are used to form the bonds to chlorine and oxygen or if the bonds are shortened for other reasons. We interpolate, nevertheless, between this chromium radius (1.13 Å) and the titanium radius (1.28 Å) to obtain a vanadium radius of 1.20 Å. Although this radius may also be slightly small, we shall employ it in our discussion; its value is the same as that assumed by Palmer (9).

A double-bond radius for chromium of 1.02 Å may be obtained by subtracting the double-bond radius of oxygen (0.55 Å) from the chromium-oxygen distance in chromyl chloride (1.57 Å). If we assume that this very reasonable difference of 0.11 Å between the single-bond and double-bond radii for chromium applies also to vanadium and titanium, we obtain 1.09 Å and 1.17 Å for the double-bond radii of these two elements, respectively.

A value for the vanadium-chlorine bond distance in vanadium tetrachloride can now be obtained. If, on the average, six orbitals are involved in bond formation to the four chlorine atoms each bond has 1/2 double bond character. From the vanadium-chlorine single bond distance of 1.20 + 0.99 = 2.19 Å and the double bond distance of 1.09 + 0.89 = 1.98 Å together with the resonance curve relating interatomic distance with the amount of double bond character (11) we predict the value 2.04 Å for the vanadium-chlorine distance; this

(11) L. Pauling, "The Nature of the Chemical Bond", second edition, p. 164 ff. Cornell University Press, Ithaca, N. Y., 1940.

value is in good agreement with the observed distance 2.03 Å. The unpaired electron in vanadium tetrachloride probably occupies one of the 3d orbitals not involved in bond formation. It is interesting that this electron does not play a significant steric role similar to that ordinarily played by an unshared electron pair in the structure of this compound; the observed tetrahedral configuration is that which would be expected if this electron were absent.

In vanadium oxytrichloride, however, five of the six orbitals are required for the three bonds to chlorine atoms and for the double bond to the oxygen atom, thus leaving one orbital to form multiple bonds. If we assume that this extra bond resonates equally among the four atoms surrounding the vanadium atom, we expect a vanadium-chlorine distance of 2.09 Å, corresponding to 1/4 double bond character, and a vanadium oxygen distance slightly shorter than the double bond distance of 1.09 + 0.55 = 1.64 Å. This shortening can be calculated from the double-bond and triple-bond distances of 1.64 Å and 1.49 Å, respectively, with the use of the resonance curve and with the assumption of 1/4 triple bond character; thus the vanadium-oxygen distance of 1.64 - 0.08 = 1.56 Å is expected. These values are in good agreement with the distances observed in vanadium oxytrichloride: V-Cl = 2.12 ± 0.03 Å and V=O = 1.56 ± 0.04 Å.

Some shortening of the vanadium-sulfur distance in the unusual crystal sulvanite (12) might also be expected from these considerations, inasmuch as the vanadium atom has only four closest sulfur neighbors, (along with six copper neighbors, somewhat further away, with which it undoubtedly interacts rather strongly). The observed distance is 2.19 Å, or 0.05 Å less than the sum of the single bond radii.

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(12) L. Pauling and R. Hultgren, Z. Krist., 84, 204 (1933).

In titanium tetrachloride we may expect a value of 2.12 Å from the sums of the single bond radii (1.28 + 0.99 = 2.27 Å) and double bond radii (1.17 + 0.89 = 2.06 Å) if we make use of the resonance curve. Similarly we might expect a value of 2.27 Å in titanium tetrabromide from the single-bond and double-bond radius sums of 2.42 Å and 2.21 Å, respectively. The observed values (10) (Ti-Cl = 2.18 ± 0.04 Å and Ti-Br = 2.31 ± 0.02 Å) are somewhat larger, suggesting somewhat less double bond character, as if titanium actually had a tendency to employ less than six orbitals in bond formation in these tetrahalides.

II. An Electron Diffraction Investigation of Dimethylketene Dimer

A. Introduction

This investigation of the molecular structure of dimethylketene dimer, which may be presumed to be 2,2,4,4-tetramethylcyclobutadione-1,3, was undertaken because of its interest in connection with the structure of diketene, which is still under active discussion. Although work on diketene was begun, it was discontinued because our diffraction photographs were unsatisfactory and because it was understood that an electron diffraction investigation is forthcoming from another Laboratory (13).

B. Experimental

The sample of dimethylketene dimer was prepared by Dr. C. W. Smith of the Shell Development Company, Emeryville, California. Dimethylketene, $\left[(CH_3)_2C=C=O\right]$, prepared from α-bromoisobutyryl bromide, was isolated and then allowed to polymerize in ethyl acetate solution. The dimethylketene dimer which was separated from this mixture melted at 113°-114°C. A rough determination of its vapor pressure gave the values 6 mm. at 52°C. and 38 mm. at 87°C. These characteristics are in agreement with those reported (14,15) in the literature for samples obtained by different syntheses. As might be expected the compound has no permanent dipole moment (14,15). Diketene, on the other hand, has a dipole moment (16) of 3.31 D, and so cannot have the cyclobutadione-1,3 structure.

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(13) S. H. Bauer, private communication.
(14) D. Hammick, G. C. Hampson, and G. I. Jenkins, J. Chem. Soc. 1263 (1938).
(15) I. E. Coop and L. E. Sutton, J. Chem. Soc. 1269 (1938).

Photographs were taken at a camera distance of 10.93 cm. with electrons of wave length 0.0610 Å as determined by standardization against zinc oxide (5). The vapor was obtained from a sample of the substance heated at 90° to 120° C in a high temperature nozzle (17).

C. Interpretation

Both the radial distribution method (6) and the correlation method (7) were used in interpreting the photographs. The radial distribution function was calculated (6) from the visual intensity curve by means of the equation

$$rD(r) = \sum_{q_i = 1,2,\ldots 100} I(q_i) \; e^{-aq_i^2} \; \sin \frac{\pi}{10} q_i r \qquad (3)$$

with a so determined that e^{-aq^2} is equal to 0.10 at $q = 90$. The theoretical intensity curves used in the correlation treatment were calculated from the simplified formula (7)

$$I^{o}(q) = \sum_{i,j}{}' \frac{Z_i Z_j}{r_{ij}} \; e^{-b_{ij}q^2} \; \sin \frac{\pi}{10} r_{ij} q \qquad (4)$$

where the constant b_{ij} in the exponential temperature factor term was given the value 0.00015 for bonded C-H terms, 0.0003 for non-bonded C...H terms and 0 for all other terms.

D. Results

The electron diffraction pattern of dimethylketene dimer is represented by curve V of Figure 2. The unobservable first feature (dotted portion of curve V), which is relatively insensitive to structure, was taken from the theoretical curves. The radial distribution function R calculated from this visual curve shows sharp peaks at 1.17 Å, 1.55 Å, 2.20 Å, and 2.58 Å, and

(16) P. F. Oesper and C. P. Smyth, J. Am. Chem. Soc., 64, 768 (1942).
(17) L. O. Brockway and K. J. Palmer, J. Am. Chem. Soc., 59, 2181 (1937).

rather broad peaks at 3.32 Å and at 4.43 Å. Its interpretation in terms of the tetramethylcyclobutadione structure is straightforward. The first peak corresponds to the C-H and C=O terms; with the assumptions that the C-H peak is at 1.09 Å, that it corresponds to a temperature factor with $b_{C-H} = 0.00015$, and that the two terms have the relative weights corresponding to those expected for tetramethylcyclobutadione, this first peak gives a C=O distance of about 1.22 Å. The peak at 1.55 Å corresponds to the C-C distances in the four-membered ring and to the $C-CH_3$ distances. These distances cannot differ greatly because the half-width (at half-height) of this peak corresponds closely with that expected from the use of the exponential term in Equation (3), namely, $w_{\frac{1}{2}} = 8.5/q_{max}$. The peak at 2.20 Å corresponds to the non-bonded C...H terms and the cross-ring C...C distances. Analysis of this peak with the assumptions C...H = 2.16 Å and $b_{C...H} = 0.0003$ yields a C...C distance of 2.21 Å, which corresponds to a C-C bond distance of 1.56 Å in the ring, in good agreement with the 1.55 Å peak. (A strict interpretation would then suggest a $C-CH_3$ distance of 1.54 Å). The peak at 2.58 Å corresponds to the shortest non-bonded C...O, $C...CH_3$, and $CH_3...CH_3$ distances, which have relative weights $n Z_i Z_j / r_{ij}$ of 20, 30, and 8. With consideration of the small width of this peak, these distances, particularly the first two, cannot differ greatly from 2.58 Å. The remaining comparisons of the distance spectrum of tetramethylcyclobutadione with the radial distribution function (as shown for model A; see Figure 2) is satisfactory if the terms corresponding to distances greater than 3 Å are given suitable temperature factors. Thus the terms which contribute to the peak at 3.32 Å give a composite term at 3.33 Å, in good agreement with the position and also with the area of this peak, but if the temperature factor is omitted the resulting peak is too narrow and too high as compared with that shown by

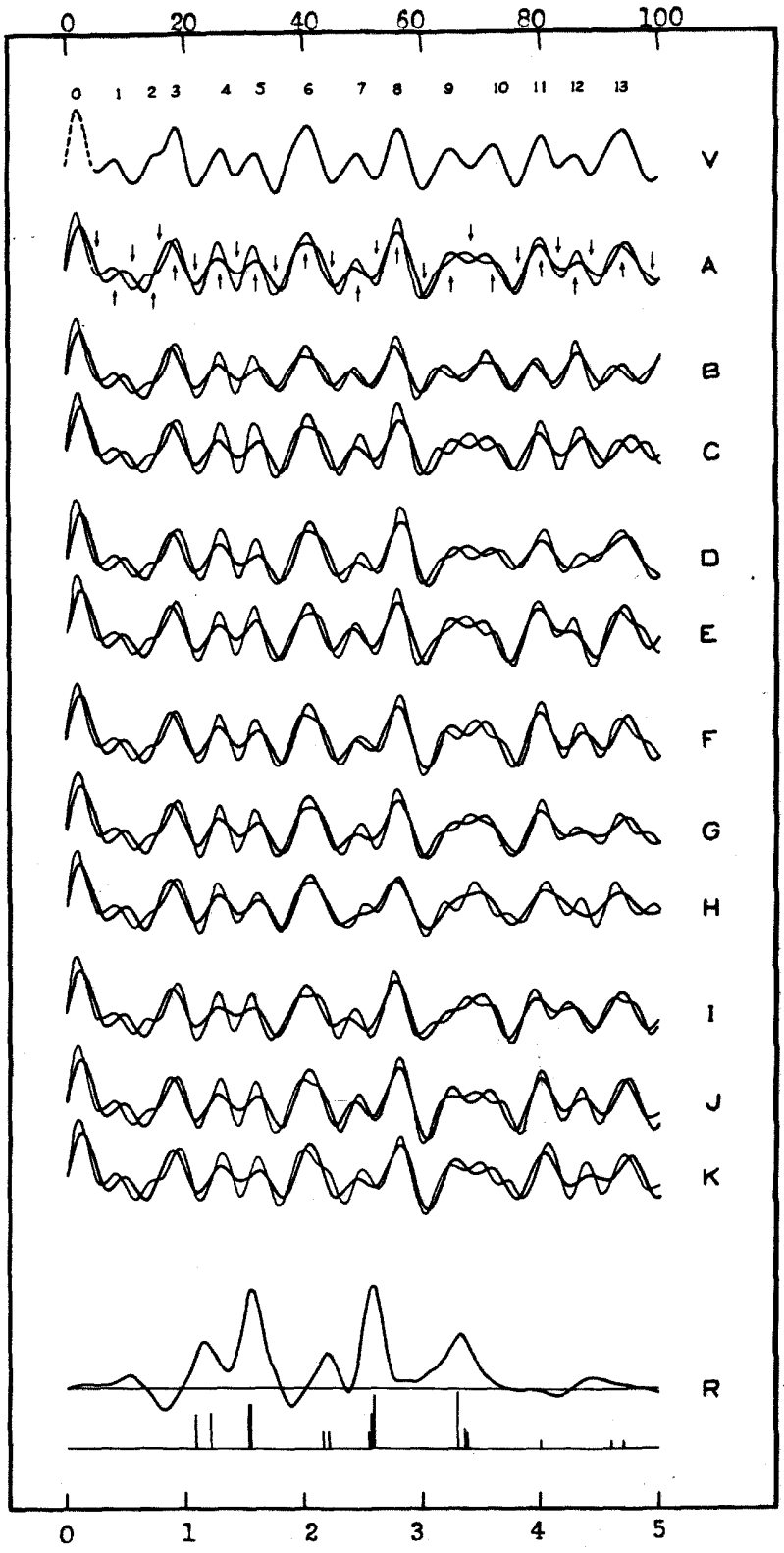

Figure 2.

Legend for Figure 2

Electron diffraction curves for dimethylketene dimer: visual curve V, theoretical intensity curves A...K, and radial distribution function R. The heavy theoretical curves were calculated (for models defined in the text) omitting distances greater than 3 Å; in the light curves all distances were included. The numbers above curve V and the arrows on curve A refer to the measured q values in Table II.

the radial distribution function. The small peak at 4.43 Å does not correspond well with the spectrum of the comparatively unimportant long distances in the molecule, but it may indicate in a general way the presence of scattering from these terms. At any rate it can be said that the discrepancies in this region represent errors in the visual curve no greater in magnitude than those demonstrated by the two sharp negative regions at 0.83 Å and 1.89 Å, and that the tetramethylcyclobutadione structure is well confirmed by the radial distribution curve.

In the correlation procedure the visual curve was compared with theoretical intensity curves calculated for tetramethylcyclobutadione models of symmetry D_{2h} (except for the hydrogen atoms) with the bonded C-H distance 1.09 Å and tetrahedral bond angles at the methyl carbon atoms. All hydrogen interaction terms except those due to the bonded and shortest non-bonded carbon-hydrogen distances were omitted, because of their relatively small weight and necessarily severe temperature factors. The five parameters of this structure may be taken as the ratio $(C\text{-}C)/(C\text{-}CH_3)$, the ratio $2(C{=}O)/[(C\text{-}C + (C\text{-}CH_3)]$, the C-CO-C (ring) angle, the $CH_3\text{-}C\text{-}CH_3$ angle, and, as size parameter, $[(C\text{-}C) + (C\text{-}CH_3)]/2$. The temperature factor for the distances greater than 3 Å also needs to be determined. In order to take account of this temperature factor two theoretical curves were calculated for each model, only the terms less than 3 Å being included for the additional, heavy curve (Figure 2). It was found that for the best models the most satisfactory agreement with the visual curve was obtained by interpolation (18)

(18) The interpolated curve lies 13% of the way from the light toward the heavy curve at $q = 15$; 42%, at $q = 30$; and 95%, at $q = 70$. For the best model the three distances contributing to the 3.3 Å peak are nearly equal. Some of the less satisfactory models tend to require somewhat different values of b_{ij}; for example, models with these distances distributed about 3.3 Å as an average require smaller values of b_{ij}.

between the heavy and light curves according to the temperature factor $e^{-b_{ij}q^2}$ for distances greater than 3 Å with b_{ij} equal to 0.0006. Disagreement is produced by variation of b_{ij} by ± 30% of this value.

Model A, which was suggested by the radial distribution function, is defined by the parameters $2(C=O)/\left[(C\text{-}C) + (C\text{-}CH_3)\right] = 1.22/1.55$, (C-C) ring/(C-$CH_3$) = 1.56/1.54, C-CO-C (ring) = 90°, CH_3-C-CH_3 = 109°28', and $\left[(C\text{-}C) + (C\text{-}CH_3)\right]/2 = 1.55$ Å, and leads to curves A in excellent agreement with the visual curve V in the sense of the interpolation just described. The slight discrepancy in regard to the relative intensities of the ninth and tenth maxima is discussed below. Reexamination of the photographs indicated that the differences in the third, fourth, fifth, and sixth maxima were exaggerated slightly in the drawing of the visual curve, and that the interpolated theoretical curve is actually in good agreement with the photographs in these respects.

A complete examination of all possible parameter variations in the neighborhood of model A was not undertaken, although each of the parameters was varied separately in the following series of models, in which, unless otherwise stated, the parameters have the same values as in model A. In considering the effects on the curves of the parameter variation it was found useful throughout to think in terms of the radial distribution function. Variation of (C-C) / (C-CH_3) to 1.61/1.49 and to 1.51/1.59 is illustrated by curves B and C; it appears that for this variation models with these two distances differing by as much as 0.09 Å are definitely inacceptable, particularly with regard to the relative intensities of the extreme outer features. Models D and E, with $2(C=O)/\left[(C\text{-}C) + (C\text{-}CH_3)\right]$ equal to 1.17/1.55 and 1.27/1.55 are somewhat outside of the range of acceptability. Of the three models, F, G, and H, in which the C-C-C angle at the carbonyl group

was given the values 85°, 95°, and 100°, F and G are nearly acceptable, while H is definitely poor. Of models I, J, and K, in which the CH_3-C-CH_3 angle was given the values 100°, 115°, and 120°, the only acceptable model is J.

Simultaneous variations of the parameters were investigated by inspection of the curves on the assumption that the effects of the variations are additive, as they must be for small variations. Combinations of variations of (C-C) / ($C-CH_3$) and 2C=O/ [(C-C) + ($C-CH_3$)] do not lead to better agreement than that shown in curve A, as may be seen by comparisons of curves B, C, D, and E; neither do they suggest that simultaneous variations of these parameters could lead to satisfactory models with parameters outside the ranges of acceptability established for the single variations. The same is true, moreover, for combined variations of these two parameters with either one of the angles. However, when simultaneous variations of the two angles are allowed a much increased range of acceptable angles values is revealed in which the angles are increased or decreased together. This is illustrated by an average of curves G and J with somewhat the greater weight for G . Indeed, slightly better agreement with the relative intensity of the ninth and tenth maxima than shown by model A is obtained by a variation in the direction of this combination without producing unsatisfactory effects elsewhere. On the other hand, simultaneous increase of one angle and decrease of the other leads very quickly to unsatisfactory curves.

On the basis of the radial distribution function, these considerations, and quantitative comparison of observed and calculated q values for models A (Table 2), C, E, G, and J the final parameters are taken as C-C = 1.56 Å, $C-CH_3$ = 1.54 Å, C=O = 1.22 Å, C-CO-C = 93°, and CH_3-C-CH_3 = 111°.

Table II

Min.	Max.	q obs.	q calcd.[a]	q calcd./q obs.
1		5.32	5.5	(1.034)
	1	8.25	8.1	(0.982)
2		11.60	11.4	(.983)
	2	14.81	14.7	(.993)
3		16.13	15.6	(.967)
	3	18.58	18.5	.996
4		22.07	22.0	.997
	4	26.09	25.8	.989
5		28.68	28.8	1.004
	5	31.87	31.8	0.998
6		35.35	35.5	1.004
	6	40.64	40.7	1.001
7		44.95	45.5	1.012
	7	49.15	49.1	0.999
8		52.41	51.8	(.988
	8	55.90	55.9	1.000
9		60.50	60.5	1.000
	9	65.02	65.2	1.003
10		68.37	68.0	0.995
	10	72.02	70.9	.984
11		76.30	75.3	.987
	11	80.28	80.0	.997
12		83.24	83.9	1.008
	12	86.06	86.7	1.007
13		88.66	90.0	1.015
	13	93.94	94.3	1.004
14		98.91	98.9	1.000
			Average	0.999
			Average deviation	.006

[a]The values of $q_{calcd.}$ were taken from the average curve obtained by weighting the light and heavy curves of model A according to the factor $e^{-0.0006q^2}$. Values in parentheses were omitted in the calculation of the average and average deviation.

Although the average of C-C and C-CH_3, which determine the position of the 1.55 Å peak of the radial distribution function, can be determined with the usual precision (± 0.02 Å), their difference cannot, the two distances being so nearly alike as to be unresolvable; this circumstance makes it necessary to assign the considerably larger value ± 0.05 Å for the limits of error (limits which we believe the error is not likely to exceed) of the separate determination of these two distances. The C-O distance, with the limits of error of ± 0.04 Å, is also not well fixed because all of the oxygen terms are either unimportant or imperfectly resolved from other terms. Limits of ± 6° can be assigned to the angle variations if simultaneous variation of the two angles is excluded; otherwise much greater limits of error, so great as almost to deprive the experimental values of any quantitative significance, must be assigned.

E. Temperature Factor and Atom Polarization

The tetramethylcyclobutadione molecule is so complex that any simple consideration of the vibrations responsible for the anomalously large temperature coefficient, which represents an increment to the average that prevails for the shorter distances in the molecule, is likely to be unsatisfactory. We wish nevertheless, to discuss a particular mode of vibration which we believe may be mainly responsible both for the anomalous temperature factor of the longer distances and the unusually large atom polarization (15), which corresponds to a root-mean-square dipole moment of about 0.7 D. Coop and Sutton (15) concluded that a different mode of vibration was responsible for the anomalous atom polarization. For each of these two modes of vibration we shall compare the root-mean-square amplitude required for the anomalous temperature factor, and that required for the anomalous atom polarization with estimates of the amplitudes to be expected

on the basis of classical temperature excitation.

The first-mentioned mode of vibration is the one in which, approximately, the $\rangle C{=}O$ groups oscillate in a plane perpendicular to that of the ring while the $\rangle C(CH_3)_2$ groups move similarly and in the opposite direction, each of the groups retaining its two planes of symmetry and the four bond angles in the ring remaining equal. If the coefficient $b_{ij} = 0.0006$ can be said to apply to the $CH_3 \cdots O$ distances, as is reasonable since these are by far the most important of the long distances for which b_{ij} was derived as an average (19) value, the root-mean-square deviation, θ, of the C=O bonds from the mean plane of the molecule is 5°. The atom polarization of the gas molecule corresponds to a root-mean-square dipole moment of 0.66 D. Reduced to 0.6 D to allow for the "normal" atom polarization (5% of P_E) which might be expected for the simpler group vibrations, this moment corresponds to a value of 7° for θ, in fair agreement with the diffraction data estimate. That these amplitudes are reasonable for this mode of vibration can be seen from a calculation of the amplitude for classical excitation at 100°C. on the assumption of a parabolic potential function (20) for bending of the ring bond angles from an (assumed) normal angle θ'' of $109\frac{1}{2}^\circ$. This amplitude, $\theta = 3.5^\circ$, is smaller than the values derived above. It may be remarked, however, that the expected anharmonicity of the potential function would lead to a considerable increase of the estimate, the ring bond angles being widely strained from their normal tetrahedral values.

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(19) Only the 3.3 Å group of distances are important. If for this group account were taken of the relatively small dependence of the $CH_3 \cdots C$ (ring) and $O \cdots C$ (ring) distances on this vibration as compared with that of the $CH_3 \cdots O$ distances this estimate of θ would be slightly increased; however, for a model with distances in the 3.3 Å region not all alike (18) it would be somewhat decreased.

(20) The constant $k = 10^{-11}$ ergs/radian^2/bond angle in the potential function $2V = k(\delta\theta''C\text{-}C\text{-}C)^2$ was estimated from the bending frequency of propane.

Coop and Sutton (15) attributed the atom polarization predominantly to oscillations of the C=O groups in the plane of the four-membered ring. In order to account for the b_{ij} value of 0.0006 by this mode of vibration alone a root-mean-square displacement, θ', of the C=O bond of 14° is required. The anomalous atom polarization requires a value of θ' of 10° if the two C=O groups are assumed to oscillate independently. With the assumption of a constant of 10^{-11} ergs/radian^2 for bending the C=O bond against the rest of the C-CO-C group, the amplitude calculated for classical excitation is found (21) to be $\theta' \pm 2^{\circ}$.

These calculations show that the very large temperature factor for the long distances in dimethylketene dimer is of the right order of magnitude to be consistent with the anomalous atom polarization. They further suggest that both of these effects may well arise predominantly from an out-of-plane vibration of the ring atoms and the attached groups rather than from vibrations of the oxygen atoms in the plane of the ring as suggested by Coop and Sutton. To be sure the argument is based on force constant estimates which are none too reliable; however, it seems unlikely that they can be so greatly in error as to invalidate the conclusion.

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(21) The bending constant used here for C=O against the C-C-C group suggests itself as a reasonable lower limit in view of the bond bending constants listed by Herzberg (Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Company, Inc., New York, N.Y., 1945, p. 193.), at least if it is assumed that the bond angle strain in the four-membered ring has no great effect. With this force constant the estimated frequency of the vibration is low enough (about 300 cm^{-1}) that the assumption of classical excitation cannot be greatly in error.

III. A Reinvestigation of the Molecular Structures of Tetrachloroethylene and Trichloroethylene by the Electron Diffraction Method

A. Introduction

Because of the difference between the molecular structures for phosgene reported by Brockway, Beach, and Pauling (22), and in a more recent investigation, by Schomaker, Stevenson, and LuValle (23) it was thought desirable to reinvestigate the structures of some of the other compounds reported in the earlier paper. Accordingly a reinvestigation of the molecular structures of the six chloroethylenes was begun in February 1942, but studies of only two, tetrachloroethylene and trichloroethylene, were substantially completed before June 1942, at which time this work was discontinued because of the press of war work. It is expected that the investigation of the entire series will be completed in the near future. Meanwhile, the results for tetrachloroethylene and trichloroethylene are here reported, and are compared with those obtained by Brockway, Beach, and Pauling (22).

B. Experimental

Eastman White Label Grade (C.P.) tetrachloroethylene and Braun Chemical Company (C.P.) trichloroethylene were fractionated in a 12-inch column packed with glass spirals. Only the middle fractions were used in the electron diffraction investigation. The refractive indices, $N_D^{20^\circ}$, of these fractions, 1.5055 for tetrachloroethylene and 1.4775 for

(22) L. O. Brockway, J. Y. Beach, and L. Pauling, J. Am. Chem. Soc., 57, 2693 (1935).

(23) V. Schomaker, D. P. Stevenson and J. E. LuValle, To be published.

trichloroethylene, are in satisfactory agreement with the reported (24) values 1.50547 and 1.4777, respectively. Photographs of both compounds were taken at camera distances of 10.95 cm. with electrons of wave length 0.0615 Å as determined by standardization against gold foil. The photographs were taken with the samples at 25° and 50°.

C. Interpretation

The appearance of the photographs is represented by curves V of Figures 3 and 5. Since the first feature (dashed portion of each of these curves), which cannot be read from the photographs, is relatively insensitive to structure, it could be estimated satisfactorily from previous experience with the theoretical curves of other more or less similar molecules. Recent reëxamination (February 1946) of the photographs without previous reference to calculated curves indicated the modifications shown by the dotted portions of curves V in Figures 3 and 5.

Both the radial distribution method (6) and the correlation method (7) were used in interpreting the photographs. The radial distribution functions were calculated from the visual intensity curves by means of Equation (3), p. , in which a was so chosen that $e^{-aq_i^2} = 0.1$ at $q = 65$ for tetrachloroethylene and at $q = 85$ for trichloroethylene. The theoretical intensity curves used in the correlation procedure were calculated (4) from the simplified formula

$$I^{o}_{(q)} = \frac{1}{(Z_{Cl} - f_{Cl})^2} \sum_{i,j}{}' \frac{(Z_i - f_i)(Z_j - f_j)}{r_{ij}} e^{-b_{ij}q^2} \sin \frac{\pi}{10} r_{ij} q \qquad (5)$$

in which account was taken of the actual ratio of scattering powers of carbon and chlorine, $(Z_C - f_C)/(Z_{Cl} - f_{Cl})$. Calculation of preliminary

(24) Handbook of Chemistry and Physics, 27th Edition, p.777, Chemical Rubber Publishing Co. Cleveland, Ohio (1943).

theoretical intensity curves for trichloroethylene showed that the scattering power of the hydrogen atom was so small compared with that of the other atoms that terms arising from its interactions could be neglected. Since none of the remaining terms appeared to require abnormally high temperature factors, the constants b_{ij} were set equal to zero.

D. Results for Tetrachloroethylene

The radial distribution function R, calculated from the (solid) visual curve (See Figure 3) shows sharp, well-resolved peaks at 1.69 Å and 4.28 Å corresponding, respectively, to the bonded C-Cl distance and the longest non-bonded Cl...Cl distance in the molecule. As will become evident in the correlation treatment the position of the small broad peak at 1.23 Å, which represents in part the small contribution of the C=C term, is inconsistent with the demands of the other, more important terms and consequently must be regarded as evidence of errors in the drawing of the visual curve. Although the peaks in the neighborhood of 3 Å, are not well resolved, it is possible to analyze these unresolved peaks in terms of the three distances and their relative contributions expected for tetrachloroethylene models. However, because of the small number of parameters needed to determine the configuration of the molecule, such an analysis was not attempted. Instead it was thought desirable to proceed with the correlation treatment.

In the correlation procedure the visual curve was compared with theoretical curves calculated from planar tetrachloroethylene models in which the symmetry D_{2h} was assumed. The bonded C-Cl distance was held constant at 1.70 Å in the models A to I, inclusive, the C=C distance and the C=C-Cl angle were given the values shown in the legend of

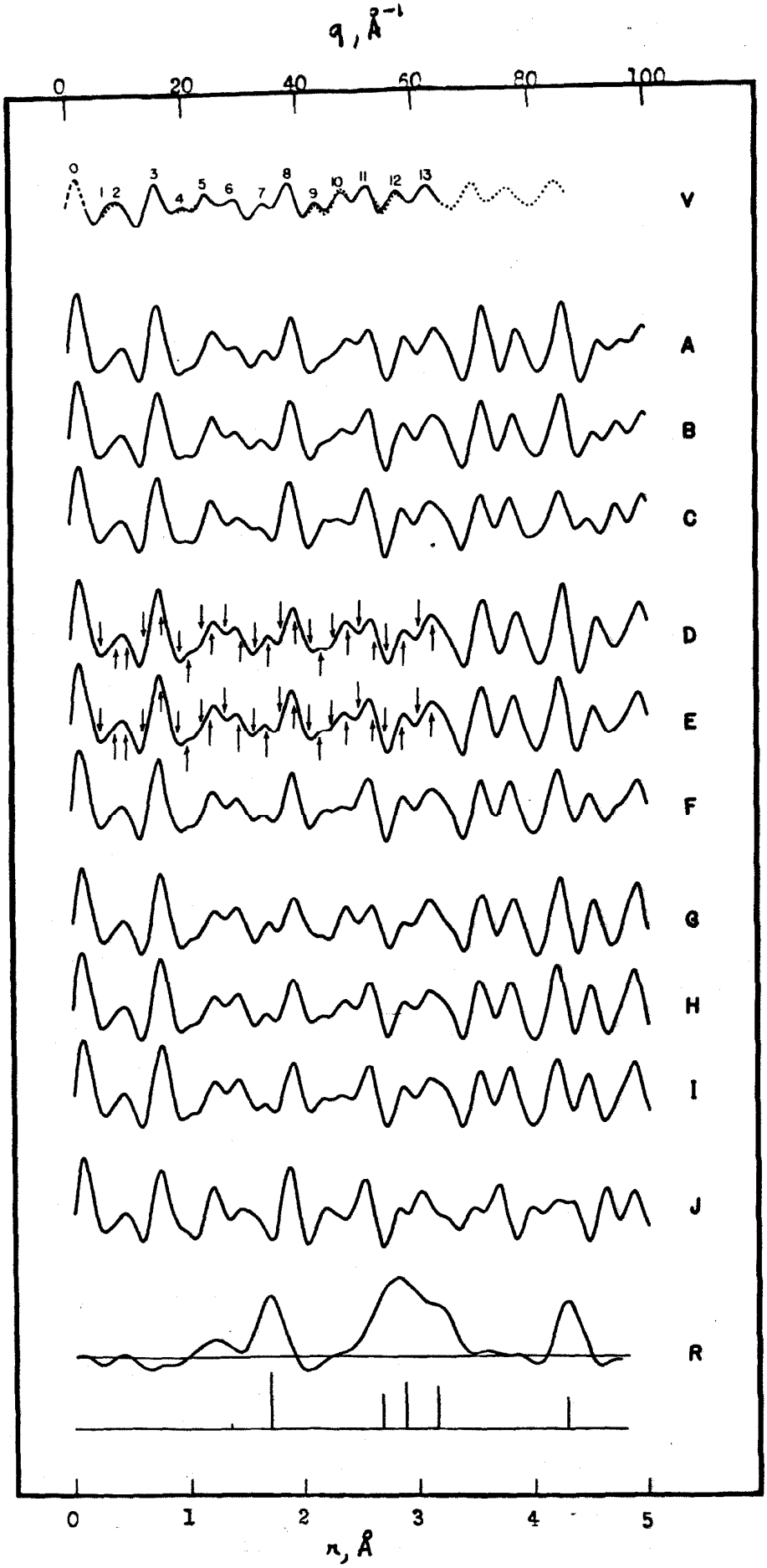

q, Å⁻¹
0
20
40
60
80
100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
V
A
B
C
D
E
F
G
H
I
J
R
0
1
2
3
4
5
r, Å

Figure 3.

Legend for Figure 3

Electron diffraction curves for tetrachloroethylene: visual curve V, theoretical curves A...J, and radial distribution function R. The numbers above curve V and the arrows on curves D and E refer to the measured q values in Table III. Parameters for the curves A...J are as follows

Model	C=C, Å	C-Cl, Å	C=C-Cl
A	1.29	1.70	123°
B	1.32	1.70	123°
C	1.35	1.70	123°
D	1.33	1.70	122°
E	1.36	1.70	122°
F	1.39	1.70	122°
G	1.39	1.70	121°
H	1.42	1.70	121°
I	1.45	1.70	121°
J	1.38	1.73	123¾°

Figure 3 and plotted in Figure 4. The range of possible models was carefully investigated by interpolation among the calculated curves of Figure 3. For any values of the C=C-Cl angle the C=C distance cannot be less than 1.29 Å or greater than 1.39 Å (with a constant C-Cl distance) without producing disagreement with the visual curve. Similarly for a constant C-Cl distance and for any C=C distance the C=C-Cl angle cannot be less than $121\frac{1}{4}^{\circ}$ or greater than $123\frac{1}{4}^{\circ}$. The relation which exists between these two variations, and the range of acceptable models is indicated by the ellipse in Figure 4. The interpolated model in best agreement with the visual curve is indicated by M. On the basis of quantitative comparison of the curves for models E and D with the visual curve (Table III), the parameters indicated for model M and the range of acceptable models (Figure 4) lead to the following final results, together with the limits of error which we believe will be exceeded only rarely: C=C = 1.34 ± 0.05 Å, C-Cl = 1.71 ± 0.02 Å, and C=C-Cl = $122\frac{1}{4}^{\circ} \pm 1^{\circ}$.

These results are not in good agreement with the model chosen by Brockway, Beach, and Pauling: C=C = 1.38 Å (assumed), C-Cl = 1.73 ± 0.02 Å, and C=C-Cl = $123.75^{\circ} \pm 1^{\circ}$. A calculated intensity curve (curve J) representing this model is shown in Figure 3. It will be observed that this model lies outside of the range of acceptability as indicated by the ellipse in Figure 4. In addition the overall size of the model chosen by them is larger than ours by about $1\frac{1}{2}$ percent, a discrepancy which may be due in part to the small number, four, of quantitative comparisons from which they derived their final model.

E. Results for Trichloroethylene

The radial distribution curve calculated from the (solid) visual

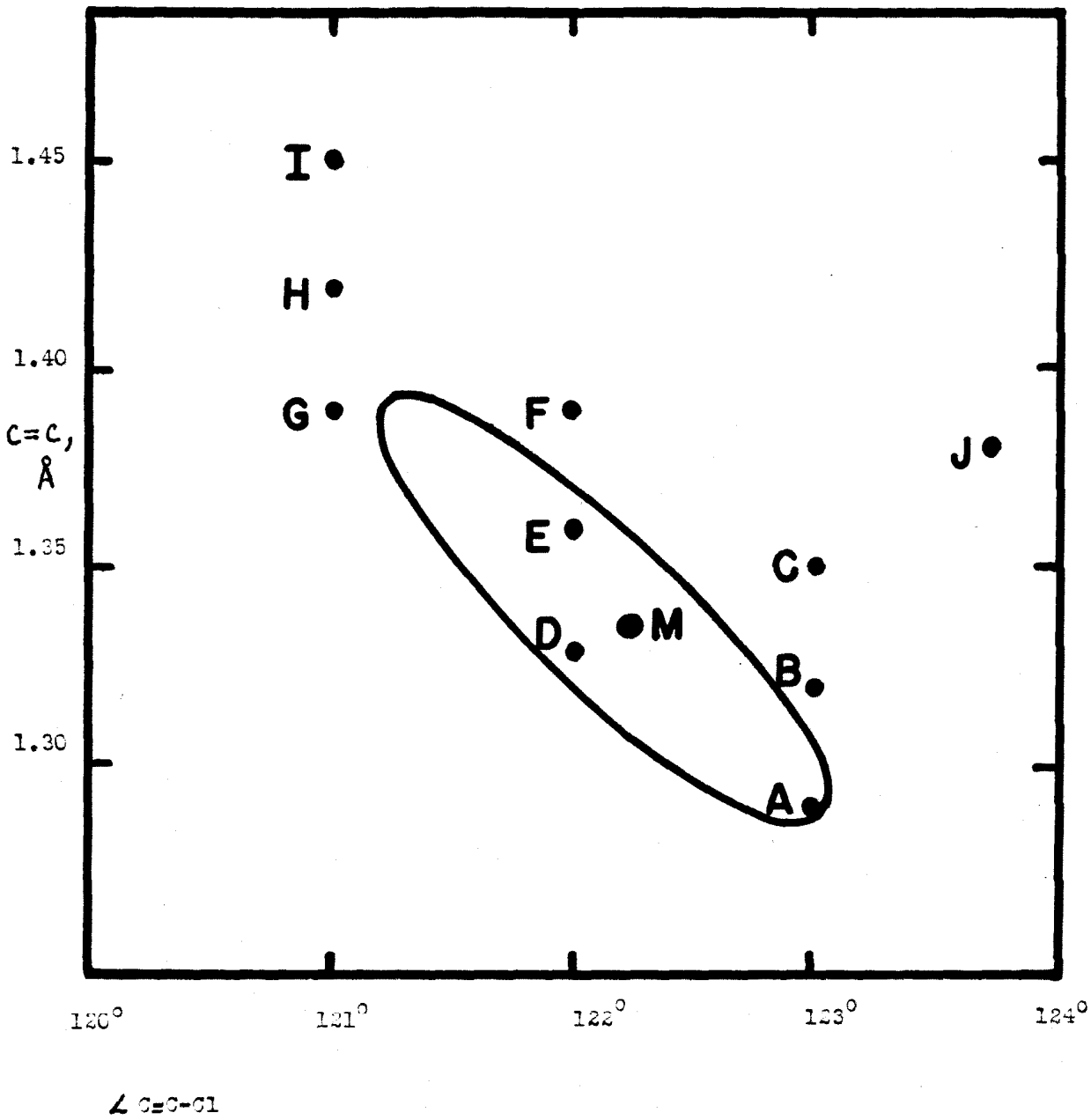


Figure 4. Parameter Values for Tetrachloroethylene Models

Table III

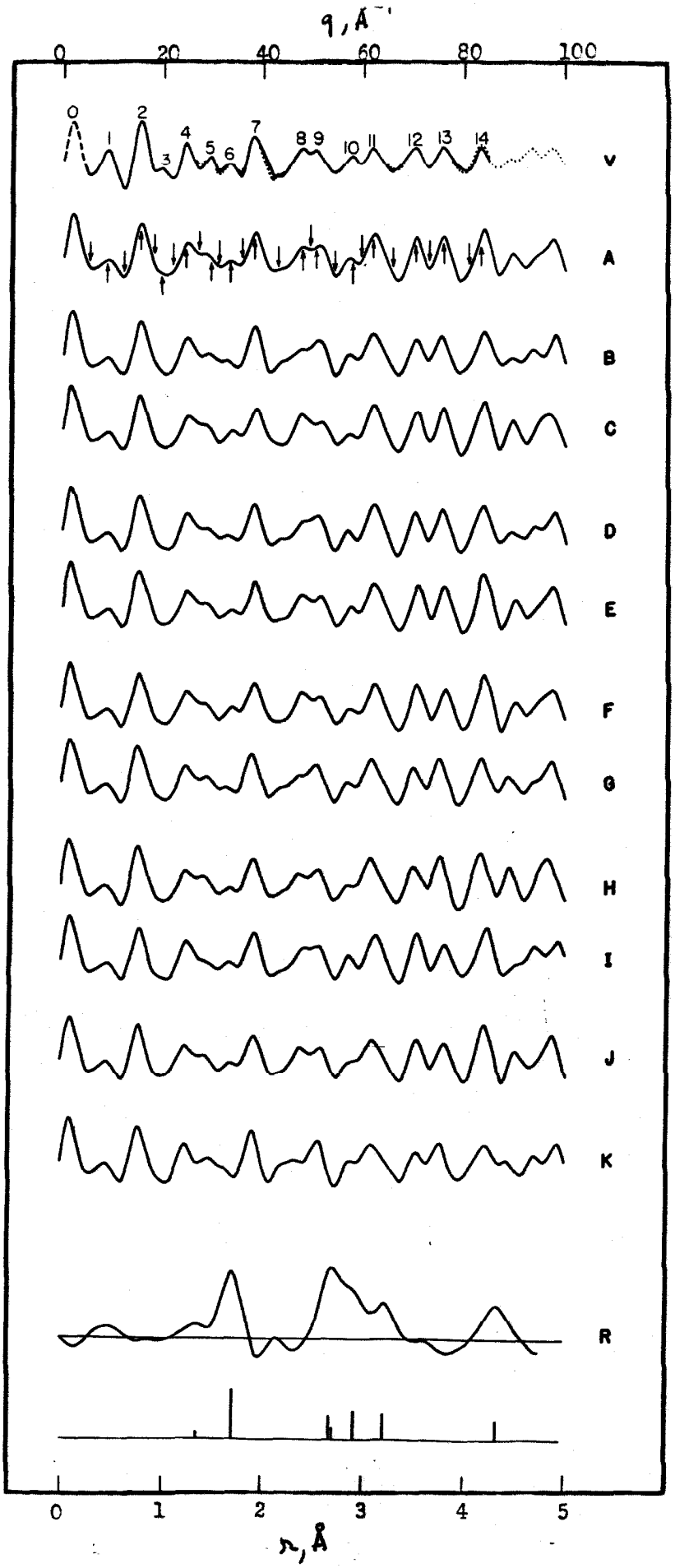
Tetrachloroethylene

		Model E			Model D	
Min.	Max.	q obs.	q calcd.	q calcd./q obs.	q calcd.	q calcd./q obs.
1		4.96	5.3	(1.069)	5.3	(1.069)
	1	7.57	9.0	---	9.1	---
	2	9.58				
3		12.29	11.9	(0.968)	11.9	(0.968)
	3	15.39	15.3	0.994	15.3	0.994
4		18.45	19.0	1.030	19.2	1.041
	4	20.21	20.5	1.014	20.6	1.019
5		22.34	21.5	0.962	21.6	0.967
	5	24.08	24.8	1.030	24.8	1.030
6		26.56	27.1	1.020	27.2	1.024
	6	29.13	28.8	0.989	28.7	0.985
7		31.52	31.7	1.006	31.7	1.006
	7	34.04	33.8	0.993	34.3	1.008
8		36.03	35.7	0.991	35.8	0.994
	8	38.72	38.6	0.997	38.8	1.002
9		41.30	41.8	1.012	42.3	1.024
	9	43.29	43.9	1.014	43.8	1.012
10		45.15	44.7	0.990	44.7	0.990
	10	47.87	47.7	0.996	48.1	1.005
11		49.79	49.5	0.994	50.3	1.010
	11	52.42	52.1	0.994	52.3	0.998
12		54.41	55.1	1.013	55.3	1.016
	12	57.45	57.9	1.008	58.2	1.013
13		59.85	59.8	0.999	59.8	0.999
	13	62.34	62.6	1.004	62.8	1.007
			Average	1.002		1.007
			Average deviation[a]	0.012		0.012

[a]Values in parentheses were omitted in the calculation of the average and average deviation.

curve for trichloroethylene is shown in Figure 5. The first significant peak, at 1.36 Å, represents the C=C term. The sharp peak at 1.72 Å is due to the bonded C-Cl term, while the isolated sharp peak at 4.33 Å is due to the longest non-bonded Cl...Cl term. The group of peaks in the neighborhood of 3 Å represent the other interatomic distances in the molecule (ignoring hydrogen terms). The highest portion (at 2.70 Å) represents the C...Cl terms, while the shoulder at about 2.95 Å and the nearly resolved peak at 3.12 Å are due to the remaining Cl...Cl terms.

A series of theoretical intensity curves based on the model suggested by the radial distribution function was then calculated. These curves (not shown) and also those in Figure 5 were calculated on the assumptions that the molecule was planar, that the bonded C-Cl distances were equal, and that the Cl-C-Cl angle was bisected by the C=C bond extended; the two C=C-Cl angles (in the CCl_2 and CHCl groups, respectively) were not assumed necessarily to be equal. From these preliminary theoretical intensity curves the curve giving best qualitative agreement with the visual curve was selected (curve A, Figure 5). Because four parameters were involved in the structural determination, a systematic study of all their possible variations with respect to one another was not attempted. Instead, a series of theoretical intensity curves was calculated in which each parameter (except the overall size parameter) was varied separately from its value in model A. The resulting curves (B to G inclusive) are shown in Figure 5; the parameter values selected for their calculation are shown in the legend. Variation of the C=C-Cl angle (CCl_2 group) by $\pm 1^\circ$ (models B and C) variation of the C=C-Cl angle (CHCl group) by $\pm 1^\circ$ (models D and E), and variation of the C=C distance by $\pm$ 0.03Å (models F and G) all


q, Å⁻¹
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20
40
60
80
100
0
1
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6
7
8
9
10
11
12
13
14
V
A
B
C
D
E
F
G
H
I
J
K
R
0
1
2
3
4
5
r, Å

Figure 5.

Legend for Figure 5

Electron diffraction curves for trichloroethylene: visual curve V, theoretical intensity curves A...K, and radial distribution function R. The numbers above curve V and the arrows on curve A refer to the measured q values in Table IV. Parameters for the curves A...K are as follows

	C=C, Å	C-Cl, Å	C-C-Cl (CCl_2 group)	C-C-Cl (CHCl group)
A	1.36	1.72	$121\frac{1}{2}^{\circ}$	124°
B	1.36	1.72	$122\frac{1}{2}^{\circ}$	124°
C	1.36	1.72	$120\frac{1}{2}^{\circ}$	124°
D	1.36	1.72	$121\frac{1}{2}^{\circ}$	125°
E	1.36	1.72	$121\frac{1}{2}^{\circ}$	123°
F	1.33	1.72	$121\frac{1}{2}^{\circ}$	124°
G	1.39	1.72	$121\frac{1}{2}^{\circ}$	124°
H	1.41	1.72	$120\frac{1}{2}^{\circ}$	123°
I	1.31	1.72	$122\frac{1}{2}^{\circ}$	125°
J	1.36	1.72	122°	122°
K	1.38	1.71	123°	123°

lead to definite disagreement with the visual curve. However, as was suggested by the rather wide range of acceptable models for tetrachloroethylene (Figure 2), simultaneous variations of these parameters lead to a larger possible range of acceptable models than do separate variations. Models illustrating this type of simultaneous variation, a decrease (or increase) of the C=C bond distance and a decrease (or increase) of the C- C-Cl angles, are shown by curves H and I in Figure 5. The most nearly satisfactory model based on equal C=C-Cl angles is represented by curve J, for which C=C ± 1.36 Å and C-Cl ± 1.72 Å. Although the curve for this model is not inacceptable, it is not in as good agreement with the visual curve as is that for Model A.

The quantitative comparison of curve A with the visual curve is shown in Table IV. The final results and the corresponding limits of error, based on quantitative comparisons of curves A,B, G, and H with the visual curve, are C=C = 1.36 ± 0.04 Å, C-Cl = 1.72 ± 0.02 Å, C=C-Cl (CCl_2 group) = $121\frac{1}{2}^\circ \pm 1^\circ$, and C=C-Cl (CHCl group) = $124^\circ \pm 2^\circ$.

These parameters are in fair agreement with those obtained by Brockway, Beach, and Pauling C=C = 1.38 Å (assumed), C-Cl = 1.71 ± 0.03 Å, C=C-Cl = $123^\circ \pm 2^\circ$. A theoretical intensity curve calculated from this model is shown in Figure 5 (curve K); it is not in very good agreement with our visual curve, particularly with regard to the relative intensities of the 8th and 9th maxima.

Table IV

Trichloroethylene

Model A

Min.	Max.	q obs.	q calcd.	q calcd./q obs.
1		5.24	5.8	(1.107)
	1	8.73	8.8	(1.008)
2		12.05	11.9	(0.988)
	2	15.29	15.3	1.001
3		18.05	18.5	1.025
	3	19.57	20.0	1.022
4		21.70	21.5	0.991
	4	24.24	24.6	1.015
5		26.88	27.1	1.008
	5	29.30	28.5	0.973
6		30.80	31.3	1.016
	6	33.25	33.3	1.002
7		35.48	35.1	0.989
	7	38.08	38.2	1.004
8		42.77	42.8	1.001
	8	47.38	47.7	1.001
9		49.12	49.3	1.004
	9	50.80	51.0	1.014
10		54.13	54.3	1.003
	10	57.65	57.1	0.990
11		59.30	58.8	0.992
	11	61.63	61.9	1.004
12		65.60	66.6	1.015
	12	70.12	70.2	1.001
13		72.64	72.7	1.001
	13	75.62	75.6	1.000
14		81.15	79.2	0.976
	14	83.13	83.3	1.003
			Average	1.002
			Average deviation[a]	0.001

[a] Values in parentheses were omitted in the calculation of the average and average deviation.

Part 2

The Crystal Structure of Methylammonium Chloride

The Crystal Structure of Methylammonium Chloride

I. Introduction

Values for the carbon-nitrogen single-bond distance in various compounds are of interest because of the occurrence of this bond in amino acids, proteins, and related substances. Numerous electron diffraction studies (1) of gas molecules have indicated the value of 1.47 Å which is consistent with the table of covalent radii (2). On the other hand distances ranging from 1.39 Å to 1.42 Å have recently been reported in simple compounds closely related to proteins (3). Incomplete results on β-glycylglycine suggested a value of about 1.49 Å for the NH_3^+-CH_2 portion of the molecule (4). Because of these many different values, it was thought desirable to investigate a simple crystal structure in which the carbon-nitrogen distance was susceptible to accurate determination. Methylammonium chloride was therefore chosen for this investigation.

Methylammonium chloride has been reported to crystallize in the tetragonal

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(1) The values obtained for this distance in various compounds are summarized in Table V, p. 60 .

(2) L. Pauling, The Nature of the Chemical Bond, Second Edition, p. 164, Cornell University Press 1940, Ithaca, N. Y.; the value 1.465 Å is given by the slightly modified values of the covalent radii as given by V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc., 63, 37 (1941).

(3) Cf. the values obtained from glycine, dl-alanine, and diketopiperazine, Table V, p. 60.

(4) The structure of this crystal has been reported by E. W. Hughes and W. J. Moore, J. Am. Chem. Soc., 64, 2236 (1943), but no value for the C-N distance was given; the value quoted above was obtained from a private communication from Dr. Hughes.

system (5). A determination of the crystal structure of this compound has been reported by Hendricks (6). The smallest unit of structure which he found compatible with his data had the dimensions a_o = 4.28 Å (obtained from powder data) and c_o = 5.13 Å (obtained from spectrum data); this unit was found on the basis of density measurements to contain one molecule of CH_3NH_3Cl. Hendricks placed the atomic positions (7) as follows: Cl^- at 000, N at $\frac{1}{2}\frac{1}{2}z_1$, and C at $\frac{1}{2}\frac{1}{2}z_2$, where the most probable values of the parameters were given as $z_1 = 0.24$ and $z_2 = 0.50$.

When the present investigation was begun it was thought only necessary to refine the above parameter values, but it soon became evident that the structure proposed by Hendricks was incorrect (8). The value of a_o was found to be larger by $\sqrt{2}$ and its direction is at 45° to that given by him; hence the unit cell actually contains two molecules of CH_3NH_3Cl.

II. The Unit Cell and Space Group

The material used for this investigation was Eastman Red Label Grade methylamine hydrochloride. Suitable crystals were grown from aqueous solutions by allowing the water to evaporate slowly. A needle-like specimen approximately 0.2-mm. in thickness and 1.5-mm. in length was selected for the single crystal photographs. Early experiments indicated that the crystals were somewhat deliquescent; hence the crystal which was selected was

(5) P. Groth, Chemische Krystallographie 1, 168 (Leipzig 1906)
(6) S. B. Hendricks, Z. Krist. 67, 106 (1928)
(7) These positions correspond to the space group P_4mm.
(8) X-ray diffraction work in collaboration with Mr. David Shoemaker indicates that Hendrick's structure for n-propylammonium chloride is also wrong, and that the correct structure is probably analogous with that of methylammonium chloride.

dipped in a mixture of paraffin wax and vaseline. This mixture not only provided a film which protected the crystal from the atmosphere but was found suitable for attaching the crystal to a quartz fiber mounted on the goniometer head. Because the protecting film obscured the faces of the crystal it was necessary to orient the crystal by trial and error by means of preliminary oscillation photographs or Laue photographs.

Complete sets of CuK_α oscillation photographs using the multiple film technique (9) were taken about the a axis and the c (needle) axis. By means of these photographs the unit cell was established as having the dimensions $a_o = 6.04$ Å and $c_o = 5.05$ Å; the probable error of each of these values is about $\pm$ 0.01 Å. These dimensions of the unit cell together with the observed density value (6), 1.23 gm./cm^3., require two molecules of CH_3NH_3Cl per unit cell. The calculated value of the density is then 1.216 gm./cm^3. which is in satisfactory agreement with the observed value.

A set of powder photographs was taken with CuK_α radiation by means of the multiple film technique (9). These photographs were successfully indexed on the new unit cell. The only systematic extinction which occurred on the oscillation and powder photographs was that for hk0 when h+k is odd.

A Laue photograph in which the X-ray beam passed along the needle axis of the crystal indicated a four fold axis and two sets of mirror planes at 45° to each other. Another Laue photograph in which the beam passed along the a axis indicated an additional mirror plane which was perpendicular to the needle axis. Hence the Laue symmetry is $\frac{4}{m}mm$.

(9) De Lange, Robertson, and Woodward, Proc. Roy. Soc. (London) A 171, 398 (1939)

The Laue symmetry $\frac{4}{m}mm.$ and the existence of all general orders of hk , hh , and Ok , together with the extinction of hkO when h k is odd indicate (10) that the space group is D_{4h}^{7} - P $\frac{4}{n}mm.$

If for the present we omit the hydrogen atoms from the discussion we have, with two atoms of each kind in the unit cell, the following possible point positions (10):

(a) 000 ; $\frac{1}{2}\frac{1}{2}0$

(b) $00\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

(c) $0\frac{1}{2}z$; $\frac{1}{2}0\bar{z}$

Now the C or N atoms cannot be in (a) or (b) and still be able to form covalent bonds; consequently we choose (c) with the following positions:

NH_3^- at $0\frac{1}{2}z_1$; $\frac{1}{2}0\bar{z}_1$

CH_3 at $0\frac{1}{2}z_2$; $\frac{1}{2}0\bar{z}_2$

If we assume the ordinary values for the van der Waals radii of the atoms, the dimensions of the unit cell place the Cl^- atoms in the positions (a) or (b). The choice between these positions is arbitrary (11); we have chosen (a):

Cl^- at 000 ; $\frac{1}{2}\frac{1}{2}0$

A consideration of the hkO intensities (See Table III, p.) also requires that the Cl^- atoms be in the position (a): The Cl^- atoms (as well as the CH_3 and NH_3^- groups) give destructive interference when h k is odd and these reflections are not observed; when h k is even those reflections for which

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(10) Internationale Tabellen zur Bestimmung von Kristallstrukturen, Gebruder Borntraeger (Berlin, 1935).

(11) The Cl^- atoms can also lie in (b), but this assignment corresponds merely to a shift of the origin by $c_o/2$.

$(h+k)/4$ is integral are of strong intensity (effect of Cl^- and $CH_3NH_3^+$ adding) and those for which $(h+k)/4$ is half-integral are weak (effect of Cl^- and $CH_3NH_3^+$ subtracting). The structure factor for the crystal is, according to the above point positions, given by the expressions

$h+k$ even

\+ if h even

\- if h odd

$$A_{hk\ell} = 2f_{(Cl^-)} \pm 2f_{(NH_3^+)} \cos 2\pi\ell z_1 \pm 2f_{(CH_3)} \cos 2\pi\ell z_2 \qquad (1)$$
$$B_{hk\ell} = 0$$

$h+k$ odd

\- if h even

\+ if h odd

$$A_{hk\ell} = 0 \qquad (2)$$
$$B_{hk\ell} = \pm 2f_{(NH_3^+)} \sin 2\pi\ell z_1 \pm 2f_{(CH_3)} \sin 2\pi\ell z_2$$

where $FF^* = A^2_{hk\ell} + B^2_{hk\ell}$.

It must be pointed out that the hydrogen atoms of a $CH_3NH_3^+$ group (in the positions (c)) cannot conform to this space group unless the group is rotating about the C-N axis or unless the hydrogens are randomly oriented with respect to rotation about this axis. A consideration of the rotation of these groups is presented in a subsequent section.

The projections of the structure on (001), (100), and (110) are shown in Figure 1.

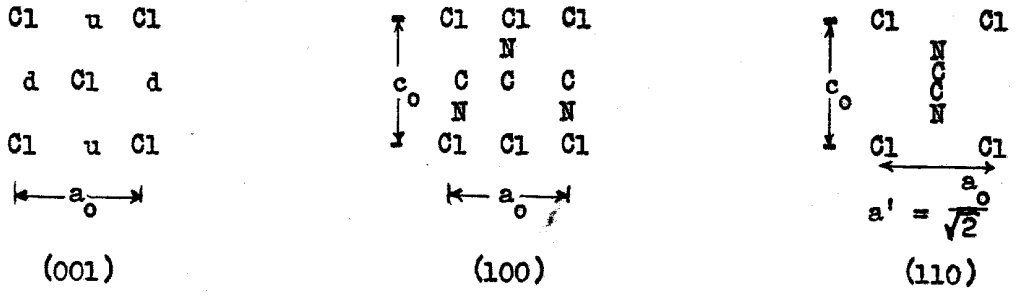

Figure 1. Projection of the Structure of CH_3NH_3Cl on Three Planes. The u and d groups are $CH_3NH_3^+$ groups with the C-N axis pointed up and down, respectively.

A further test of the structure, and incidentally one which distinguishes our structure from the one proposed by Hendricks, is the pyroelectric test (12). His structure, which has no center of symmetry, consists of alternate layers of Cl^- atoms, NH_3^+ groups, and CH_3 groups and is therefore strongly polar. It should therefore show a strong pyroelectric effect. Our proposed structure has a center of symmetry (at $\frac{1}{4}\frac{1}{4}0$, etc.) and hence should show no pyroelectric effect. The test was carried out as follows: The crystal was attached to a single fiber of silk by means of a microscopic drop of cement. The crystal was suspended in liquid air and then removed. Since the crystal then showed no tendency to be attracted to the neck of the Dewar and since no anisotropic growth of ice crystals was observed, it was concluded that the pyroelectric test was negative.

III. Determination of the Parameters

A. Preliminary Results

The intensities of the lines on the powder photographs were estimated visually. The structure factors listed in Table IV (p. 47) were then calculated from these estimates after correction for the Lorentz and polarization factors, and for the multiplicity factors for the occurrence of various planes having the same indices with various signs. The signs of the structure factors were obtained from a preliminary assumption of $z_1 = 0.21$ for NH_3^+ and $z_2 = 0.50$ for CH_3. These preliminary values were based on accepted interatomic distances. The electron density function $\rho(0,\frac{1}{2},z)$ was then calculated

(12) Methods for carrying out this test are described by Wooster, Crystal Physics, p. 223 f, (Cambridge 1938)

from the usual Fourier expression

$$\rho(x,y,z) = \frac{1}{V}\left[\sum A_{hk\ell} \cos 2\pi(hx+ky+\ell z) + B_{hk\ell} \sin 2\pi(hx+ky+\ell z)\right], \quad (3)$$

where V is the volume of the unit cell and the coefficients $A_{hk\ell}$ and $B_{hk\ell}$ are obtained from the observed structure factors. (Table IX) The function $\rho(0,\frac{1}{2},z)$ had maxima at $z_1 = 0.205$ and $z_2 = 0.490$ but there was an additional maximum (and a corresponding minimum) which had a height about 1/6 of that of the real maxima. This residual maximum and minimum indicated poor convergence of the function $\rho(0,\frac{1}{2},z)$ and hence the parameters indicated by this calculation were not regarded as accurate.

Complete sets of CuK_α oscillation photographs using the multiple film technique had already been obtained about the a axis, [100], and the c axis, [001]. A Fourier projection on (100) could be obtained from the $h0\ell$ reflections from the a axis photographs by means of a modification of Equation (3). This projection would resolve the CH_3 groups well but would resolve the NH_3^+ group only very poorly (See Figure 1). In order to resolve suitably the NH_3^+ group it is necessary to calculate the projection on (110), for which the $hh\ell$ reflections are required. Accordingly a complete set of CuK_α oscillation photographs using the multiple film technique was taken about [110]. In order to calculate the projection the $hh\ell$ reflections (zero layer line) were reindexed on an orthorhombic unit cell with a and b axes in the plane of and at 45° with respect to the basal tetragonal axes. The axial lengths of the new cell are $a = a_o\sqrt{2}$ and $b = a_o\sqrt{2}$; the volume of this unit is the same as that of the tetragonal unit. Thus the $hh\ell$ reflections became $h'0\ell$ reflections; the Fourier projection was calculated from the expression

$$\rho'(x',z) = \frac{1}{A'}\sum_{h'\ell} F_{h'0\ell} \cos 2\pi(h'x'+\ell z), \quad (4)$$

where the area A' is $A/\sqrt{2}$ (where A is the area of the hOℓ projection), and the sine terms have dropped out since $B_{hk\ell} = 0$. Therefore $A_{hk\ell} = F_{hh\ell} = A_{h'0\ell} = F_{h'0\ell}$.

Sections of the Fourier projections for the hOℓ and hhℓ reflections were then calculated along the line x = 0 for the hOℓ data and x = $\frac{1}{2}$ for the hhℓ data. These sections gave broad peaks at the atomic positions and also indicated poor convergence of the series. Since a reestimation of all of the intensities gave essentially the same result it was concluded that the difficulties were due to the absence of higher order reflections and to absorption of the CuK_α radiation. In order to obtain the hOℓ and hhℓ data it was necessary to mount the needle axis of the crystal horizontally; hence the incident and reflected X-ray beams for various reflections were required to traverse widely different path lengths inside the crystal. Thus it is reasonable that large errors may be introduced because of absorption of the CuK_α radiation. The hkO data, on the other hand, were obtained with the needle axis of the crystal in a vertical position; in general for these reflections the path length of the radiation through the crystal was small and approximately the same for all reflections. The hkO data which appear in Table III were therefore those obtained with CuK_α radiation; no additional photographs of this zone were taken with MoK_α radiation.

B. Determination of the Parameters from the Fourier Projections

Since MoK_α radiation has a much lower linear absorption coefficient than does CuK_α radiation, and since higher order reflections would appear on the film because of the smaller wave length of MoK_α radiation (0.710 Å as compared with 1.54 Å for CuK_α radiation), complete sets of oscillation photographs were

taken about [100] and [110] using MoK_α radiation filtered through a 100 μ Zr filter. The multiple film technique was used for these photographs; in order to reduce the intensity by a desirable factor, 0.001-inch copper sheets were interleaved between the films.

Since the needle axis of the crystal was horizontal, the effect of absorption of the MoK_α radiation was minimized by allowing the X-rays to pass only through the region near one end of the crystal (13). Only the reflections which passed through the small length of path at the end of the crystal were estimated (Figure 2).

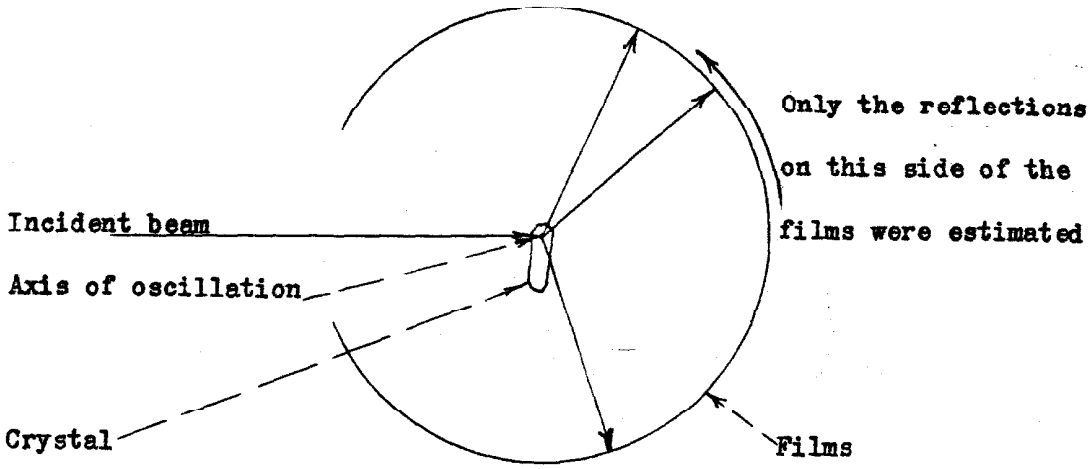

Figure 2. Experimental Arrangement Designed to Minimize the Effect of Absorption

The intensities of the reflections on the zero layer lines of the [100]

(13) Because of the hygroscopic nature of the crystal, no attempt was made to avoid absorption difficulties by suitable modification of its shape.

and [110] photographs were estimated with the aid of an Eastman Densitometer, Model B. The factor by which the intensity was reduced when the reflections passed through one film and one copper sheet was found, by means of the densitometer, to be 4.0. The reflections in the density range from 0.09 to 0.6 were measured with the densitometer, and then all of the reflections were estimated visually using the densitometered values as a basis. In the densitometered range the intensity was taken proportional to the maximum density of a reflection minus the density of the background near that reflection.

Slight differences in the intensities of the same reflections on different films were attributed to variations in the intensity of the incident beam and to the immersion of a different total volume of the crystal in the X-ray beam for the different oscillation photographs. In order to correct for these discrepancies the estimated intensities were corrected for Lorentz and polarization factors and the corresponding structure factors were calculated. The structure factors on each film were then compared with those obtained from the powder photographs and hence a relative scale was established for the various oscillation photographs. The adjustment of the structure factors of a given zone to an absolute scale was made by the method of least squares as described in a subsequent section.

The observed structure factors for the h0ℓ and hhℓ reflections are shown in Tables I and II, respectively. These values were used, with the signs indicated on the calculated values, to calculate the sections of the Fourier projections shown in Figures 3 and 4; these sections represent $\rho(0,z)$ for the h0ℓ zone and $\rho'(\frac{1}{2},z)$ for the hhℓ zone, respectively. The carbon parameter, obtained from the function $\rho(0,z)$, is 0.489. The nitrogen parameter, obtained

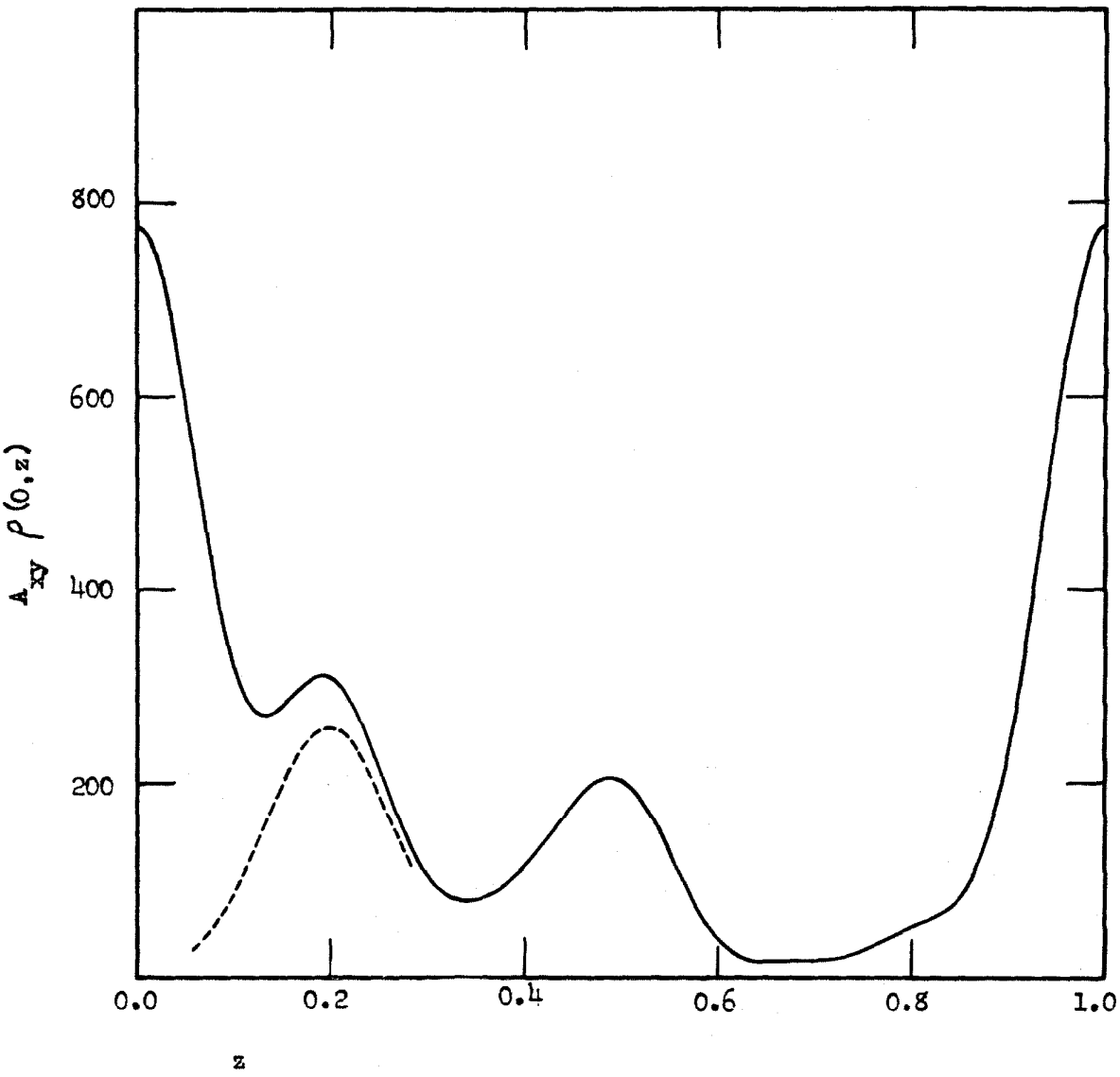

Figure 3. Section of the Fourier projection $\rho(x,z)$ for $x = 0$. The dotted curve was obtained after subtraction of the contribution of Cl^- (right side of curve).

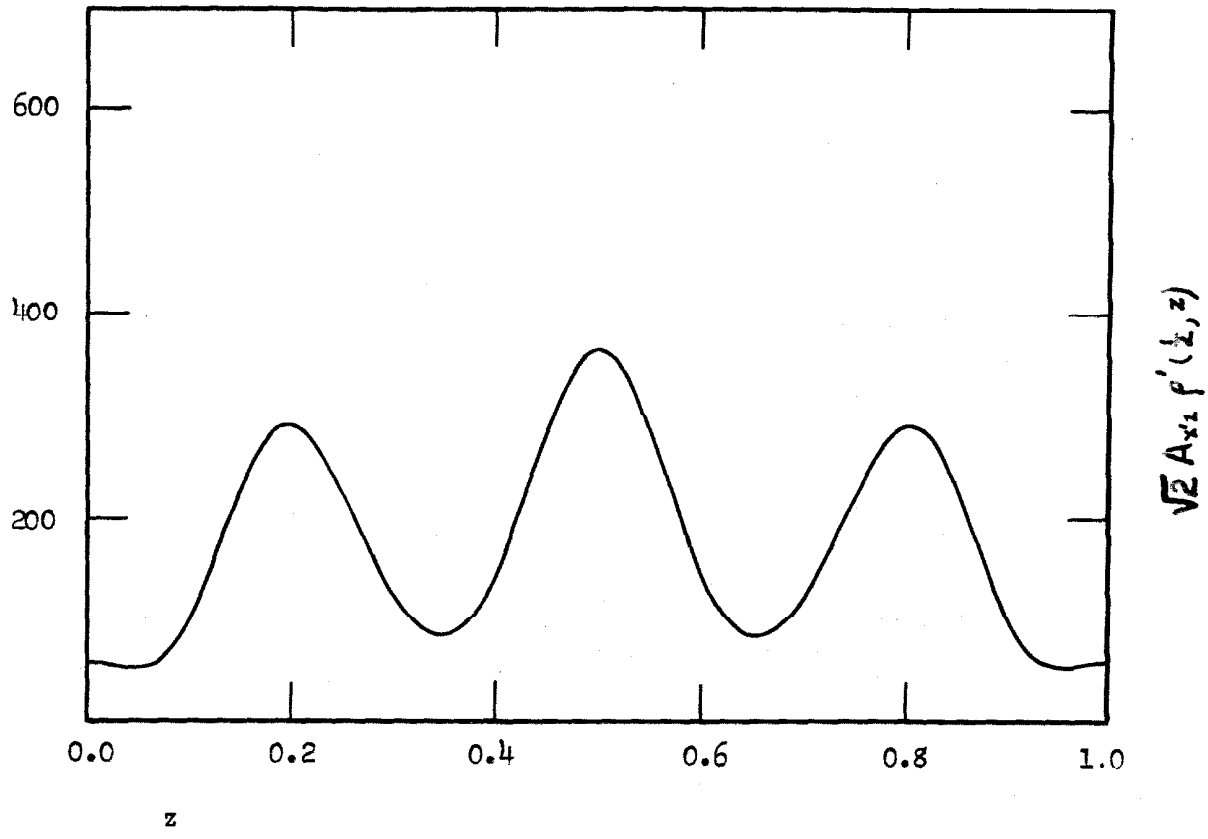

Figure 4. Section of the Fourier projection $\rho'(x', z)$ for $x' = \frac{1}{2}$.

from the function $\rho'(\frac{1}{2},z)$, is 0.198. The nitrogen parameter can also be estimated, with somewhat greater uncertainty, from the function $\rho(0,z)$ shown in Figure 3: If the curve for the Cl^- atom, obtained from the right side of the curve, is subtracted from the left side, the dotted curve is obtained; this curve represents approximately the contribution of the NH_3^+ group. The nitrogen parameter is 0.199 from this curve. The agreement between these two values for the nitrogen parameter is quite satisfactory.

The probable errors, r_{z_1} and r_{z_2}, of the parameters z_1 and z_2 were calculated from the hhℓ data and the h0ℓ data, respectively, by means of the following expression, which is derived in Appendix I, where the choice

$$r_{z_i}^2 = \frac{2\pi^2}{\left[\frac{\partial^2(\rho V)}{\partial z^2}\right]_i^2} \sum_{hk\ell} r_{hk\ell}^2 \, \ell^2 \, (1 \pm \cos 4\pi \ell \, z_i), \qquad (5)$$

of signs is + if h+k is odd and - if h+k is even. The values of $\left[\frac{\partial^2(\rho V)}{\partial z^2}\right]_i$ were estimated from the Fourier projections. The values of $r_{hk\ell}$ were obtained from the residuals, F(observed) - F(calculated), by the method outlined in Appendix I. The calculated structure factors were those labelled F_4 in Tables I and II; the method by which these quantities were calculated is described in a subsequent section.

The probable errors of both z_1 and z_2 were found to be $\pm$ 0.001 by this method. A somewhat larger probable error was assigned to the value of z_1 obtained from the h0ℓ projection after subtraction of the Cl^- atom (see Figure 3); this probable error was set at $\pm$ 0.002.

The values of the structure factors were then calculated using the parameter values $z_1 = 0.200$ and $z_2 = 0.490$. The hydrogens were introduced into the scattering factors of the carbon and nitrogen atoms by use of the difference

Table I

Structure Factors of the h0ℓ Reflections

	Calculated				Observed
h0ℓ	F_1	F_2	F_3	F_4	F
001	21.9	21.4	21.3	21.5	19.7
101	11.2	11.0	10.1	10.1	11.6
200	39.8	40.2	39.5	39.0	39.2
201	17.2	17.3	17.4	17.4	17.1
002	19.9	18.2	19.7	19.8	18.9
102	3.4	3.3	5.3	5.2	5.4
202	15.7	14.6	15.0	14.7	14.6
301	5.2	5.0	5.1	5.0	5.8
003	7.5	5.4	4.2	4.4	3.2
103	-1.8	-1.7	-2.2	-1.9	2.4
302	1.9	1.8	1.2	1.3	1.3
400	18.7	19.3	19.3	18.7	20.6
203	6.7	5.5	4.6	4.8	4.5
401	10.3	11.2	11.1	11.0	11.6
402	9.9	9.9	10.0	9.6	8.6
303	-1.2	-1.1	-1.1	-0.9	1.3
004	12.3	9.2	9.2	9.1	9.2
104	-2.8	-2.5	-2.5	-2.5	2.8
501	2.2	2.0	2.1	2.0	3.5
204	10.7	8.1	8.4	8.3	8.2
403	4.8	4.4	4.1	4.1	4.1
502	0.9	0.8	0.9	0.7	1.3
304	2.1	1.8	-2.0	-1.9	1.3
005	5.9	4.1	4.0	4.0	4.2
600	9.4	10.4	10.8	10.0	9.6
105	0.4	0.3	0.2	0.3	1.3
601	5.4	6.7	6.6	6.1	6.7
503	-0.6	-0.5	-0.6	-0.5	1.3
404	7.6	6.0	6.0	5.8	6.1
205	5.9	3.6	3.5	3.6	3.9
602	5.5	6.1	6.1	5.7	4.9
305	0.4	0.3	0.3	0.4	1.2
504	-1.4	-1.1	-1.1	-1.0	2.2
603	2.4	2.8	2.8	2.7	2.6
701	1.1	0.8	0.9	0.8	1.2
006	5.3	2.8	2.8	2.8	2.8
405	3.9	2.7	2.7	2.6	2.5
106	0.6	0.5	0.5	0.3	1.2
702	0.4	0.3	0.3	0.3	1.2
206	4.7	2.5	2.5	2.5	2.6
604	4.3	3.6	3.6	3.3	3.1 *
306	0.5	0.4	0.3	0.3	1.2
505	0.2	0.2	0.2	0.2	1.2
703	-0.4	-0.3	-0.2	-0.2	1.2
800	4.2	5.0	5.1	4.4	3.8
801	2.2	3.3	3.3	3.0	3.1
406	2.6	1.8	1.9	1.8	1.6
802	2.4	3.1	3.2	2.8	2.8
007	1.4	0.1	0.1	0.3	1.2
107	0.6	0.4	0.4	0.4	1.2
704	-0.7	-0.5	-0.5	-0.5	1.6
605	2.4	1.7	1.7	1.5	1.9

* Limit of CuK_α radiation

Table II

Structure Factors of the hhℓ Reflections

	Calculated				Observed
hhℓ	F_1	F_2	F_3	F_4	F
001	21.9	21.4	21.3	21.5	19.7
110	5.5	6.0	5.4	5.5	5.5
111	29.3	29.0	28.9	28.7	29.4
002	19.9	18.2	19.7	19.8	18.9
112	18.6	17.2	16.6	16.5	17.6
220	28.7	29.0	28.4	28.0	28.8
221	14.3	14.7	14.9	14.6	15.2
003	7.5	5.4	4.2	4.4	3.2
222	13.1	12.6	12.7	12.5	12.4
113	18.6	16.1	17.1	16.7	17.3
330	5.9	7.5	7.3	7.1	8.4
331	12.1	12.9	13.0	12.5	12.7
223	6.1	5.0	4.5	4.6	5.5
004	12.3	9.2	9.2	9.1	9.2
332	9.4	9.5	9.5	9.1	10.2
114	6.6	4.2	4.1	4.4	4.6
333	10.5	9.4	9.6	9.3	8.4
224	9.4	7.4	7.6	7.3	7.6
440	10.5	11.5	11.9	11.1	10.8
441	6.1	7.5	7.4	6.8	8.4
005	6.8	4.1	4.0	4.0	4.2
442	6.3	6.8	6.8	6.4	6.0
115	5.9	3.4	3.4	3.4	3.2
334	3.9	3.0	2.9	3.0	3.7
225	5.2	3.2	3.2	3.2	3.9
443	2.8	3.1	2.9	2.9	3.4
550	2.1	3.9	3.8	3.5	3.6
551	4.7	5.8	5.7	5.2	4.5
006	5.3	2.8	2.8	2.8	2.8
116	2.6	0.8	0.9	1.0	1.6
335	3.7	2.4	2.3	2.3	2.7
444	4.9	4.0	4.0	3.7	3.7
552	3.5	4.2	4.1	3.8	5.4
226	4.2	2.3	2.3	2.2	2.5 **
553	4.1	3.8	4.1	3.7	4.1
445	2.6	1.8	1.9	1.8	2.0
007	1.4	0.1	0.1	0.3	1.7
660*	3.4	4.1	4.1	3.5	
117	3.1	1.5	1.6	1.4	1.7
554	1.5	1.6	1.5	1.4	1.7
661	1.8	2.9	2.9	2.5	3.4
227	1.2	0.2	0.1	0.2	1.7
662	1.9	2.6	2.6	2.2	2.2

* Not observed because of experimental arrangement

** Limit of CuK_α radiation

Table III

Structure Factors of the hk0 Reflections

	Calculated				Observed
hk0	F_1	F_2	F_3	F_4	F
110	5.5	6.0	5.4	5.5	5.5
200	39.8	40.2	39.5	39.0	39.2
220	28.7	29.0	28.4	28.0	28.8
310	6.9	8.2	8.9	8.8	8.9
400	18.7	19.3	19.3	18.7	20.6
330	5.9	7.5	7.3	7.1	8.4
420	15.7	16.6	16.8	16.1	16.4
510	4.6	6.5	6.2	5.9	6.9
440	10.5	11.5	11.9	11.1	10.8
530	3.8	5.8	5.4	5.0	5.8
600	9.4	10.4	10.8	10.0	9.6
620	8.3	9.3	9.4	8.7	9.3
550	2.1	3.9	3.8	3.5	3.6
710	2.1	3.9	3.8	3.5	3.6
640	6.1	6.9	6.9	6.2	6.2
730	1.7	3.3	3.3	2.9	3.1

Table IV

Intensity Data from the Powder Photographs

hkℓ	$\frac{\sin\theta}{\lambda}$	Observed* I	Calculated* I
001	0.099	780	920
110	.117	120	120
101	.129	1080	820
111	.153	6920	6580
200	.166	6150	6080
201	.193	2340	1420
002	.198	710	780
211	.210	730	780
102	.215	230	220
112	.230	2480	2180
220	.234	3320	3130
221	.254	1850	1700
202	.258	1710	1730
310	.262	630	620
301	.267	270	200
212	.271	160	120
311	.280	5120	4520
003	.297	200	40
222	.307	1230	1250
103	.308	190	30
321	.314	370	240
302	.318	200	10
113	.319	2390	2230
312	.328	2550	2380
400	.331	1700	1400
203	.340	160	180
401	.346	1070	970
213	.350	370	230
330	.351		
411	.356	280	140
322	.358	240	20
331	.364	1290	1250
420	.370	2150	2070
223	.378	240	170
421	.384	1420	1410
402	.386	490	740
303	.387		
412	.394	3000	2440
004	.396		
313	.396		
332	.403	830	660
104	.405	310	50
114	.413	170	160

Table IV Continued

Intensity Data from the Powder Photographs

hkℓ	$\frac{\sin\theta}{\lambda}$	Observed* I	Calculated* I
422	.420	1240	1220
323	.420		
510	.422	380	280
501	.425	350	100
431	.425		
204	.429	540	550
511	.433	1400	1570

* These observed values were obtained from photographs made with filtered CuK_α radiation. Observed and calculated values have been corrected for Lorentz - polarization factors. The calculated values of I correspond to the values of F_4 in Tables I, II, and III. Very few reflections were resolved for values of sin θ/λ greater than 0.433.

between the scattering factors for oxygen and oxide ion (10). As a first approximation the Debye-Waller temperature factor, $e^{-B(\frac{\sin\theta}{\lambda})^2}$, was assumed to be the same for all of the atoms in the crystal. The value of B, as determined by the least squares treatment given below, was approximately 3.3. These calculated values are labelled F_1 in Tables I, II, and III. Although the agreement between the calculated and observed structure factors was fairly good, numerous reversals of the observed values with respect to some of the calculated values were noted. These discrepancies were shown not to be due to errors in the estimated values because a complete reestimation of the intensities gave essentially the same results. The reason for the difficulty did not become apparent until the complete projections were calculated, the results of which are shown in Figures 5 and 6. These calculations were made using the punched card method and International Business Machines (14). The series (Equations 3 and 4) were summed at intervals of $a_o/100$ and $c_o/125$ ($h0\ell$ projection) and $a'/50$ and $c_o/100$ ($hh\ell$ projection).

The small negative areas which occurred in the Fourier projections are not shown in the figures; the lowest level of these areas is -4 for the $h0\ell$ projection (height of Cl^- peak, 770), and -4 for the $hh\ell$ projection (height of the 2 Cl^- peak, 1117).

The elliptical shape of the Cl^- atom is the most striking observation to be made on the projections shown in Figures 5 and 6. Although these two projections represent independent sets of experimental data (except for the 00ℓ reflections), they both indicate a strong anisotropy of the temperature

(14) P. A. Shaffer, Jr., Thesis 1942, California Institute of Technology

vibration of the Cl^- atom. A treatment of this anisotropy is presented in the following section on least squares.

Another observation is the indications of the effect of the hydrogen atoms, especially on the methyl group of the hOℓ projection (Figure 5). Although the positions of the hydrogen atoms cannot be determined from these data, it seems reasonable that the introduction of these atoms in their approximate positions in the structure would improve the agreement between the observed and calculated structure factors. Accordingly, such a calculation is also included in the section of least squares.

C. Least Squares Determination of Parameters

The parameters to be determined by the least squares treatment include not only the distance parameters but also the temperature factors. The general method of the least squares treatment was the same as that used by Dr. Hughes in the melamine paper (15). Using trial parameters for the temperature factors and distance parameters approximate equations are set up in the form

$$w_{hk\ell}\left[\sum_i \left(\frac{\partial F_{hk\ell}}{\partial z_i}\right)' \Delta z_i + \sum_j \left(\frac{\partial F_{hk\ell}}{\partial B_j}\right)' \Delta B_j = \sqrt{w_{hk\ell}}\,(F_{hk\ell} - F'_{hk\ell}). \quad (6)$$

The primes indicate that the quantities have been evaluated from the trial parameters. The $F_{hk\ell}$ is the observed structure factor and the Δz_i and ΔB_j are the corrections being sought. The weighting factor $w_{hk\ell}$ governs the

(15) E. W. Hughes, J. Am. Chem. Soc., 63, 1737 (1941)

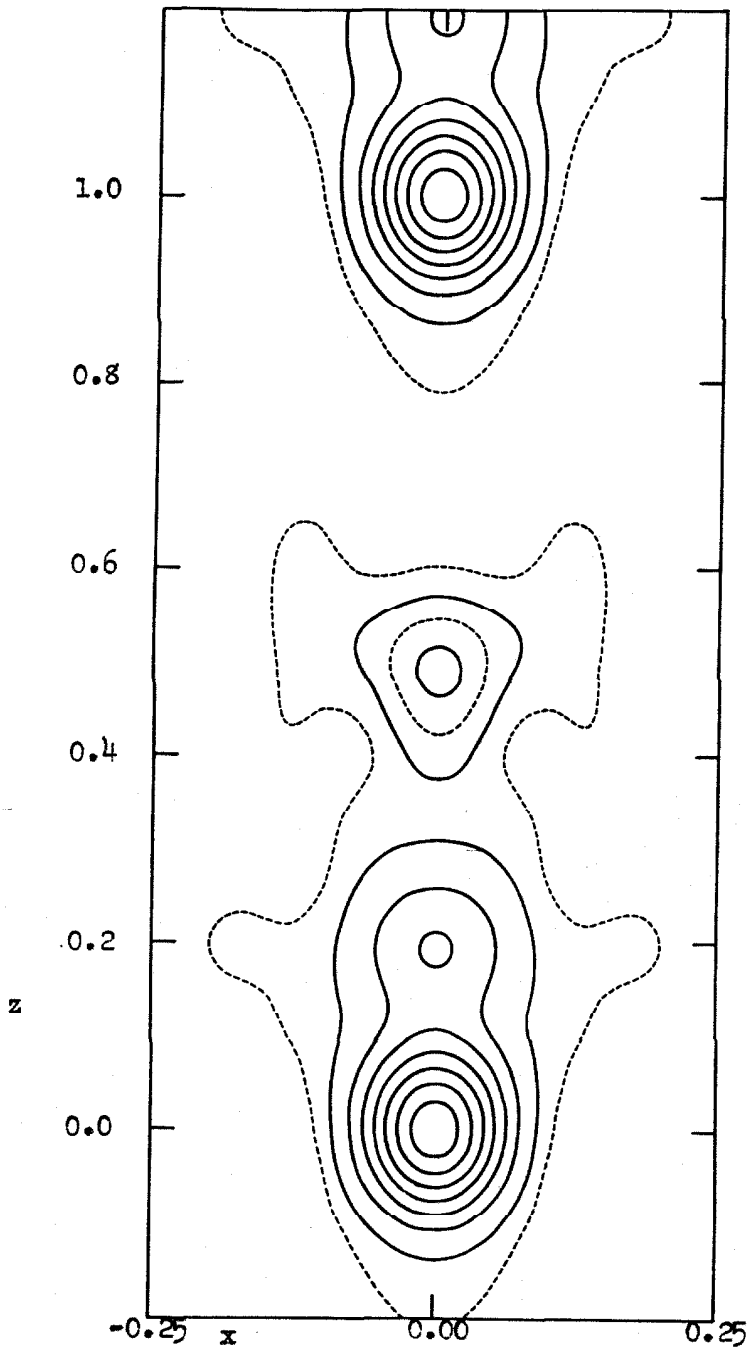

Figure 5. Fourier Projection on (100). The function calculated was $A_{xz}\,\rho(x,z) = \sum_{h,\ell} A_{h0\ell} \cos 2\pi(hx+\ell z) + B_{h0\ell} \sin 2\pi(hx+\ell z)$. Solid contours are drawn at intervals of 100n, where n = 1,2, ... 7; dotted contours are drawn for n = $\frac{1}{2}$ and $\frac{3}{2}$.

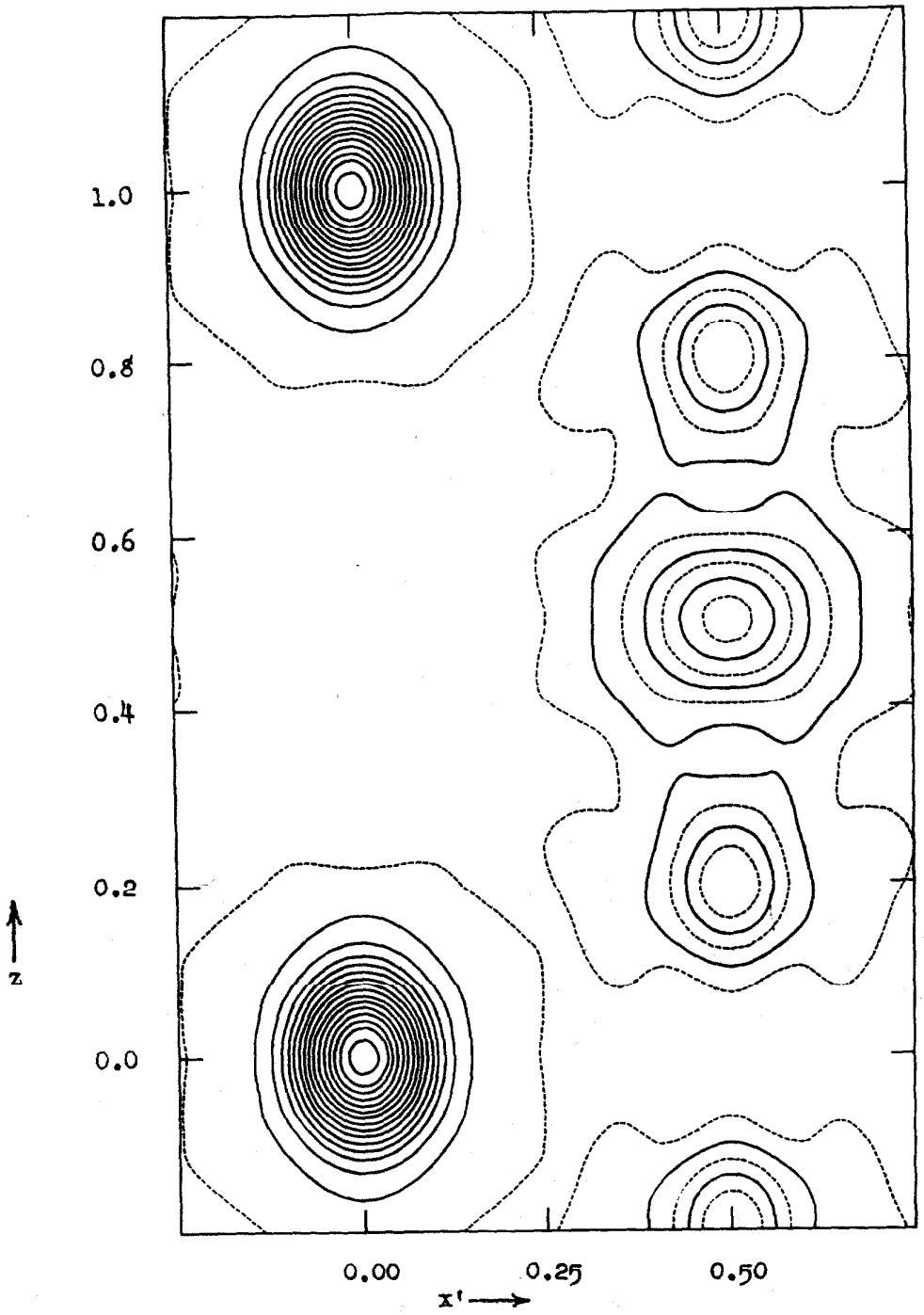

Figure 6. Fourier Projection on (110). The function calculated was $A'_{x'z}\rho(x',z) = \sum_{h,\ell} F_{hh\ell} \cos 2\pi(hx'+\ell z)$. Solid contours are drawn at intervals of (100 n)/$\sqrt{2}$ where n = 1,2,$\cdots$15; dotted contours are drawn for n = $\frac{1}{2}$ and, in part, for n = $\frac{3}{2}$ and $\frac{5}{2}$.

relative importance of the various equations of the above type for each of the observed $F_{hk\ell}$'s.

In the final least squares treatment the weights were chosen by the method previously described by Dr. Hughes (15). For this treatment $w_{hk\ell}$ was taken proportional to $1/F^2_{hk\ell}$ for $F_{hk\ell} \geq 4F_{min.}$ and proportional to $1/(16\ F^2_{min})$ for $F_{hk\ell} \leq 4\ F_{min.}$ This system of weighing implies that the percentage probable error in the F's is constant for $F_{hk\ell} \geq 4\ F_{min.}$, and that the probable error for F's below that range is constant. This can only be considered a rough approximation which is easy to apply in practice, but there is some basis for this choice in the methods which were used to estimate the intensities. A slightly different weighting system, which was later discarded in favor of the above system was used in the preliminary least squares treatments; the results obtained with the two weighting systems differed by an amount comparable with the probable errors of the parameters.

The proper absolute scale was chosen before the least squares treatment was begun, and a new absolute scale was determined after each refinement of the parameter values. The scale factor, α, for a given zone was chosen to make the function

$$w_{hk\ell}\ (\alpha\ F_{hk\ell} - F'_{hk\ell})^2$$

a minimum, i.e.

$$\alpha = \frac{\sum w_{hk\ell}\ F_{hk\ell}\ F'_{hk\ell}}{\sum w_{hk\ell}\ F^2_{hk\ell}} . \qquad (7)$$

A scale factor was determined for each zone separately before each least

squares treatment was started. It was observed that the scale factor approached unity as successive refinements were made in the parameters.

Although in the final least squares treatment both the temperature factors and distance parameters were allowed to vary simultaneously, several preliminary least squares treatments were made for the temperature factors using approximately those values of the parameters indicated by the Fourier projections ($z_1 = 0.200$ and $z_2 = 0.490$). On the basis of these preliminary treatments the values of the structure factors listed in Tables I, II, and III were calculated. The various methods of calculation are described in the following sections.

1. Calculation of F_1

As a first approximation all of the atoms were assumed to have the same temperature factor $e^{-B(\frac{\sin\theta}{\lambda})^2}$. The least squares treatment of the h0ℓ, hhℓ, and hk0 data for the temperature factor B gave the value B = 3.3; the structure factors F_1 were calculated using this value. As was pointed out previously the general agreement between observed and calculated F's was fairly good but some of the intensities were not in agreement even on a relative scale.

2. Calculation of F_2

After the complete Fourier projections had been calculated it was obvious that the introduction of an anisotropic temperature factor for the Cl^- atom together with a single temperature factor for the $CH_3NH_3^+$ group would improve considerably the agreement between the observed and calculated

F's. The anisotropic temperature factor (16) for the Cl^- atom was written in the same form as that used by Dr. Hughes in the melamine paper (15).

$$f = f_o\, e^{-(B_1 + B_2 \cos^2\varphi)(\frac{\sin\theta}{\lambda})^2}, \qquad (8)$$

where B_1 and $B_1 + B_2$ are the constants for planes parallel and perpendicular, respectively, to the direction of maximum vibration, and φ is the angle between the normal to the reflecting plane and the direction of maximum vibration. For our tetragonal crystal in which the direction of maximum vibration has been taken along the c axis we have the relation

$$\cos^2\varphi = \frac{l^2}{\left(\frac{c_o}{a_o}\right)^2\left[h^2 + k^2 + \left(\frac{a_o}{c_o}\right)^2 l^2\right]}.$$

The temperature factor of the $CH_3NH_3^+$ group was assumed to be $e^{-B_3(\frac{\sin\theta}{\lambda})^2}$.

A least squares treatment using these expressions and the distance parameters $z_1 = 0.200$ and $z_2 = 0.490$ gave the results:

$$B_1 = 2.5, \qquad B_1 + B_2 = 5.5, \qquad \text{and } B_3 = 4.0.$$

The values of F_2 (Tables I, II, and III) were calculated using these parameter values. The agreement between observed and calculated F's was improved by this treatment. Of the small discrepancies which remain those for the reflections 102 and 003 seem to be the greatest. It was believed that the introduction of the hydrogen atoms in their proper positions would reduce these discrepancies.

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(16) The use of an anisotropic temperature factor was first described by L. Helmholz, J. Chem. Phys., 4, 316 (1936).

3. Calculation of F_3

The hydrogen atoms of the $CH_3NH_3^+$ groups, which are assumed to be rotating about the C-N axes, were introduced by a method suggested by Professor V. Schomaker (17). The contribution of a single atom, e.g. a hydrogen atom, to the scattering factor may be written as follows

$$f_{i_{hk\ell}} = f_i \, e^{2\pi i \underline{h}\cdot\underline{r}} = f_i e^{2\pi i \underline{h}\cdot (\underline{r}_o + \Delta\underline{r})},$$

where $\underline{r}$ is the position vector from the origin to the atom i, and $\underline{r}_o$ is the vector to the center of the circle of radius $\rho' = |\Delta\underline{r}|$. If we now average over the circle described by the rotating atom we obtain

$$f_{i_{hk\ell}} = f_i \, e^{2\pi i \, \underline{h}\cdot\underline{r}_o} \, J_o(u) \, , \qquad (9)$$

where $u = 2\pi \frac{\rho'}{a_o}\sqrt{h^2 + k^2}$, and $J_o(u)$ is the zero order Bessel function.

The contribution of the hydrogen atoms to the scattering factor of the crystal were calculated from Equation (9) assuming one scattering electron per hydrogen atom, and assuming that the CH_3 group is equivalent to C + 3H and the NH_3^+ group is equivalent to N + 2H. Slight deviations from these assumptions would not produce results which are significantly different. The hydrogen atoms were assumed to be about 1Å from the atom to which they are bonded; tetrahedral bond angles were assumed.

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(17) Private communication from Professor V. Schomaker, February 13, 1945. Calculations of this sort have been described by the following authors: D. Coster, Verslag, Akad. Wetenschappen Amsterdam, 28, 391 (1919); N. H. Kolkmeyer, ibid., 28, 767 (1920); J. M. Bijvoet, Rec. trav. chim., 42, 874 (1932); and J. M. Bijvoet and J. A. A. Ketelaar, J. Am. Chem. Soc., 54, 625 (1932).

The structure factors F_3 in Tables I, II, and III were calculated using the same temperature factors and distance parameters for F_2, but with the hydrogens introduced according to Equation (9). Very few of the structure factors were changed appreciably and all of these have low values of $\sin\theta/\lambda$, e.g. the 103 and 003 reflections. Because of the negligible change of the structure factors having the higher values of $\sin\theta/\lambda$ it was not considered necessary to redetermine separately the temperature factors. The agreement between the observed structure factors and the calculated values F_3 is excellent.

4. Comparison of observed and calculated structure factors

The observed structure factors may be most easily compared with the calculated values, F_1, F_2, or F_3, by calculation of the sum of squares of residuals. The following result was obtained, after summing over the $h0\ell$, $hh\ell$, and $hk0$ data:

$$\sum (F_1 - F_{obs})^2 = 208 ,$$
$$\sum (F_2 - F_{obs})^2 = 50 , \text{ and}$$
$$\sum (F_3 - F_{obs})^2 = 40 ,$$

where, in these calculations, the weighting factors were omitted. Thus considerable improvement was obtained by introduction of the anisotropic temperature factor. Introduction of the hydrogens in approximately their proper positions instead of by the oxygen minus oxide ion correction produced a less striking but significant improvement in the agreement between the observed and calculated F's. The order in which these two improvements was carried out probably has little effect on the sum of squares of residuals

because the hydrogens are important only at the smaller values of sin θ/λ while the anisotropic temperature factor is important chiefly at the higher values of sin θ/λ.

5. Final least squares treatment

A final least squares treatment in which the distance parameters and temperature factors were allowed to vary simultaneously was carried out using the trial parameters

$$B_1 = 2.5 ,$$
$$B_1 + B_2 = 5.5 ,$$
$$B_3 = 4.0 ,$$
$$z_1 = 0.200 , \text{ and}$$
$$z_2 = 0.490.$$

The calculated values F_3 were used in this treatment; the following final values were obtained by the least squares method:

$$B_1 = 2.8 ,$$
$$B_1 + B_2 = 5.4 ,$$
$$B_3 = 4.3 ,$$
$$z_1 = 0.198 , \text{ and}$$
$$z_2 = 0.485.$$

The differences between the trial parameters and these final least squares parameters are due in part to interaction of the Δz_i's and ΔB_j's and in part to the slight difference in the weighting systems used in the preliminary and final least squares treatments.

6. Probable errors of the distance parameters which were determined by the least squares method

The probable errors of the parameters z_1 and z_2 were determined from the least squares data by the method outlined in Appendix I. The values which were obtained were $r_{z_1} = \pm 0.002$ and $r_{z_2} = \pm 0.004$.

D. Final Values of the Parameters; Calculation of F_4

The values of the distance parameters which were obtained by the two methods are summarized in the following tabulation:

Fourier Method	Least Squares Method
$z_1 = 0.198 \pm 0.001$ (hhℓ proj.)	$z_1 = 0.198 \pm 0.002$
$z_1 = 0.199 \pm 0.002$ (h0ℓ proj.)	
$z_2 = 0.489 \pm 0.001$ (h0ℓ proj.)	$z_2 = 0.485 \pm 0.004$

The value of $z_2 = 0.485$ obtained from the least squares treatment may well be in error because of an inadequate treatment of the temperature factors for the CH_3 and NH_3^+ groups; indeed the hhℓ projection (Figure 6) suggests that the CH_3 group has an anisotropy in its temperature vibration. A treatment of this effect by the method of least squares was not carried out, however. Because of the possibility of interference of this temperature anisotropy with the parameter determination and because of the relatively large probable error in z_2 as calculated by the least squares method, somewhat less significance was attached to this value of z_2.

From the determinations listed in the preceeding tabulation the following final values of the parameters were obtained:

$z_1 = 0.198 \pm 0.001$ — NH_3^+ parameter

$z_2 = 0.488 \pm 0.001$ — CH_3 parameter

$B_1 = 2.8$

$B_1 + B_2 = 5.4$ — Cl^- atom

$B_3 = 4.3$ — $CH_3NH_3^+$ group

The calculated structure factors, F_4, in Tables I, II, and III, and the calculated intensities in Table IV ($I_{hk\ell} = mF^2_{hk\ell}$, where m is the multiplicity factor) were obtained with the use of these final values of the parameters.

IV. Discussion of the Results

A. Interatomic Distances

From the final values of the parameters and the unit cell dimensions ($a_o = 6.04$ Å and $c_o = 5.05$ Å) the following interatomic distances were calculated to the nearest 0.005 Å:

$$C \text{ —— } N = 1.465 \pm 0.01 \text{ Å},$$
$$C \text{ ... } Cl^- = 3.900 \pm 0.005 \text{ Å},$$
$$C \text{ ... } Cl^- = 3.975 \pm 0.005 \text{ Å}, \text{ and}$$
$$N \text{ ... } Cl^- = 3.180 \pm 0.005 \text{ Å}.$$

It is thus very unlikely that the C - N distance is in error by more than ± 0.03Å, or that the other distances are wrong by more than ± 0.015 Å.

The predicted value of the C - N distance (2) is 1.47 Å if we ignore the formal charge correction, or 1.44 Å if we take it into account. If we

consider the ionic radius (18) for Cl^- (1.81 Å), the van der Waals radius for the methyl group (2.0 Å), and the ionic radius for the NH_4^+ ion (1.4 Å) corrected for the effect of change of coordination number (19) we calculate the non-bonded distances C...Cl^- = 3.8 Å, and N ... Cl^- = 3.2 Å. Thus the observed values are in satisfactory agreement with those predicted on the basis of previous structural determinations in other compounds. The formal charge of the NH_3^+ group does not seem to shorten the C - N bond appreciably below the normal covalent value of 1.47 Å.

B. Partial Summary of Carbon-Nitrogen "Single-Bond" Distances

A partial summary of carbon-nitrogen single-bond distances obtained in the most recent available X-ray and electron diffraction studies of various compounds is shown in Table V.

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(18) Reference (2), pp. 352 and 189.

(19) The NH_4^+ ... Cl^- distance found in "low" NH_4Cl (3.35 Å) by R. J. Havighurst, E. Mack, Jr., and F. C. Blake, J. Am. Chem. Soc., 46, 2368 (1924) yields an ionic radius of 1.54 Å for NH_4^+ when the ionic radius for Cl^- is subtracted. This value may be corrected for change of coordination number from eight to four (Reference (2), p. 368) to give the NH_4^+ ionic radius of 1.41 Å.

Table V

Values of the Carbon-Nitrogen Single-Bond Distance in Various Compounds

X-Ray Investigations

Distance in Å.	Compound
1.465	Methylammonium chloride (20)
1.49	Geranylamine hydrochloride (21)
1.45	Hexamethylenetetramine (14)
1.42	dl-Alanine (22)
1.39	Glycine (23)
1.41	Diketopiperazine (24)
1.48	Tetramethylammonium chloride (25)

Electron Diffraction Investigations

Distance in Å.	Compound
1.48	Hexamethylenetetramine (14)
1.44	Methyl isocyanide (26)
1.49	Trimethylamine oxide (27)
1.47	Dimethylchloroamine (28)
1.47	Tetranitromethane (29)
1.46	Dimethylamine (30)
1.53	Borinetrimethylammine (31)
1.47	Methyl azide (32)
1.47	Trimethylamine (33)
1.46	Nitromethane (34)

(20) This determination.

(21) G. A. Jeffrey, Proc. Roy. Soc., A 183, 388 (1945); L. Bateman and G. A. Jeffrey, Nature, 152, 446 (1945).

(22) H. A. Levy and R. B. Corey, J. Am. Chem. Soc., 63, 2095 (1941).

(23) G. A. Albrecht and R. B. Corey, ibid., 61, 1087 (1939).

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(31) S. H. Bauer, ibid., 59, 1804 (1937).

(32) L. Pauling and L. O. Brockway, ibid., 59, 13 (1937).

(33) L. O. Brockway and H. O. Jenkins, ibid., 58, 2036 (1936).

(34) L. Pauling and L. O. Brockway, ibid., 59, 13 (1937).

Appendix I

Calculation of the Probably Errors in Parameter Values

Methods for the calculation of probable errors of parameter values obtained by the least squares method and by the Fourier method are outlined in the following sections. These methods were compiled, for the most part, from private connumications received from Dr. Hughes; they are presented here because some of the final expressions were used in the preceeding pages, and because not all of the results have been published in the literature.

A. Probable Error of a Parameter Determined by the Least Squares Method

We define the following quantities:

w = weight,

v = residual = observed value - most probably value: $v_{hk} = F_{obs} - F_{calc.}$,

n = number of observations,

q = number of variables,

u = mean error,

a = average deviation, and

r = probable error.

When these quantities refer to a particular structure factor we shall use the subscript hk ; when they refer to a parameter we shall use the subscript z_1, z_2, etc.

Now the mean error and the probable error may be calculated as follows (34)

(34) Whittaker and Robinson, "Calculus of Observation", Chapter IX, Blackie and Son, London 1929

$$u = \sqrt{\frac{\sum w_{hk\ell}\, v^2_{hk\ell}}{n - q}}, \qquad \text{and } a = \frac{\sum |w_{hk\ell}|\ \sqrt{w_{hk\ell}}}{\sqrt{n(n - q)}} .$$

For a normal distribution of errors we may calculate the probable errors from either of these quantities as follows

$$r = (0.6745)\, u, \qquad \text{or} \qquad r = (0.8453)\ \text{a.d.} ,$$

and for a large number of observations the values of r calculated by these two methods will agree closely if the errors follow a normal distribution. In the final least squares determination the values of r found by the two methods outlined above were 0.395 and 0.397, respectively.

The probable error of the i th parameter may then be calculated from the equation

$$r_{z_1} = \frac{r}{\sqrt{w_{z_1}}} , \qquad \text{where} \quad w_{z_1} = D/A_{ii} ;$$

D is the determinant of the normal equations in the least squares treatment, and A_{ii} is the ii th minor of the determinant (15).

B. Probable Error of a Parameter obtained by the Fourier method

From the value of r as calculated from the residuals $v_{hk\ell}$ and weights $w_{hk\ell}$ by the methods outlined in the previous section we may find the probable error of a given $F_{hk\ell}$ from the equation

$$r_{hk\ell} = \frac{r}{\sqrt{w_{hk\ell}}} .$$

Now in general the parameter z_i is a function of the $F_{hk\ell}$'s; hence we find

a change in z_i is related to a change in the $F_{hk\ell}$'s by the expression

$$\Delta z_i = \sum_{hk\ell} \frac{\partial z_i}{\partial F_{hk\ell}} \Delta F_{hk\ell} \quad .$$

If we take the average and convert to probable errors we find

$$r_{z_i}^2 = \sum_{hk\ell} \left(\frac{\partial z_i}{\partial F_{hk\ell}} \right)^2 r_{hk\ell}^2 \quad .$$

Hence in order to find r_{z_i} from $r_{hk\ell}$ we need only know the values of $\frac{\partial z_i}{\partial F_{hk\ell}}$; these values are calculated in the following way:

The general expression for the electron density function is

$$\rho(x,y,z) = \frac{1}{V} \left[\sum_{hk\ell} A_{hk\ell} \cos 2\pi (hx+ky+\ell z) + B_{hk\ell} \sin 2\pi (hx+ky+\ell z) \right] .$$

Now at the coordinates of the i <u>th</u> atom we have

$$x = x_i,\ y = y_i,\ z = z_i, \quad \frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial y} = \frac{\partial \rho}{\partial z} = 0 \quad .$$

The expression obtained from $\frac{\partial \rho}{\partial z} = 0$ is of interest for our case; it is

$$\sum_{hk\ell} \ell \left[A_{hk\ell} \sin 2\pi (hx_i + ky_i + \ell z_i) - B_{hk\ell} \cos 2\pi (hx_i + ky_i + \ell z_i) \right] = 0$$

If we differentiate this expression with respect to some F, say $F_{h'k'\ell'}$, we find, after solving for

$$\frac{\partial z_i}{\partial F_{h'k'\ell'}} \quad ,$$

$$\frac{\partial z_i}{\partial F_{h'k'\ell'}} = \frac{2\pi\ell'}{\left[\frac{\partial^2(\rho V)}{\partial z^2}\right]_i} \left[\sin 2\pi(h'x_i + k'y_i + \ell'z_i) \frac{\partial A_{h'k'\ell'}}{\partial F_{h'k'\ell'}} - \cos 2\pi(h'x_i + k'y_i + \ell'z_i) \frac{\partial B_{h'k'\ell'}}{\partial F_{h'k'\ell'}} \right].$$

This expression may be substituted back into our equation for probable errors; we find, after dropping primes, that

$$r_{z_i}^2 = \left[\frac{4\pi^2}{\frac{\partial^2(\rho V)}{\partial z^2}}\right]_i^2 \sum_{hk\ell} \ell^2 r_{hk\ell}^2 \left[\sin 2\pi(hx_i+ky_i+\ell z_i) \frac{\partial A_{hk\ell}}{\partial F_{hk\ell}} - \cos 2\pi(hx_i+ky_i+\ell z_i) \frac{\partial B_{hk\ell}}{\partial F_{hk\ell}}\right]^2$$

The remaining partial derivatives are especially simple for our compound; we have

for h + k even $\qquad B_{hk\ell} = 0 \ , \ \frac{\partial A_{hk\ell}}{\partial F_{hk\ell}} = 1$, and

for h + k odd $\qquad A_{hk\ell} = 0 \ , \ \frac{\partial B_{hk\ell}}{\partial F_{hk\ell}} = 1.$

These give, for the probable error of a parameter z_i in our crystal,

$$r_{z_i}^2 = \frac{2\pi^2}{\left[\frac{\partial^2(\rho V)}{\partial z^2}\right]_i^2} \cdot \sum_{hk\ell} \ell^2 r_{hk\ell}^2 \left[1 \pm \cos 4\pi(hx_i + ky_i + \ell z_i)\right],$$

where we choose - if h + k is even and + if h + k is odd.

The weighting factors $w_{hk\ell}$ are, of course, assumed to allow for the possible errors due to absorption and extinction in addition to the relative ease in estimation of the intensities. Additional factors which must be

considered in the assignment of a probable error from the Fourier projection are the possibility of errors in sign of some of the structure factors, and the effect of the structure factors which are missing from the calculation either because the corresponding intensities were too small or because their values of $(\sin \theta)/\lambda$ were so large that these reflections did not appear on the films.

Summary

Electron diffraction studies of vanadium tetrachloride, dimethylketene dimer, tetrachloroethylene, and trichloroethylene have been completed. Vanadium tetrachloride has the regular tetrahedral structure with the bond distance V-Cl = 2.03 ± 0.02 Å. For dimethylketene dimer the 2,2,4,4-tetramethylcyclobutadione-1,3 structure is confirmed, a notable feature of which is the large temperature factor that must be ascribed to the distances greater than 3 Å. Reinvestigation of two of the six chloroethylenes by the electron diffraction method gave the following parameters: tetrachloroethylene, C=C = 1.34 ± 0.05 Å, C-Cl = 1.71 ± 0.02 Å, and C=C-Cl = $122\frac{1}{4}^\circ$ ± 1°; trichloroethylene, C=C = 1.36 ± 0.04 Å, C-Cl = 1.72 ± 0.02 Å, C=C-Cl (CCl_2 group) = $121\frac{1}{2}^\circ$ ± 1°, and C=C-Cl (CHCl group) = 123° ± 2°.

The crystal structure of methylammonium chloride has been determined. The unit cell was found to be tetragonal with the dimensions a_o = 6.04 Å and c_o = 5.05 Å; this cell contains two molecules of CH_3NH_3Cl. The space group was found to be D_{4h}^7 - $P\frac{4}{n}nm$; the Cl^- atoms are placed at 000 and $\frac{1}{2}\frac{1}{2}0$, the N atoms at $0\frac{1}{2}z_1$ and $\frac{1}{2}0\bar{z}_1$, and the C atoms at $0\frac{1}{2}z_2$ and $\frac{1}{2}0\bar{z}_2$. The z parameters of the carbon and nitrogen atoms were determined by the methods of Fourier projection and least squares. The values which were found were z_1 = 0.198 ± 0.001 and z_2 = 0.488 ± 0.001. The carbon-nitrogen distance was found to be 1.465 ± 0.017 Å.

Acknowledgements

I am very grateful to Professor Linus Pauling for his advice, encouragement, and interest, without which these investigations could not have been undertaken. I am also greatly indebted to Professor Verner Schomaker for his many interesting, stimulating, and informative discussions and for his continued interest in my research work. I wish to thank the principal collaborators with whom certain portions of these investigations were carried out. These include Professor V. Schomaker (Parts 1 and 3), Mr. A. Greenville Whittaker (vanadium tetrachloride), Dr. Edward W. Hughes (Part 2), Dr. Robert B. Corey (Part 3), and Professor J. H. Sturdivant and Dr. T. R. Rubin (Part 4). I am also indebted to my wife for assistance with many calculations and for assistance in the preparation of this thesis.

Propositions

1. As an aid in the identification of alcohols in dilute aqueous solutions, the 3-5 dinitrobenzoates can conveniently be prepared by addition of a benzene solution of 3-5 dinitrobenzoyl chloride to a strongly alkaline aqueous solution of the alcohol (1).

2. The mode of vibration of 2,2,4,4-tetramethylcyclobutadione responsible for the anomalously large atom polarization is probably not predominantly that proposed by Coop and Sutton (2) but rather the one described approximately by an out of plane (of the four-membered ring) vibration of the $\rangle C=O$ groups and a similar but opposite motion of the $\rangle C(CH_3)_2$ groups (3).

3. Comparison of the relative intensities of two X-ray reflections by means of the multiple film technique can lead to errors if due regard is not exercised for the apparent change in relative intensity by change of the order of superposition of the two films. This phenomenon is attributed primarily to multiple scattering of light by the backgrounds of the two films.

4. When the absolute scale of observed and calculated structure factors is not known, a more satisfactory scale factor than that ordinarily used is $\alpha = \sum w_{hk\ell} F_{hk\ell} F'_{hk\ell} / \sum w_{hk\ell} F^2_{hk\ell}$ where α multiplies the observed structure factor $F_{hk\ell}$, $w_{hk\ell}$ is a weighting factor, and $F'_{hk\ell}$ is the calculated structure factor.

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(1) W.N. Lipscomb and R.H. Baker, J. Am. Chem. Soc., 64, 179 (1942).
(2) I.E. Coop and L.E. Sutton, J. Chem. Soc., 1269 (1938).
(3) Thesis, p. 19 .

5. Plots (Λ vs. $\sqrt{C}$) of the conductance data reported (4) for M , HF_2^- salts having the assumed positive ions H_3O^+ , $CH_3OH_2^+$, $C_2H_5OH_2^+$, and $n\text{-}C_3H_7OH_2^+$ in HF(ℓ) result in curves having anomalously high limiting slopes (β = 0.94 to 0.74) as compared with curves for the positive ions Ag^+ and K^+ (β = 0.54). A possible explanation of this anomaly is that these ions really exist partly or completely as H_4O^{++} , $CH_3OH_3^{++}$, etc. in HF(ℓ).

6. (a) The viscosity of HF(ℓ) at -15°C. can be calculated from the conductance data (4) and the dielectric constant data (5) by means of the Debye-Hückel-Onsager equation. The result, 0.0057 poise, may deviate from the actual value if the conductance of the HF_2^- ion proceeds in part by a chain mechanism. This deviation may be discussed in terms of that which occurs in a similar calculation of the viscosity of water from the conductance data for acids or bases.

(b) Experimental determinations of the viscosities of HF(ℓ) at various temperatures are desirable.

7. (a) It seems very probable that the highly polar crystal structures assigned (6) to methylammonium bromide and iodide and to n-propylammonium chloride, bromide, and iodide are incorrect. Actually the $CH_3NH_3^+$ or $CH_3CH_2CH_2NH_3^+$ groups probably have their polar axes aligned in opposite directions in the structures rather than in the same direction, with the result that these structures are centrosymmetric.

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(4) Fredenhagen and Cadenbach, Zeits. f. Phys. Chem., 146, 257 (1930).
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(6) S.B. Hendricks, Z. Krist., 67, 106, 465 (1928).

(b) By crystallization of methylammonium chloride (or the n-propylammonium halides) in the presence of a strong electric field it may be possible to prepare crystals having the highly polar structures described by Hendricks (6).

8. The possibility of separating mixtures of organic or inorganic crystals which have different dielectric constants by application of a non-uniform field to a suspension of them in a liquid with intermediate dielectric constant should be considered as an available laboratory technique (7).

9. Confidential.

10. Confidential.

11. (a) Research and study at the Institute have been unnecessarily hampered by the present policy of not heating the buildings on week-ends.

(b) Manure should not be used as a fertilizer on ground adjacent to the Campus Coffee Shop.

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(7) G.L. Rosenholtz and D.T. Smith, American Mineralogist, 21, 115 (1936).

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