Mean-Square Amplitudes and Force Constants of Tetrahedral Molecules. II. Silicon Tetrachloride*

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In a preceding paper,[1] we have proposed a new method for determining the force field of molecules by the use of the mean-square amplitudes in addition to the vibrational frequencies, and have shown that the application of the method to germanium tetrachloride and carbon tetrachloride molecules provides reasonable sets of the force constants. In the present report, the results of the application of the same method to silicon tetrachloride will be shown, with a special emphasis on the estimation of the uncertainties of the results by a statistical consideration.

In order to use the mean-square amplitudes for the determination of the force field, it is essential to ascertain the precise experimental values of the amplitudes, with their uncertainties. Accordingly, possible sources of experimental errors are discussed in this paper.

The failure of the first Born approximation is often regarded as a serious error for an atom pair with very different atomic numbers. Fortunately, however, silicon tetrachloride has the advantage that the error caused by the Born approximation is negligibly small; the correction is only 1% for the Si–Cl pair, in contrast to about 20% for the Ge–Cl pair in germanium tetrachloride, or 10% for the C–Cl pair in carbon tetrachloride.[2] The finite sample size is another source of the error,[3,4] and presumably the largest one for this molecule. It is assumed in the theory of gas diffraction that the scattering occurs at an infinitesimal point, but in a practical experiment the diffracted beams come from a finite cross-section of the primary beam in the gas stream. A needle-type nozzle is, therefore, employed in this study in order to reduce the sample delocalization, and at the same time, the correction for the finite sample size was estimated on the basis of the distribution of the gas molecules along the primary beam, which was measured with a special device which will be described in detail in a following paper.[5]

The atomic distances in the silicon tetrachloride molecule have been determined by the visual method by Wierl,[6] Brockway and Wall,[7] Pauling and Brockway,[8] and Iwasaki et al.[9] The Si–Cl distances obtained are 2.02 Å, 2.02 Å, 2.00±0.02 Å and 2.01±0.02 Å respectively and the tetrahedral structure has been established, although the mean-square amplitudes have not been reported any of the above papers.

Experimental

The apparatus used for the electron diffraction measurement is the same as that reported in a previous paper,[1] except for a few improvements. Diffraction photographs were obtained on Fuji Process Hard plates through an r^3-sector, with camera lengths of 11.8 cm. and 27.9 cm. The accelerating voltage was about 45—47 kV., and its fluctuation and drift were regulated to within 0.1%. The sample of silicon tetrachloride was kindly provided by the Shin-Etsu Chemical Industrial Co., Ltd. The gaseous sample was held in a glass flask of about 1 l. at a pressure of about 30 mmHg, and the gas flow was controlled by a needle valve at the rate of decrease in the gas pressure in the flask of about 1 mmHg/min. The exposure time was varied from 2 to 5 min. Two kinds of nozzles were used. One was of a drum-type, the same as that reported by Kuchitsu;[4] it is shown in Fig. 1. The other, a needle-type nozzle, was made of a straight tube of stainless steel with an inner diameter of 0.55 mm. The drum-type nozzle gives a wider spread of the gas distribution at the diffraction center, and it presumably leads to an apparent increase in the mean-square amplitudes. Therefore, the needle-type nozzle is more suitable for obtaining the precise values of the mean-square amplitudes. The drum-type nozzle was, then, used as an auxiliary nozzle for calibrating the scale factor of the needle-type nozzle, because the needle-type nozzle had no space

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* A preliminary report on this work was presented at the International Conference on Magnetism and Crystallography, Kyoto, 1961.

[1] Y. Morino, Y. Nakamura and T. Iijima, *J. Chem. Phys.*, **32**, 643 (1960).

[2] L. S. Bartell and L. O. Brockway, *Nature*, **171**, 978 (1953).

[3] I. L. Karle and J. Karle, *J. Chem. Phys.*, **18**, 963 (1950).

[4] K. Kuchitsu, This Bulletin, **32**, 748 (1959).

[5] Y. Morino and Y. Murata, ibid., **38**, 114 (1965).

[6] R. Wierl, *Ann. Physik*, **8**, 521 (1931).

[7] L. O. Brockway and F. T. Wall, *J. Am. Chem. Soc.*, **56**, 2373 (1934).

[8] L. Pauling and L. O. Brockway, ibid., **57**, 2684 (1935).

[9] M. Iwasaki, A Kotera, A. Tatematsu and K. Yamasaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **69**, 104 (1948).

on which to attach a reference gold-foil without disturbing the gas flow near the nozzle.

The beam current was about 0.02 μamp. for the short camera length and about 0.005 μamp. for the long camera length when the drum-type nozzle was used. In the case of the needle-type nozzle, it was necessary to increase the beam current by five times. The photographs were developed at 20°C for 5 min. with an FD-131 developer diluted twice. The photographs were scanned with a Rigaku-Denki MP-3 microphotometer. The optical densites of the plates were regulated to be less than 0.6. It has been confirmed by Morino and Iijima(10) that the intensity is directly proportional to the photographic density in the range of density less than 0.6.

The wavelength of the electron beam was calibrated with reference to the diffraction pattern of the gold-foil on the assumption that the camera length for the gas pattern was equal to that for the gold-foil pattern. After a gas pattern had been taken, the gas nozzle was replaced by the gold-foil and the scattering pattern of the reference was taken on the same photographic plate, beside the gas pattern, by sliding the plate holder. In order to make a precise calibration, it was thought important to make sure that the reference gold-foil was placed in exactly the position of the gas diffraction center, and that the photographic plate was set in exactly the same position when the photographic plate was moved for the reference pattern to be taken; the latter test was necessary because the plate may not be exactly perpendicular to the beam axis due to a mechanical imperfection in the construction of our plate-holder.

For the former test, the gas pattern was taken at a reversed orientation where the nozzle, together with the gold-foil, was rotated around the axis by 180°, keeping their relative positions fixed (see Fig. 1.). The difference in the camera lengths, if there is any, should have a reverse effect by the same amount on the diffraction pattern at the reversed orientation. In fact, about a 0.22% increase in the atomic distance was observed after this reversal of the nozzle, as is shown in Table I. For the latter test, the difference in the camera length was measured by taking gold-foil patterns at the center of the photographic plate, where, in our normal operation, the gas pattern was taken, and also at the place where the reference pattern was normally taken; the difference in the camera length thus found was corrected for each gas pattern.

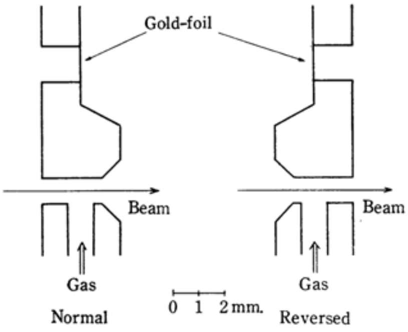

Fig. 1. Normal and reversed orientations of the drum-type nozzle.

A slight blackening by an extraneous scattering was observed by a blank experiment near the outer periphery of the pattern. The density of the blank photograph was subtracted from each photograph in order to correct for the extraneous scattering.

Analysis

A small fluctuation from the defined opening, $\theta = cr^3$, was observed in the r^3-sector used in this experiment. The variations in the parameters caused by the correction for this sector deficiency were -0.0013 Å and $+0.0009$ Å for the Si–Cl and the Cl–Cl distances respectively, and -0.0021 Å and $+0.0017$ Å for the mean amplitudes of Si–Cl and Cl–Cl respectively. These corrections were especially important for the mean amplitudes in comparison with their total errors, even though the defects in the sector were less than 1%.

In order to calculate the molecular intensities, a correction for the so-called non-nuclear scattering was made by Bartell's method.(11) For the atomic scattering factors of the silicon and chlorine atoms, appropriate averages of the factors given by Viervoll and Ögrim(12) and those by Tomiie and Stam(13) were used. The values of the inelastic scattering factors were taken from the table given by Bewilogua,(14) and the values of $\Delta\eta(\theta)$, from the table of Ibers and Hoerni.(15)

The reduced molecular intensity curves thus obtained were compared with the theoretical expression:

$$qM(q) = \frac{10}{\pi} \sum_i \sum_j{}' k_{ij} \frac{1}{r'_{aij}} \frac{Z_i Z_j}{\sum_k (Z^2_k + Z_k)} \times \mu_{ij} \cos \Delta\eta_{ij} \exp\left(-\frac{1}{2}(l'_{aij})^2 s^2\right) \times \sin(sr'_{aij} - s^3\kappa_{ij}) \quad (1)$$

by a procedure essentially the same as that used in a previous paper:(1) the parameters to be determined by the least-squares calculation were the atomic distances, r'_a(Si–Cl) and r'_a(Cl–Cl), the mean amplitudes, l'_a(Si–Cl) and l'_a(Cl–Cl), and the indices of resolution, k(Si–Cl) and k(Cl–Cl). As was described in

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10) Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).

11) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

12) H. Viervoll and O. Ögrim, *Acta Cryst.*, **2**, 277 (1949).

13) Y. Tomiie and C. H. Stam, ibid., **11**, 126 (1958).

14) L. Bewilogua, *Physik. Z.*, **32**, 740 (1931).

15) J. A. Ibers and J. A. Hoerni, *Acta Cryst.*, **7**, 405 (1954).

a previous paper,[16] the indices of resolution varied independently for each atomic pair. The r'_a and l'_a constants are not equal to the molecular constants, r_a and l_a respectively, since the effect of gas distribution at the diffraction center is involved in the former. The anharmonicity constants, κ(Si–Cl) and κ(Cl–Cl), were fixed at approximate values (perhaps a very crude one for κ(Cl–Cl)) as follows.

If a potential funtion of the Morse-type is assumed for the bonded Si–Cl pair,[17] the anharmonicity parameter, κ, and the so-called anharmonic term of the internuclear distance, $\langle \Delta z\rangle$, may be approximately represented by:[18]

$$\kappa=\frac{a}{6}l^4 \qquad (2)$$

and

$$\langle \Delta z\rangle=\frac{3}{2}al^2 \qquad (3)$$

where a is the asymmetry constant of the Morse function and may be obtained on the basis of the parameters given by Lippincott and Schroeder.[19] The parameter κ(Si–Cl) is thus found to be 1.21×10^{-6} Å^3.

The anharmonicity parameter κ for the non-bonded Cl–Cl pair may be obtained if the actual motion of the two chlorine atoms along the line connecting their equilibrium positions is approximated by a motion under a Morse potential. In such a case, the following relation is derived from relations 2 and 3:

$$\kappa=\frac{1}{9}l^2\langle \Delta z\rangle \qquad (4)$$

where l is the mean amplitude of the atom pair and can be obtained by measurements. On the other hand, the $\langle \Delta z\rangle$ value for the pair is given by:

$$\langle \Delta z\rangle(\text{Cl–Cl})=2\sqrt{\frac{2}{3}}\langle \Delta z\rangle(\text{Si–Cl}) \qquad (5)$$

since there is no totally symmetric deformation vibration for a tetrahedral molecule.[20] The parameter κ(Cl–Cl) thus obtained is 7.11 $\times10^{-6}$ Å^3.*

As will be mentioned in the next section, it is reasonable to assume that the weight matrix is given by a diagonal form when the observations are made in the interval of $\Delta q=1$. Thus, the statistical weight given in Fig. 1(c) of Ref. 16 was used in the present analysis.

As is shown in Table I; the least-squares fit was carried out on several observed molecular intensity curves for each of the three kinds of nozzles; for the drum-type nozzle in the normal and reversed positions and for the needle-type nozzle. Ten sets of parameters with their standard deviations were obtained by making the respective least-squares outputs converge.[21] Table I shows the average values for each nozzle with the estimated standard deviations σ_1 and σ_2; σ_1 denotes the standard deviation for the average value of the atomic distances obtained by the least-squares fit, and σ_2, the standard deviation obtained from the deviations of the several observed values from the average value.[16] The calculation was carried out by means of two digital computers, PC-1 and PC-2, in the University of Tokyo.

It has already been mentioned that the atomic distances obtained by the reversed orientation of the nozzle were larger than those obtained by the normal orientation.** Because there are four observations corresponding to the normal position and two to the reversed position, the most probable values of the observed atomic distances may be given according to an ordinary statistical theory, by means of the arithmetic means of each averaged value, with their standard deviations $(\sqrt{3}/4\sqrt{2})(6\sigma_-{}^2+\sigma_+{}^2)^{1/2}$, where σ_- and σ_+ denote their standard deviations. However, the values of σ_+ obtained in this experiment is not considered to be reliable, because it was obtained

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[16] Y. Morino, K. Kuchitsu and Y. Murata, ibid., to be published.

[17] K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2470 (1962).

[18] K. Kuchitsu and L. S. Bartell, ibid., **35**, 1945 (1961).

[19] E. R. Lippincott and R. Schroeder, ibid., **23**, 1131 (1955).

[20] Y. Morino, S. J. Cyvin, K. Kuchitsu and T. Iijima, ibid., **36**, 1109 (1962).

* In the analysis mentioned above, the anharmonicity constants were fixed as the estimated values. However, when they were taken as variable parameters in the least-squares analysis, the following values were obtained for the most probable values and their standard deviations (in 10^{-6} Å^3 units):

		Average	σ_1	σ_2
Needle-type nozzle:	κ(Si-Cl)	2.2	1.3	0.3
	κ(Cl-Cl)	11.3	4.1	3.3
Drum-type nozzle:	κ(Si-Cl)	−2.1	1.7	1.7
	κ(Cl-Cl)	−1.1	5.9	6.3

The negative values of κ obtained for the drum-type nozzle may be caused by the effect of finite sample distribution. When this nozzle is used, some of the scattered electrons are screened by the edge of the nozzle because of the finite spread of the gas molecules, and they do not reach the photographic plate at larger scattering angles. Therefore, the center of gravity of the distribution of gas molecules, by which electrons are scattered to a given point on the photographic plate, changes with the scattering angle; the change makes the effective κ values significantly different from the ideal values. By using the distribution function of the gas molecule obtained for the drum-type nozzle,[5] the shift, . κ, caused by the above shielding effect was approximately determined by a numerical calculation to be -1×10^{-5} Å^3 and -2×10^{-5} Å^3 for Si–Cl and Cl–Cl respecitively. The deviations in atomic distances obtained in this analysis were taken into account in estimating the systematic errors caused by uncertainties in the assumed κ values.

[21] Y. Morino, K. Kuchitsu, T. Iijima and Y. Murata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 803 (1962).

** This discrepancy may be explained by an asymmetric distribution of the gaseous sample, as will be described in a following paper.[5]

TABLE I. AVERAGE VALUES OF THE PARAMETERS
(r and l in Å units)

Nozzle-type	Parameter	Average	σ_1	σ_2
D-N	r'_a(Si-Cl)	2.0159	0.0004	0.0011
	r'_a(Cl-Cl)	3.2893	0.0008	0.0021
	l'_a(Si-Cl)	0.0495	0.0008	0.0013
	l'_a(Cl-Cl)	0.0943	0.0011	0.0010
	k(Si-Cl)	0.998	0.010	0.043
	k(Cl-Cl)	0.979	0.016	0.027
D-R	r'_a(Si-Cl)	2.0204	0.0005	0.0003
	r'_a(Cl-Cl)	3.2963	0.0011	0.0029
	l'_a(Si-Cl)	0.0482	0.0011	0.0010
	l'_a(Cl-Cl)	0.0944	0.0016	0.0022
	k(Si-Cl)	0.992	0.013	0.012
	k(Cl-Cl)	0.989	0.022	0.030
N	r'_a(Si-Cl)	2.0182	0.0002	—
	r'_a(Cl-Cl)	3.2935	0.0005	0.0007
	l'_a(Si-Cl)	0.0479	0.0005	0.0006
	l'_a(Cl-Cl)	0.0905	0.0007	0.0009
	k(Si-Cl)	1.055	0.007	0.013
	k(Cl-Cl)	1.063	0.011	0.003

D-N : The drum-type nozzle in the normal direction.
Four observed curves were used to obtain the average values.
D-R : The drum-type nozzle in the reversed direction.
Two observed curves were used.
N : The needle-type nozzle.
Four observed curves were used.
r'_a and l'_a: See text.

TABLE II. FINAL RESULTS OF THE LEAST-SQUARES ANALYSIS
(r and l in Å units)

Parameter	Most probable value	σ_1	σ_2
r_a(Si-Cl)	2.0182	0.0003	0.0010
r_a(Cl-Cl)	3.2928	0.0006	0.0018
l'_a(Si-Cl)	0.0479	0.0005	0.0006
l'_a(Cl-Cl)	0.0905	0.0007	0.0009
k(Si-Cl)	1.020	0.005	0.019
k(Cl-Cl)	1.015	0.009	0.017

from only two observations. On the other hand, σ_- is somewhat more reliable since it was obtained from four observations. Therefore, it seems more reasonable in this case to assume $\sigma_+^2 \sim 2\sigma_-^2$ since both experimental procedures are essentially the same, and the standard deviation for the most probable values is taken to be $(\sqrt{3}/2)\sigma_-$.

After the series of corrections mentioned above, the final results for the observed atomic distances and their standard deviations shown in Table II have been obtained. As has been mentioned above, the values obtained by using the needle-type nozzle are suitable for determining the mean amplitudes, while the average of all the observed values were used for the indices of resolution, because the latter are not influenced by the sample delocalization around the nozzle.5)

The scale factor for the needle-type nozzle was adjusted to give the atomic distances consistent with those obtained with the drum-type nozzle. Fortunately, the apparent increment or decrement of the atomic distances in the drum-type nozzle, Δr, was in almost the same ratio for Si–Cl and Cl–Cl; the Cl–Cl distance obtained by the needle-type nozzle was longer by 0.0007 Å than that obtained by the other nozzle, but this discrepancy is smaller than the uncertainty of the Cl–Cl distance.

The photographs taken with the long camera distance ($q=8-36$) were analyzed separately because their index of resolution was much larger than that derived from the photographs taken with the short camera distance. These results will be described in the Appendix.

The Estimation of the Uncertainties of the Molecular Constants

Atomic Distances.—Let us first consider the uncertainties of the observed atomic distances. The standard deviation of each least-squares fit, σ_1, was found to be about 0.0003 Å and 0.0006 Å for the Si–Cl and the Cl–Cl pairs respectively (Table II), whereas the σ values of the fluctuations among the mean values of the atomic distances obtained by the respective least-squares fit, σ_2, were 0.0010 Å and 0.0018 Å respectively. If the experimental conditions were kept strictly the same for all photographs, the latter should have been equal to the former. The difference between σ_1 and σ_2 may be attributed mainly to the difference between the accelerating voltages when the photographs of the sample and those of the gold-foil reference were taken, to the failure in locating the center of the halos when the plates were photometered, to the difference in the gas spread among different exposures, to the difference in the conditions of developing the photographic plates, and to random errors in the determination of the camera lengths for the sample and for the reference. In our present experiment, none of these sources of difference can be corrected for by the measurement of the deviations. All of them can occur randomly and, hence, they must be included in the random errors, σ_2, described above.

The systematic errors consist of all the uncertainties which do not occur at random and which can, in principle, be estimated. Uncertainties of various corrections made of the observed values should also be included in these errors. For instance, the true lattice constant of the gold-foil used in this experiment may have been different from the assumed value, 4.070Å; this difference should give an uncertainty to the scale factor. It was reported by Morino and Iijima that the error of this origin may be 0.05%.[10] A gradual drift of the accelerating potential during the measurement may be another source of the uncertainty: it was found to be within 0.1%, corresponding to 0.05% in λ.

The inclination of the plates has been corrected for by the procedure described in the Experimental Section. The σ in the measurement of the correction gives an uncertainty of 0.03% to the final result concerning the atomic distance.

Another error may originate from the difference in the camera lengths between the sample and the reference, as has been pointed out in the preceding section.

The failure in estimating the correct anharmonicity constants may possibly lead to some uncertainty in the final results, because the anharmonicity constant has an intensive correlation with the interatomic distance. In order to estimate these uncertainties, the parameters κ were either taken as variable parameters or were fixed as constants of various estimated values. The uncertainties thus estimated are 0.0010Å and 0.0025Å for the Si–Cl and Cl–Cl distances respectively.

If the accuracy of the measurement be expressed by the limit of errors, two-and-a-half times the standard deviation plus the systematic errors, it corresponds to taking a 99% confidence interval. Because the individual errors are considered to be all mutually independent, the square roots of their squared sums, 0.0034Å and 0.0062Å (as is shown in Table III), are taken as the limit of errors of the Si–Cl and Cl–Cl pairs respectively.

TABLE III. ERRORS OF THE ATOMIC DISTANCES (in Å units)

Source of error	r(Si–Cl)	r(Cl–Cl)
Random error (2.5σ)	0.0025	0.0045
Drift of voltage	0.0010	0.0017
Lattice constant	0.0010	0.0017
Inclination of plate	0.0015	0.0025
Effect of κ	0.0010	0.0025
Total error	0.0034	0.0062

Mean-Square Amplitudes. — The errors in the mean amplitudes are estimated in the following way. The standard deviations obtained by the least-squares method for each of the four molecular intensities, σ_1, were 0.0005Å and 0.0007Å for Si–Cl and Cl–Cl respectively, while those of the fluctuations from the mean values, σ_2, were found to be 0.0006Å and 0.0009Å respectively. As the standard deviations, σ_1 and σ_2, are almost equal in magnitude, either of them can be taken as a measure of the random error of the mean amplitude.

It should be mentioned in this connection that an appropriate interval of the observations, Δq, should be taken if a diagonal weight matrix is used in the least-squares analysis. It appears plausible to take the interval Δq as unity in our experiment because of the following consideration.

(1) If the interval Δq decreases, the standard deviation, σ_1, decreases while σ_2 is expected to remain almost invariant. Since the observations made at an unreasonably small interval can not be regarded as mutually independent, such a σ_1 value is of little statistical significance; for a proper treatment, a weight matrix with off-diagonal elements must be used in such a case.[22] In other words, only for the range of Δq for which σ_1 is not smaller than σ_2 may the weight matrix be approximated by a diagonal form. (2) The standard deviations, σ_1, obtained by the least-squares analysis of $f(r)$ by using diagonal matrices are of almost the same magnitude as those shown in Table I(b) of Ref. 16, where the number of the observations was the same as in the case of the analysis of $qM(q)$, where the interval was taken to be $\Delta q=1$. It, therefore, seems likely that the observations are mutually independent if the interval is taken to be as small as unity.

The above arguments are based on somewhat indirect reasoning. It may, nevertheless, be a plausible approximation for the weight matrix in a diagonal form corresponding to $\Delta q=1$ to be taken in our experiment. The random errors obtained by taking two-and-a-half times the present standard deviations, 0.0015Å and 0.0023Å for Si–Cl and Cl–Cl respectively, will, therefore, be statistically adequate.

Of the uncertainties which belong to the systematic errors, those from the drift of the accelerating voltage and from the lattice constant are both about 0.05%, while that from the fluctuation of the camera length is 0.08%, as has already been described. The contribution from the multiple sacttering may not be important, because the indices of resolution were found to be roughly unity. Even if the multiple scattering were present, it would have a significant effect only on the effective damping factor in the range $q \lesssim 10$.[23] Since the

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[22] Y. Murata and Y. Morino, *Acta. Cryst.*, to be published.

[23] J. A. Hoerni, *Phys. Rev.*, **102**, 1530 (1956).

mean amplitudes were determined in the range $q=18$—100, the effect of the multiple scattering on the mean amplitude may be ignored. The effect of the finite sample size has been corrected for by estimating the distribution of the gas molecules.⁵⁾ The uncertainty in the theoretical approximation for this procedure was estimated to be about 10%, as will be described in a following paper.⁵⁾ The uncertainty caused by the experimental error in the intensity measurement cannot be estimated in a reliable way. However, even if it were assumed to be 50%, which is certainly an overestimate, it would have no appreciable influence on the final results. The failure of the Born approximation, and the imperfection in the assumption of a linear relationship between the photographic darkness and the electron intensity, is so slight that the errors in their corrections are negligible. The error caused by the correction for the extraneous scattering is probably included in σ_2. The final values of the limit of errors are 0.0016 Å for Si–Cl and 0.0024 Å for Cl–Cl, as is shown in Table IV.

TABLE IV. ERRORS OF THE MEAN AMPLITUDES*
(in Å units)

Source of error	l(Si–Cl)	l(Cl–Cl)
Random error (2.5σ)	0.0015	0.0023
Sample size	0.0005	0.0007
Total error	0.0016	0.0024

* Errors of negligible magnitude are excluded from the table.

The uncertainties in the indices of resolution are considered to arise from the same origins as those in the mean amplitudes, except for the finite sample size, which makes no appreciable contribution to the uncertainties in the former. The standard deviations obtained from the ten plates, σ_2, were 0.019 and 0.017, and the σ_1 values for each least-squares fit were 0.005 and 0.009 for k(Si–Cl) and k(Cl–Cl) respectively. The limit of errors in the indices of resolution are, therefore, taken to be 0.05 and 0.04.

Results

Atomic Distances and Mean-Square Amplitudes. — The atomic distance obtained by the least-squares fit of the observed curve to the molecular intensity function, $qM(q)$, is neither the equilibrium distance, r_e, nor the mean value of the internuclear probability distribution function, r_g. When r'_a is corrected to r_a to compensate for the difference in the camera lengths, the observed distance, r_a, is approximately equal to the mean value with respect to the radial distribution function; it is related to r_g as follows;¹⁾

$$r_g=r_a+l^2/r_a \qquad (6)$$

The observed mean amplitude, l_a, for which the effect of the sample size is corrected, is approximately equal to l_g, the mean amplitude referred to r_g as will be shown below. It is assumed that the internuclear probability distribution function is represented by:

$$P(r)=[1+\beta_1(r-r_e)+\beta_2(r-r_e)^2 \\ +\beta_3(r-r_e)^3]P_h(r) \qquad (7)$$

where $P_h(r)$ is a probability distribution function corrected to the harmonic oscillator. The observed mean-square amplitude, $l_a{}^2$, is represented by:

$$l_{\mathrm{a}}{}^2=l_\alpha{}^2+l_\alpha{}^4\{2(\beta_2+\gamma\beta_1)-(\beta_1+\gamma)^2 \\ -6l_\alpha{}^2(\beta_3+r\beta_2)(\beta_1+\gamma) \\ -9l_\alpha{}^4(\beta_3+\gamma\beta_2)^2\}+l_\alpha{}^4\{(1/r_e{}^2) \\ +6l_\alpha{}^2(\beta_3+\gamma\beta_2)/r_e\} \qquad (8)$$

and $l_g{}^2$ is represented by:

$$l_g{}^2=l_\alpha{}^2+l_\alpha{}^4\{2(\beta_2+\gamma\beta_1)-(\beta_1+\gamma)^2 \\ -6l_\alpha{}^2(\beta_3+\gamma\beta_2)(\beta_1+\gamma) \\ -9l_\alpha{}^4(\beta_3+\gamma\beta_2)^2\} \qquad (9)$$

where $\gamma=(\langle\varDelta x^2\rangle+\langle\varDelta y^2\rangle)/2\langle\varDelta z^2\rangle r_e$ and l_α is the mean amplitude referred to the harmonic oscillator. The last term in Eq. 8 is of the order of $(l/r)^2$. Therefore, l_a is approximately equal to l_g.¹⁷⁾ It may easily be shown that almost the same result can be obtained if the Morse potential is assumed, in which case the term of $(r-r_e)^6$ is significant.

It should also be noted that the difference in the observed mean amplitudes, l_g, from the amplitudes, l_α, which refer to the harmonic oscillators, is negligibly small when it is compared with their experimental errors; accordingly, l_g may be used directly for the computation of the force constants.

We have recently proposed an internuclear distance parameter, r_α:²⁴⁾

$$r_\alpha=r_g-(\langle\varDelta x^2\rangle+\langle\varDelta y^2\rangle)/2r_e-\delta r \qquad (10)$$

where δr is the correction for the centrifugal distortion; it is negligibly small for this molecule. For a tetrahedral molecule, XY_4, the perpendicular amplitudes, $\langle\varDelta x^2\rangle$ and $\langle\varDelta y^2\rangle$, are given by,

for the X-Y pair:

$$\langle\varDelta x_1{}^2\rangle=\langle\varDelta y_1{}^2\rangle=\frac{\mu_{\mathrm{Y}}}{4}\langle Q_2{}^2\rangle+\left\{\frac{2}{\sqrt{3}}\mu_{\mathrm{X}}L^{-1}{}_{33} \\ -\left(\frac{4}{\sqrt{3}}\mu_{\mathrm{X}}+\frac{\sqrt{3}}{2}\mu_{\mathrm{Y}}\right)L^{-1}{}_{34}\right\}^2\langle Q_3{}^2\rangle$$

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24) Y. Morino, K. Kuchitsu and T. Oka, *J. Chem. Phys*˙, **36**, 1108 (1962).

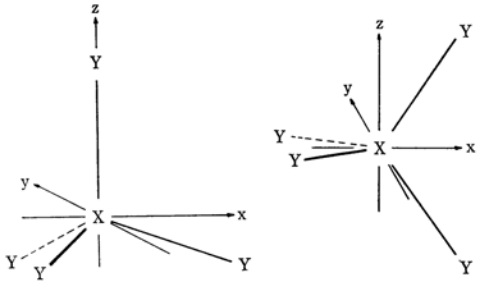
$$+\left\{\frac{2}{\sqrt{3}}\mu_X L^{-1}{}_{43} - \left(\frac{4}{\sqrt{3}}\mu_X + \frac{\sqrt{3}}{2}\mu_Y\right) L^{-1}{}_{44}\right\}^2 \langle Q_4{}^2\rangle \qquad (11)$$

and for the Y–Y pair:

$$\langle \Delta x_2{}^2\rangle = \frac{2}{3}\mu_Y{}^2 (L^{-1}{}_{33} + L^{-1}{}_{34})^2 \langle Q_3{}^2\rangle + \frac{2}{3}\mu_Y{}^2 (L^{-1}{}_{43} + L^{-1}{}_{44})^2 \langle Q_4{}^2\rangle \qquad (12)$$

$$\langle \Delta y_2{}^2\rangle = \mu_Y \langle Q_2{}^2\rangle, \qquad (14)$$

where μ_i denotes the reciprocal mass and $L^{-1}{}_{ij}$ the i, j element of the $\boldsymbol{L}^{-1}$ matrix. The x and y axes are taken to be as shown in Fig. 2. The values of r_α obtained in this way are shown in Table V. The uncertainties listed in Table V are the 99% confidence limit of errors, including the systematic errors, as has been discussed above.



(a) (b)

Fig. 2. Cartesian coordinates. The z_i axes (i=1 or 2) are taken in the direction of the atomic pair at their equilibrium positions, the x_i axes are taken on the plane Y-X-Y and perpendicular to z_i, and y_i are perpendicular to x_i and z_i.

TABLE V. FINAL RESULTS OF THE MOLECULAR CONSTANTS (r, l and δ in Å units)

r_g	2.0193±0.0034	3.2953±0.0062
r_α	2.016 ±0.004	3.293 ±0.007
l_g	0.0470±0.0016	0.0892±0.0024
k	1.020 ±0.048	1.015 ±0.043
δ_g	0.0022±0.0032	

In this type of molecule, there is no totally-symmetric deformation mode; hence, the shrinkage of the Y–Y distance can be evaluated only by means of quadratic potential constants, just as in the case of linear molecules.[20] It is shown to be 0.0036 Å for Cl–Cl. The observed shrinkage, δ_g, on the other hand, is 0.0022±0.0032 Å. It should be noted here that the shrinkage is not influenced by the uncertainty in the scale factor; it is given by the difference between two large quantities, both of which vary in the same ratio, when the scale factor changes.

The distance r_α does not show any shrinkage effect, because by definition it does not include the perpendicular vibration. The experimental result satisfies this requirement, although the uncertainty in the measurement does not give any clear evidence for the presence of the shrinkage effect in r_g or for its absence in r_α.

Force Constants.—It has already been pointed out that, in the tetrahedral molecules, all of the force constants in the general quadratic form cannot uniquely be determined from the vibrational frequencies alone. Accordingly, mean-square amplitudes cannot be calculated simply by using the frequencies. Since there are four frequencies in contrast to five constants, one degree of freedom is left undetermined. The two mean-square amplitudes which are compatible with the four vibrational frequencies, if taken as a set of coordinates, are given by a point on a closed curve given by the following set of relations:

$$l^2(\text{Si–Cl}) = \frac{1}{4}G_{11}\langle Q_1{}^2\rangle + \frac{3}{4}G_{33}\langle Q_3{}^2\rangle - \frac{3}{4}L_{34}{}^2(\langle Q_3{}^2\rangle - \langle Q_4{}^2\rangle) \qquad (14)$$

$$l^2(\text{Cl–Cl}) = \frac{2}{3}G_{11}\langle Q_1{}^2\rangle + \frac{1}{9}G_{22}\langle Q_2{}^2\rangle + \frac{1}{6}(4G_{33} + 4G_{34} + G_{44})\langle Q_3{}^2\rangle - \frac{1}{6}(2L_{34} + L_{44})^2(\langle Q_3{}^2\rangle - \langle Q_4{}^2\rangle) \qquad (15)$$

$$(G_{33} - L_{34}{}^2)(G_{44} - L_{44}{}^2) = (G_{34} - L_{34}L_{44})^2 \qquad (16)$$

where the G_{ij}'s are the elements of the $\boldsymbol{G}$-matrix, and the $\langle Q_i{}^2\rangle$'s are the squared mean

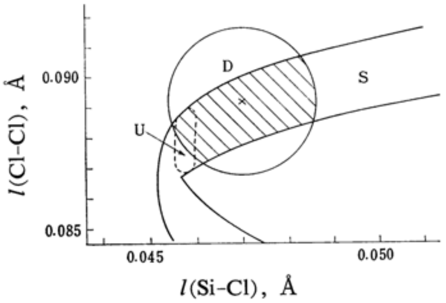


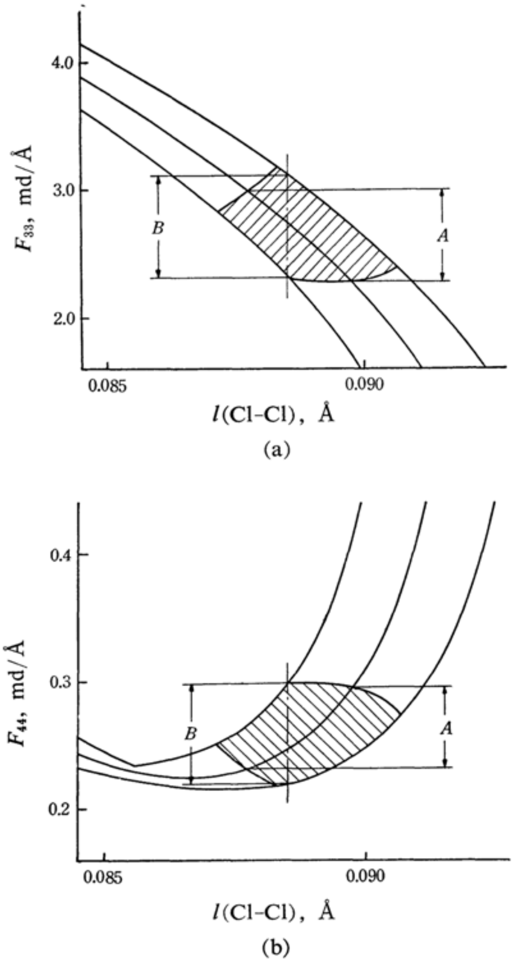
Fig. 3. Correlation curve of two mean amplitudes. The shaded area indicates the values which are compatible with both the diffraction and spectroscopic data.
D: Observed values by electron diffraction.
S: Calculated values from spectroscopic data.
U: Calculated values corresponding to the Urey-Bradley force field.

values of the displacements of the normal coordinates. The curve is shown in Fig. 3.

For the tetrahedral molecules, all fundamentals are Raman active, while only two frequencies of the symmetry F_2 are active in the infrared; for silicon tetrachloride one of them has a frequency too small to be observed by an ordinary infrared spectrometer. For the calculation of the force constants, we must use the normal frequencies of the molecule in the gaseous state. Since no observations of the Raman spectrum of this molecule in the vapor state had been reported, the measurement of the gaseous Raman spectrum was undertaken. The details of the experiment have beed reported elsewhere.25) The vibrational frequencies obtained in this measurement are used in the calculations except for ν_3, for which the fundamental frequency obtained by the infrared spectrum in the gaseous state25) was used.

It is not practicable to make the correction of fundamental frequencies to the normal frequencies, because we have no exact knowledge on the anharmonicity factors of the potential function as a basis for calculating the correction. A tentative assumption regarding the potential function shows that the correction may be of the same order of magnitude as the uncertainties of the frequencies. The uncertainties in the frequencies cause the spread of the position and the size of the curve shown in Fig. 3. On the other hand, the mean amplitudes obtained by the electron diffraction experiment are expressed by an area enclosed by a circle which represents the limit of errors around the observed values. Thus, any point included in the overlapping area, the shaded portion in Fig. 3, is compatible with both the observed mean amplitudes and the observed vibrational frequencies within the limit of errors. As is clearly indicated in Figs. 4a and 4b, the uncertainties of the force constants originate from the mean amplitudes by the same order of magnitude as from the vibrational frequencies.

Table VI gives the force constants of the potential function in the general quadratic form in terms of the symmetry coordinates and of the internal coordinates. The force constants of the Urey-Bradley force field, with the additional assumption proposed by Shimanouchi that $F' = -(1/10)F$,26) were computed by using the observed vibrational frequencies; the results are shown in Table VII. The possible range of the mean amplitudes calculated on the basis of these force constants is shown by the area enclosed in a broken ellipse in Fig. 3. Since a half of this area is located inside the limit of errors of the observed mean amplitudes, it may be inferred that the



(a)

(b)

Fig. 4. Correlation curves of the force constants and l(Cl-Cl). The ranges A indicate the limits of the force constants for which the errors of frequencies are disregarded, while the ranges B show those for which the error of l(Cl-Cl) is ignored. Though only the diagonal elements of F-matrix are shown in this figure, the curve of F_{34} is similar to F_{44} in shape. (a) F_{33}, and (b) F_{44}.

TABLE VI. FORCE CONSTANTS OBTAINED BY USING THE MEAN AMPLITUDES (in md./Å units)

Symmetry coordinate system		Internal coordinate system	
F_{11}	3.77 ± 0.02	k_r	2.97 ± 0.34
F_{22}	0.154 ± 0.004	k_{rr}	0.26 ± 0.12
F_{33}	2.71 ± 0.45	$k_\alpha - k_{\alpha\alpha'}$	0.26 ± 0.04
F_{34}	0.07 ± 0.13	$k_{\alpha\alpha} - k_{\alpha\alpha'}$	0.05 ± 0.02
F_{44}	0.26 ± 0.04	$k_{r\alpha} - k_{r\alpha'}$	0.05 ± 0.10

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25) Y. Morino, Y. Murata, T. Ito and J. Nakamura, *J. Phys. Soc. Japan*, **17**, Supplement B-II, 37 (1962).

26) T. Shimanouchi, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **74**, 266 (1953).

TABLE VII. FORCE CONSTANTS IN THE SYMMETRY-COORDINATE SYSTEM (in md./Å) AND MEAN AMPLITUDES (in Å) OBTAINED IN TERMS OF THE UREY-BRADLEY FORCE FIELD WITH THE ADDITIONAL ASSUMPTION THAT $F'=-(1/10)F$.

F_{11}	$3.77\ \pm 0.02$
F_{22}	$0.154\ \pm 0.004$
F_{33}	$3.02\ \pm 0.03$
F_{34}	$0.161\ \pm 0.006$
F_{44}	$0.23\ \pm 0.01$
l(Si-Cl)	0.0458 ± 0.0002
l(Cl-Cl)	0.0877 ± 0.0011

assumption of the Urey-Bradley type with $F'=-(1/10)F$ is approximately permissible in the case of silicon tetrachloride.

Summary

The atomic distances and the mean-square amplitudes of silicon tetrachloride have been determined by the sector-microphotometer method. The possible sources of experimental errors have been thoroughly examined. The quadratic force constants of the potential function have been determined by the use of the mean-square amplitudes thus obtained, by combining them with the vibrational frequencies obtained from the Raman spectrum in the gaseous state. It has been shown that the errors of the force constants originate from those of the mean-square amplitudes by the same order of magnitude as from those of the frequencies.

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Appendix

The Analysis of Small-Angle Intensities.—As has been described in this text, the atomic distances and the mean-square amplitudes of silicon tetrachloride have been determined precisely by the analysis of the electron diffraction halos taken by the short camera length, 11.8 cm. ($q=18$—97). On the other hand, the errors of the atomic distances and mean amplitudes are inversely proportional to s and s^2 respectively, and the error caused by the uncertainty in the μ-factor increases in the range of small q-values. It would be of interest to see what results can be obtained by the analysis of the photographs of silicon tetrachloride taken by the long camera distance at smaller scattering angles ($q=8$—36).

Since there are four humps in this range, as is shown in Fig. 5, reasonable background curves were obtained by Karle's method.[27] An analysis was made by the same procedure as that used in the analysis for the short camera distance except for the few points given below. In view of the limited number of observations (less than 30 for $\Delta q=1$), it was thought advantageous to make the number of variables for the analysis as small as possible. Therefore, by assuming that the Si–Cl and Cl–Cl distances have equal indices of resolution, the index was taken as one of the parameters instead of having both indices varied. A conventional weight function was used, since the use of other weight functions caused little change in this case. Four photographs were used for the analysis.

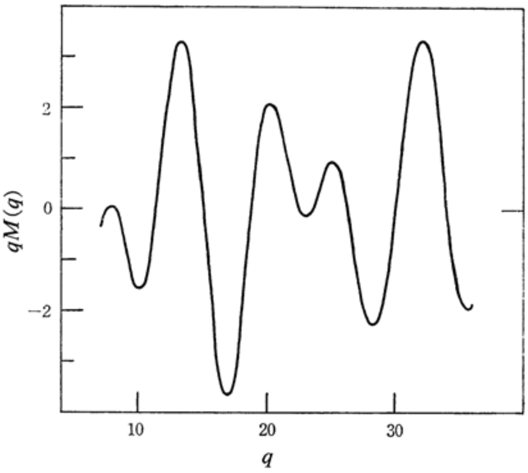

Fig. 5. Molecular intensity curve of $SiCl_4$ obtained by the long camera distance.

In the small-angle scattering ($s \lesssim 10$), the theoretical atomic form factor is strongly dependent on the original wave function used in the calculation. Therefore, the analysis of the intensity taken by the long camera distance, as separated from that taken by the short camera distance, was useful as a test of the effect of the atomic form factors on our analysis by using the various values listed below. The atomic form factors for silicon and chlorine have been obtained by Viervoll and Ögrim[12] on the basis of Hartree's wave function; by Ibers and Hoerni,[15] who reported $|f|$ based on the Thomas-Fermi model, and by Tomiie and Stam,[13] whose calculation was based on Slater's wave function. Three kinds of atomic form factor, were, threfore, used in the present analysis; (the first obtained by Viervoll and Ögrim, the second given by Tomiie and Stam for the silicon and chlorine atoms, and the third obtained by the

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[27] I. L. Karle and J. Karle, *J. Chem. Phys.*, **18**, 565 (1950).

arithmetic mean values of $f(\mathrm{Si}^{4+})$ and $f(\mathrm{Si})$, and $f(\mathrm{Cl}^{-})$ and $f(\mathrm{Cl})$, for silicon and chlorine respectively, and given by Tomiie and Stam) since the Si–Cl bond in the silicon tetrachloride molecule is likely to have about a 50% ionic character at the chlorine atom, as estimated from the pure quadrupole resonance frequency[28] of ^{35}Cl. Two kinds of the inelastic scattering factors which were obtained by Bewilogua[14] and Freeman[29] were used for calculating the μ-factors. Unfortunately, however, the inelastic scattering factor for the chlorine atom was not calculated by Freeman; hence, an approximate value was estimated for our use.

Four sets of μ-factors were obtained for Si–Cl and Cl–Cl, as is shown in Fig. 6; by using these μ-factors and each of the four observed intensity curves, the corresponding average values and the standard deviations of the parameters were obtained by the method of the least squares,[21] as is shown in Table VIII. It was found that the most probable values of the parameters in the first three sets were almost equal to one another, but that they are significantly different from the values obtained with the short camera distance, especially for the mean amplitudes. The last set agreed with the values obtained by the short camera distance. The μ-factor is little affected by the change in the atomic form factor, since the change of the numerator is seemingly cancelled by that of the denominator. The inelastic scattering factor, on the other hand, is included only in the denominator of the μ-factor, since, on the basis of the basic assumption, the inelastic scattering makes no contribution to the molecular term. The change in the inelastic scattering factor, therefore, has an appreciable effect on the molecular intensity in the small-angle region.

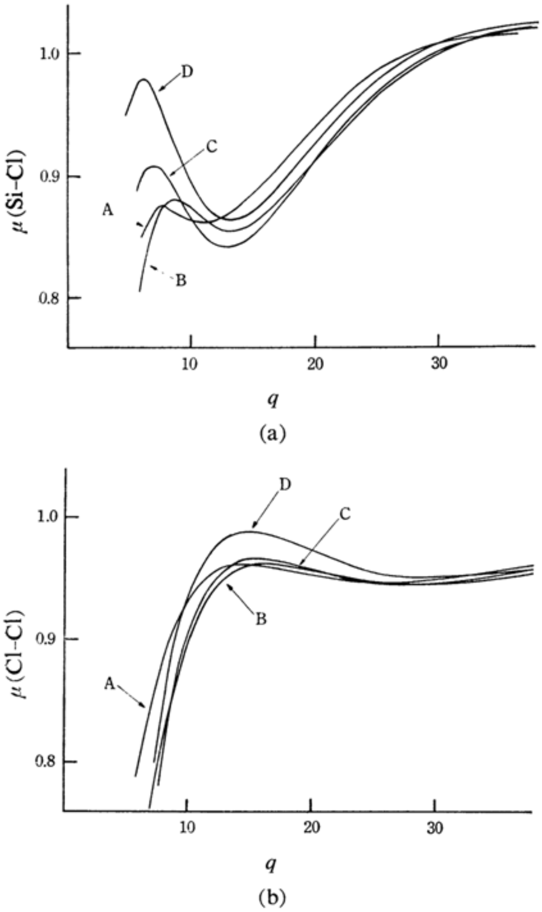

Fig. 6. The μ-factors obtained by the combinations of the atomic form factors and the inelastic scattering factors shown in Table III. (a) Si–Cl, and (b) Cl–Cl.

TABLE VIII. DEPENDENCE OF PARAMETERS ON THE CHOICE OF VARIABLE μ-FACTORS (r and l in Å units)[a]

	r(Si–Cl)	σ_1	σ_2	r(Cl–Cl)	σ_1	σ_2
A	2.0173	0.0010	0.0028	3.2949	0.0012	0.0007
B	2.0175	0.0011	0.0028	3.2949	0.0012	0.0007
C	2.0172	0.0012	0.0029	3.2949	0.0013	0.0009
D	2.0172	0.0012	0.0028	3.2951	0.0014	0.0007

	l(Si–Cl)	σ_1	σ_2	l(Cl–Cl)	σ_1	σ_2
A	0.0520	0.0032	0.0018	0.0949	0.0021	0.0017
B	0.0520	0.0032	0.0018	0.0949	0.0021	0.0017
C	0.0520	0.0036	0.0017	0.0943	0.0024	0.0016
D	0.0467	0.0041	0.0019	0.0918	0.0025	0.0017

	k	σ_1	σ_2
A	1.098	0.011	0.018
B	1.098	0.011	0.018
C	1.096	0.012	0.019
D	1.065	0.012	0.018

a) The atomic form factors and the inelastic scattering factors used for calculating the μ-factors were taken in the following combinations: A(a, d); B(b, d); C(c, d); and D(c, e).

a: The atomic form factor given by Viervoll and Ögrim.

b: The atomic form factor given by Tomiie and Stam.

c: The atomic form factor given by Tomiie and Stam in which the 50% ionic character was taken into account.

d: The inelastic scattering factor obtained by Bewilogua.

e: The inelastic scattering factor obtained by Freeman.

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[28] H. C. Dehmelt, *J. Chem. Phys.*, **21**, 380 (1953); R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).

[29] A. J. Freeman, *Acta Cryst.*, **12**, 929 (1959).