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The Molecular Structure of Tin Tetrachloride as Determined by Gas-electron Diffraction

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The molecular structure of tin tetrachloride was determined by the sector-microphotometer method of gas-electron diffraction. By taking into account the phase-shift for the Sn-Cl pair, the following results were obtained: the tetrahedral structure with $r_g(\text{Sn–Cl})=2.280_8\pm0.003_7$ Å, $l(\text{Sn–Cl})=0.049_9\pm0.003_3$ Å, and $l(\text{Cl}\cdots\text{Cl})=0.108_6\pm0.005_0$ Å. These values, especially that of the mean amplitude, l(Sn–Cl), are different from those previously reported by other workers. This is because the effect of the phase shift was neglected in the previous investigations.

Schomaker and Glauber first pointed out the fault of the first Born approximation for the interpretation of the electron-diffraction patterns of molecules containing both heavy and light atoms;[1] subsequently, Hoerni and Ibers calculated the complex atomic-scattering factors for electrons by the partial-waves method in order to explain the observed intensities of UF_6 at 40 and 11 keV.[2,3] Since then, the angle-dependent phase factor in the scattering of electrons has been the subject of several theoretical and experimental investigations.[3] Especially, the studies carried out by Seip[4] and also Kimura *et al.*[3a] have provided extensive experimental data for solving this phase problem. The molecules treated in these experimental studies contain both very heavy and light atoms, and their diffraction patterns show distinct cut-off points in intensities at moderate scattering angles. However, the influence of the phase factor on structure analysis is not limited to such molecules. If this effect is not taken into consideration, inaccurate structure parameters might be yielded, even for molecules whose diffraction patterns have no cut-off point. The tin tetrachloride molecule is considered to be one such molecule.

There have been a few structure determinations of tin tetrachloride by electron diffraction;[5-7] the values reported by Livingston and

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[1] V. Schomaker and R. Glauber, *Nature*, **170**, 290 (1952).

[2] J. A. Hoerni and J. A. Ibers, *Phys. Rev.*, **91**, 1182 (1953).

[3] See, *e.g.*, (a) M. Kimura, V. Schomaker, D. W. Smith and B. Weinstock, *J. Chem. Phys.*, **48**, 4001 (1968); also (b) H. M. Seip, "Selected Topics in Structural Chemistry," Universitetsforlaget, Oslo (1967), pp. 26—68.

[4] H. M. Seip and R. Seip, *Acta Chem. Scand.*, **20**, 2698 (1966) and the preceding papers.

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

[6] L. O. Brockway and F. T. Wall, *J. Amer. Chem. Soc.*, **56**, 2373 (1934); L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

[7] R. L. Livingston and C. N. R. Rao, *J. Chem. Phys.*, **30**, 339 (1959).

Rao,7) $r(\text{Sn–Cl})=2.31\pm0.01_5$ Å, $r(\text{Cl}\cdots\text{Cl})=3.77\pm0.03_0$ Å, $l(\text{Sn–Cl})=0.08$ Å and $l(\text{Cl}\cdots\text{Cl})=0.10$ Å, have often been quoted as the interatomic distances and mean amplitudes of the molecule. These values, however, have not been accurate enough to withstand recent critcal discussion of the molecular structure, for they were determined by the visual-sector method, without taking into account the phase shift for the Sn–Cl atom pair. Since, in structure analysis, the mean amplitude of the Sn–Cl stretching vibration is correlated very closely with the effect of the phase shift, the experimental mean amplitudes reported by Livingston and Rao may be larger than the true values.

It is well-known that the mean amplitudes can be calculated from the molecular geometry and the internal force field which satisfies the normal frequencies, while, conversely, unknown force constants of the internal force fields can be determined by using the observed mean amplitudes as additional information. Morino *et al.* determined, in this way, the force constants for the tetrachloride molecules, CCl_4,8) $SiCl_4$9) and $GeCl_4$.8) The force constants of an internal force field can also be determined by the use of the relative intensities of the Raman lines in addition to the fundamental frequencies.10) Chantry and Woodward applied this method to tetrahalide molecules, MX_4 (M=C, Si, Ge, and Sn; X=Br and Cl).11) However, this method gives four sets of force constants accounting for the vibration of species, F_2, and specifies no unique set of force constants. Therefore, they selected one set from among the four by consulting the experimental mean amplitudes of vibration. Because of the inevitable ambiguities of the results for $SnCl_4$, Chantry and Woodward's choice of the force constants for $SnCl_4$ is not decisive.

Recently, Bürger and Ruoff12) and also Kebabçioglu *et al.*13) independently determined the force constants for the tetrachloride molecules of the group-IV_b elements by the use of the Coriolis coupling constants, which were estimated from a separation between the P and R branches of the F_2 band. The results for $SiCl_4$ and $GeCl_4$ were in reasonable agreement with each other, and also with those determined from the mean amplitudes and the relative intensities of the Raman lines. However, it seems that the values previously reported for $SnCl_4$ are inconsistent with one another. In these circumstances it is very desirable to determine the precise interatomic distances and mean amplitudes of tin tetrachloride by the sector-microphotometer method of electron diffraction. Especially, the values of the mean amplitudes are expected to be revised significantly by taking into account the phase shift for the Sn–Cl pair.

Experimental

The sample of tin tetrachloride was loaded in a sample holder by manipulating it in a dry box filled with nitrogen. The vapor pressure of the sample was about 20 Torr at 20°C.

Photographs were taken at 18°C with an r^3-sector at camera lengths of 24.430 cm and 10.930 cm; the exposure times were about 40 sec, with a beam current of about 0.15 μA. The fluctuations of the accelerating voltage (about 47.5 kV) were maintained within 0.1 per cent throughout a sequence of exposures. Carbon disulfide was employed as a reference material in determining the wavelength.14)

The intensities of the diffraction patterns of $SnCl_4$ decreased rapidly with an increase in scattering angles, so that intensity measurements were practically impossible in a range beyond about $q=100$. This is certainly due to the effect of the phase shift in addition to the damping effect caused by molecular vibrations. This suggests that information can be obtained by using photographs taken at a long camera distance. Therefore, three plates from the long camera distance were selected for analysis; hereafter, they will be referred to as plates 1, 2, and 3 for the sake of convenience. The wavelength for each plate was determined by the use of two plates of carbon disulfide taken in the same sequence of exposures.

With a double-beam microphotometer, Model NLM-III, of the Nalumi Co., Ltd., the optical densities of the diffraction patterns were measured by the following two methods:

(1) This microphotometer was equipped with a cam converting transmission into optical density and a pen-recorder. Optical densities were read at intervals of $\Delta q=1$ on the left and right sides of the diffraction center. In this method the optical densities were determined by averaging the corresponding observed values on the two sides (the pen-recording method).

(2) By connecting an integrating digital voltmeter to the microphotometer, the values of the output voltages from the photomultiplier of the microphotometer were perforated in digits directly onto an input tape for an electronic computer. From these values, taken every one-third of a milimeter on a plate, the optical density at every integral number of q was obtained by interpolation by a second-degree polynomial which passes through the three observed points closest to each q. In this case, the diffraction center was determines so as to minimize the value of $\sum_i [D_{li}-D_{ri}]^2$, where

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

9) Y. Morino and Y. Murata, This Bulletin, **38**, 104 (1965).

10) M. Wolkenstein, *C. R. Acad. Sci. U. R. S. S.*, **32**, 185 (1941); D. A. Long, *Proc. Roy. Soc.*, **A217**, 203 (1953).

11) G. W. Chantry and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 1110 (1960).

12) H. Bürger and A. Ruoff, *Spectrochim. Acta*, **A24**, 1863 (1968).

13) a) C. J. Peacock, A. Müller, R. Kebabçioglu, *J. Mol. Spectry.*, **27**, 351 (1968). b) R. Kebabçioglu, A. Müller, C. J. Peacock and L. Lange, *Z. Naturforsch.*, **23A**, 703 (1968).

14) C. Kato, S. Konaka, T. Iijima and M. Kimura, This Bulletin, **42**, 2148 (1969).

the D_{li} denotes the optical density at $q=i$ on the left side of the diffraction center, and the D_{ri}, the corresponding value on the right side. Thus, by this method two sets of the observed optical densities, D_l and D_r, were obtained for each plate (the digital method). The whole process was performed by the use of an electronic computer.

The optical densities measured by the two methods differ from each other by only one per cent at most. Since the observed optical densities for all plates were below 0.7, it was assumed that the optical densities are proportional to the scattering intensities, I_T^{obs}.15) The observed intensities ranging from $q=10$ to 70 were adopted for analysis.

Analysis and Results

The observed molecular scattering intensity, $qM(q)^{obs}$, was obtained from the I_T^{obs} and the smooth background, I_B^{obs}, according to the equation:

$$qM(q)^{obs} = q(I_T^{obs}-I_B^{obs})/I_B^{obs} . \tag{1}$$

The corresponding theoretical expression is:

$$qM(q)^{theor} = k\sum_{i,j}{}' A_{ij}\mu_{ij} \cos(\Delta\eta_{ij})\exp[-a_{ij}q^2] \times \sin\left[\frac{\pi}{10}q\left\{r_{aij}-\left(\frac{\pi}{10}q\right)^2\kappa\right\}\right], \tag{2}$$

$$a_{ij} = \frac{1}{2}(\pi/10)^2 l_{ij}{}^2 , \tag{3}$$

$$A_{ij} = \frac{Z_iZ_j}{\sum_k Z_k(Z_k+1)}\cdot\frac{20}{\pi r_{aij}} \tag{4}$$

$$\mu_{ij} = \frac{\sum_k Z_k(Z_k+1)}{Z_iZ_j}\cdot\frac{|F_i|\,|F_j|}{\sum_k\{|F_k|^2+S_k\}} , \tag{5}$$

$$|F_k| = h^2s^2|f_k|/8\pi^2me^2 , \quad s = \left(\frac{\pi}{10}\right)q . \tag{6}$$

Here, all the notations follow usual usage. Starting from a trial experimental background described below, the final I_B^{obs} and $qM(q)^{obs}$ were determined according to Karle's non-negativity criterion16) by repeating a few times the calculation of the radial distribution curve and its inverse Fourier transformation for the $r=0.00$—1.60 Å range. The trial experimental background was determined in the following way: By replacing the $q(Mq)^{obs}$ in Eq. (1) by the theoretical molecular intensity, $q(Mq)^{theor}$, the observed background can be expressed as:

$$I_B^{obs} = I_T^{obs}\frac{q}{q+kqM(q)^{theor}} .$$

From this equation a preliminary background can be calculated by using $qM(q)^{theor}$ for a reasonable molecular model and an appropriate k value.

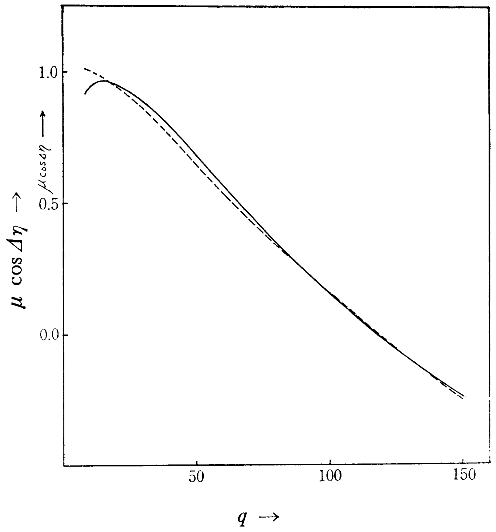

Fig. 1. $\mu_{SnCl}\cos(\Delta\eta_{SnCl})$ (the solid line) and $\chi_{SnCl}(q)$ (the broken line).

By fitting the background to a polynomial in terms of q, $\sum_{n=0}^{5} a_nq^n$, a smooth trial background, I_B^{obs}, was obtained.

Since the $\mu_{SnCl}\cos(\Delta\eta_{SnCl})$ values are far from unity, as may be seen in Fig. 1, the corrections for the non-nuclear scattering in the calculation of the radial distribution cannot be made satisfactorily by the conventional form, $1-\mu_{SnCl}\cos(\Delta\eta_{SnCl})$. Generally, the $\mu_{ij}\cos(\Delta\eta_{ij})$ values for an i and j atom pair can be approximated by the following function, $\chi_{ij}(q)$:17)

$$\chi_{ij}(q) = \alpha_{ij} + \beta_{ij}\cos\left(\frac{\pi}{10}\Delta r_{ij}\cdot q\right) + \gamma_{ij}\exp[-\delta_{ij}q^2] , \tag{7}$$

where the α_{ij}, β_{ij}, γ_{ij} and δ_{ij} are positive constant coefficients. The correction term, then, becomes:

$$\Delta qM(q) = \sum_{i,j}{}' A_{ij}\sin\left(\frac{\pi}{10}qr_{ij}\right)\exp[-a_{ij}q^2] \times \{\chi_{ij}(q)-\mu_{ij}\cos(\Delta\eta_{ij})\} , \tag{8}$$

and the corresponding radial distribution curve, $f(r)$, is given by:

$$\begin{aligned} f(r) = {} & \sum_{i,j}{}' \frac{A_{ij}}{4}\sqrt{\frac{\pi}{a_{ij}+b}}\exp\left[-\frac{\pi^2}{400}\frac{(r-r_{ij})^2}{a_{ij}+b}\right]\alpha_{ij} \\ & + \sum_{i,j}{}' \frac{A_{ij}}{4}\sqrt{\frac{\pi}{a_{ij}+b}} \times\left\{\exp\left[-\frac{\pi^2}{400}\frac{(r-r_{ij}+\Delta r_{ij})^2}{a_{ij}+b}\right] + \exp\left[-\frac{\pi^2}{400}\frac{(r-r_{ij}-\Delta r_{ij})^2}{a_{ij}+b}\right]\right\}\frac{\beta_{ij}}{2} \\ & + \sum_{i,j}{}' \frac{A_{ij}}{4}\sqrt{\frac{\pi}{a_{ij}+b+\delta_{ij}}} \times\exp\left[-\frac{\pi^2}{400}\frac{(r-r_{ij})^2}{a_{ij}+b+\delta_{ij}}\right]\gamma_{ij} . \end{aligned} \tag{9}$$

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

16) J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).

17) S. Konaka, T. Ito and Y. Morino, This Bulletin, **39**, 1146 (1966).

Here, the b is an artificial damping factor, and the Δr_{ij} corresponds to an apparent splitting of the i and j interatomic distance due to the phase difference. The Δr_{ij} value was estimated from the $(\pi/10)\Delta r_{ij}\cdot q_c=\pi/2$ relation, with a theoretical first cut-off point, q_c. The anharmonicity parameter, κ, in Eq. (2) can be ignored in the calculation of the radial distribution. It readily be seen from Eq. (9) that the non-negativity criterion holds for this radial distribution curve.

In the case of $SnCl_4$ we employed the functions of $\chi_{ij}(q)$ with the following coefficients:

$\alpha_{Sn-Cl}=0$ $\alpha_{Cl-Cl}=1.20$

$\beta_{Sn-Cl}=0.625$ $\beta_{Cl-Cl}=0$

$\gamma_{Sn-Cl}=0.4$ $\gamma_{Cl-Cl}=0.3$

$\delta_{Sn-Cl}=0.00039$ $\delta_{Cl-Cl}=0.00014$

$\frac{\pi}{10}\Delta r_{Sn-Cl}=0.01333$

The broken line in Fig. 1 indicates the $\chi_{SnCl}(q)$. The final molecular intensity, $qM(q)^{obs}$, and the corresponding radial distribution, $f(r)$, are shown in Figs. 2 and 3 respectively.

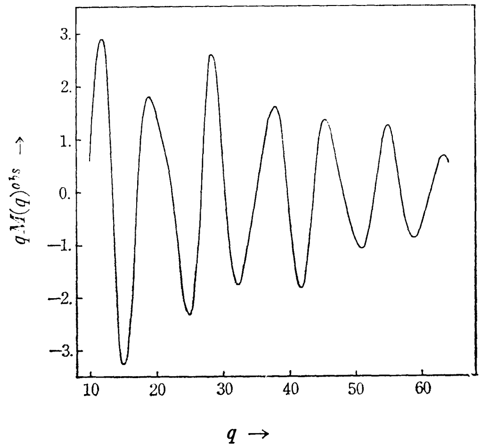

Fig. 2. The molecular intensity curve, $qM(q)^{obs}$.

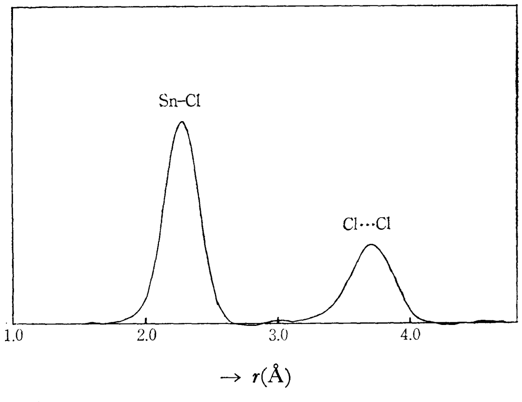

Fig. 3. The radial distribution curve, $f(r)$.

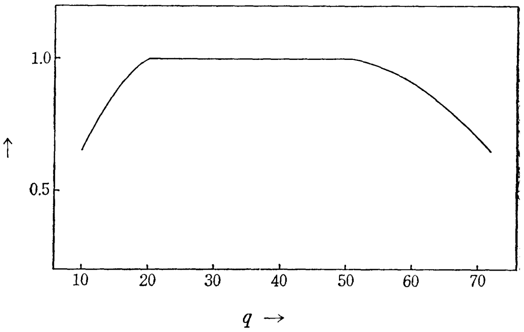

Fig. 4. The weight function employed for the least-squares fitting.

The molecular parameters were determined by the least-squares method applied to the $qM(q)^{obs}$, with the weight function shown in Fig. 4. A regular tetrahedral symmetry was assumed.

The atomic scattering factors, $|F|$, and the phase shift, $\Delta\eta$, used in the $qM(q)^{theor}$ are those calculated by Kimura *et al*,[18] the inelastic scattering factors, S, for Cl and Sn are those calculated by Tavard *et al*[19] and by Bewilogua[20] respectively.

The anharmonicity parameters, κ, fixed in the least-squares treatment were estimated to be 16×10^{-7} Å^3 for Sn–Cl and 100×10^{-7} Å^3 for Cl··· Cl by following the method applied to $SiCl_4$ by Morino and Murata.[9] Errors based on the uncertainties in κ were included in the total errors, which will be described in the next section.

The measurements of the optical densities were carried out by the digital and the pen-recording methods. Table 1 shows the values of r_a observed by the digital method. The results obtained from the D_l and the D_r agree with each other within their standard deviations. The final values of r_a for each plate were determined by multiplying the averages of the two values by the scale factor. The final results obtained by the two methods for plate 1 are compared in Table 2. The two results agree with each other, but the standard deviations are about a half as much in the digital method as in the pen-recording method. This is because the smoother intensity curve was obtained by the former method than by the latter. Therefore, the results by the digital method were adopted as the final values for plates 1 and 2. Plate 3 was measured only by the pen-recording method.

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[18] M. Kimura, S. Konaka and M. Ogasawara, *J. Chem. Phys.*, **46**, 2559 (1967); M. Ogasawara, S. Konaka and M. Kimura, *ibid.*, **50**, 1488 (1969).

[19] C. Tavard, D. Nicolas and M. Roualt, *J. Chim. Phys.*, to be published.

[20] L. Bewilogua., *Physik. Z.*, **32**, 740 (1931).

TABLE 1. RESULTS OBTAINED FROM THE OPTICAL DENSITIES MEASURED BY THE DIGITAL METHOD[a)]

		from D_l[b)]	from D_r[b)]	Average
Plate 1	k	0.995 ± 0.011	0.993 ± 0.011	0.994 ± 0.011
	r_a(Sn-Cl)	2.2795 ± 0.0008	2.2777 ± 0.0008	2.2786 ± 0.0008
	l(Sn-Cl)	0.0513 ± 0.0017	0.0519 ± 0.0017	0.0516 ± 0.0017
	r_a(Cl···Cl)	3.7119 ± 0.0030	3.7125 ± 0.0029	3.7122 ± 0.0030
	l(Cl···Cl)	0.1117 ± 0.0027	0.1086 ± 0.0027	0.1102 ± 0.0027
Plate 2	k	0.965 ± 0.012	0.971 ± 0.014	0.968 ± 0.014
	r_a(Sn-Cl)	2.2796 ± 0.0009	2.2797 ± 0.0010	2.2797 ± 0.0010
	l(Sn-Cl)	0.0494 ± 0.0019	0.0500 ± 0.0022	0.0497 ± 0.0022
	r_a(Cl···Cl)	3.7165 ± 0.0033	3.7117 ± 0.0038	3.7141 ± 0.0038
	l(Cl···Cl)	0.1104 ± 0.0029	0.1104 ± 0.0034	0.1104 ± 0.0034

a) Distances and mean amplitudes in Å unit. The errors are the standard deviations obtained from the least-squares treatments.

b) See text.

TABLE 2. COMPARISON OF THE RESULTS FOR PLATE 1 OBTAINED SEPARATELY FROM THE OPTICAL DENSITIES BY THE PEN-RECORDING AND THE DIGITAL METHOD*

	Pen-recording	Digital
k	0.952 ± 0.020	0.994 ± 0.011
r_a(Sn-Cl)	2.2795 ± 0.0015	2.2796 ± 0.0008
l(Sn-Cl)	0.0505 ± 0.0031	0.0516 ± 0.0017
r_a(Cl···Cl)	3.7132 ± 0.0052	3.7139 ± 0.0030
l(Cl···Cl)	0.1043 ± 0.0047	0.1102 ± 0.0027

* Distances and mean-amplitudes in Å unit. The errors are the standard deviations obtained from the least-squares treatment. The r_a values in the third column are those in Table 1 multiplied by the scale factor.

The results of the least-squares refinements for the three plates are summarized in Table 3. The σ_1 and σ_2 values, which represent the standard deviations for the average values, were estimated according to these formulas: $\sigma_1^2 = \langle\sigma\rangle^2/3$ and $\sigma_2^2 = \sum V_i^2/6$. Here, $\langle\sigma\rangle$ is the average of the standard deviations for the three plates, while V_i is the residual of the value for the ith plate subtracted from the average value.[9)] All the σ_1 values are larger than the corresponding values. The final random errors were, then, given by $2.5\sigma_1$, corresponding to the 99 per cent confidence intervals. Two plates of carbon disulfide were measured in order to determine the scale factor for each plate and were analyzed in the same way as were the sample plates. Therefore, various systematic errors involved in the experiment and analysis may be regarded as included in the error of the scale factor.[14)] The practical procedure is to determine the scale factor for each plate by comparing the results of analysis at a presumed wavelength with the true structure of carbon disulfide. Analysis was made by assuming the two independent interatomic distances, r(C–S) and r(S···S). Then, the scale factor obtained from one plate of carbon disulfide may be given by a weighted mean of the scale factors determined from the two individual distances, while its standard deviation is given by $\sigma = [1/\sigma_{cs}^2 + 1/\sigma_{ss}^2]^{-1/2}$.[*1] The final scale factor and its standard deviation were determined using the results for the two plates of carbon disulfide. The limit of error of the scale factor was taken as 2.5 times the standard deviation thus obtained, corresponding to 0.12 per cent in interatomic distance.

TABLE 3. SUMMARY OF RESULTS (in Å)

	Plate 1	Plate 2	Plate 3	Average	σ_1	σ_2	2.5σ
k	0.994 ± 0.011	0.968 ± 0.014	0.982 ± 0.018	0.981	0.008	0.008	0.020
r_g(Sn-Cl)	2.2808 ± 0.0008	2.2818 ± 0.0010	2.2797 ± 0.0013	2.2808	0.0006	0.0006	0.0015
l(Sn-Cl)	0.0516 ± 0.0017	0.0497 ± 0.0022	0.0484 ± 0.0029	0.0499	0.0013	0.0009	0.0033
r_g(Cl···Cl)	3.7172 ± 0.0030	3.7191 ± 0.0038	3.7142 ± 0.0046	3.7168	0.0022	0.0014	0.0055
l(Cl···Cl)	0.1102 ± 0.0027	0.1104 ± 0.0034	0.1053 ± 0.0042	0.1086	0.0020	0.0017	0.0050
δ_g	0.0073 ± 0.0033	0.0071 ± 0.0041	0.0085 ± 0.0051	0.0076	0.0024	0.0004	0.0060
method	digital	digital	pen-recording				

[*1] The off-diagonal element of the error matrix, $B^{-1}{}_{cs,ss}$, is one to two hundredth as small as the diagonal elements, $B^{-1}{}_{cs,cs}$ and $B^{-1}{}_{ss,ss}$. Therefore, even if the least-squares treatment is performed under the condition that the distances, r(C–S) and r(S···S), are not independent of each other, the results do not change.

The errors associated with the ambiguity of κ were estimated from the results of the least-square fittings carried out by assuming various κ values. They were ±0.0020 Å for r_g(Sn–Cl) and ±0.0040 Å for r_g(Cl···Cl).

The total errors for the interatomic distances were estimated by regarding these errors independent of one another. Systematic errors for the mean amplitudes were ignored, for their magnitudes may be considered to be much smaller than the random errors. The final parameters are given in Table 4.

Table 4. Molecular parameters of tin tetrachloride at 18°C

r_g(Sn–Cl)	$2.280_8 \pm 0.003_7$ Å
r_α(Sn–Cl)	$2.274_9 \pm 0.003_7$ Å
l(Sn–Cl)	$0.049_9 \pm 0.003_3$ Å
r_g(Cl···Cl)	$3.716_8 \pm 0.008_2$ Å
r_α(Cl···Cl)	$3.712_7 \pm 0.008_2$ Å
l(Cl···Cl)	$0.108_6 \pm 0.005_0$ Å
δ_g	$0.007_6 \pm 0.006_0$

Discussion of the Results

The r_g(Sn–Cl) value, 2.281±0.004 Å, determined by the present study is about 0.03 Å shorter than those reported by the previous studies[5–7] and 0.11 Å less than the sum of the covalent radii, 2.39 Å. From the results of the electron-diffraction studies of $SiCl_4$[9] and $GeCl_4$[8] the corresponding values of bond shortening are estimated to be 0.14 Å for the Si–Cl bond in $SiCl_4$ and 0.10 Å for the Ge–Cl bond in $GeCl_4$. It may be noted here that the amount of bond shortening for the Sn–Cl bond is smaller than that for the Si–Cl bond, but virtually equal to that for the Ge–Cl bond. These bond shortenings were explained by the partial ionic and the partial double-bond character of these bonds reported to Pauling.[21] From the fact that the same electronegativity value, 1.8 in Pauling's scale, is given to Si, Ge, and Sn atoms, it is reasonable to expect the same partial ionic character; consequently, the bond shortening is the same for all of the Si–Cl, Ge–Cl, and Sn–Cl bonds. Thus, the amounts of bond shortening, 0.14 Å for the Si–Cl, 0.10 Å for the Ge–Cl, and 0.11 Å for the Sn–Cl, become a measure of the extent of their double-bond character. By using the results previously reported by Pauling and Brockway[6], *i.e.*, 2.30 Å for the Sn–Cl bond length and the bond shortening of 0.07 Å, Gordy has mentioned that the quantities of double-bond character decrease in the order of the Si–Cl, Ge–Cl, and Sn–Cl bonds and that a tendency to form multiple bonds decreases with an increase in the size of the atoms.[22] It was found in the present study, however, that the amount of bond shortening for the Sn–Cl bond was similar to that for the Ge–Cl bond. It seems that, for these two bonds, the effect of the increase in atomic size from Ge to Sn is compensated for by that of the decrease in promotion energy from *p* to *d* orbitals, and that, as a result, the Ge–Cl and Sn–Cl bonds have almost the same double-bond character.

The r_g values can be converted to r_α by using the relation: $r_\alpha = r_g - [\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle]/2r_g - \delta r$, where $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ are the perpendicular mean amplitudes, and δr, the centrifugal stretching. Using the force constants determined from the fundamental frequencies and the Coriolis coupling constants,[13] the values of the perpendicular mean amplitudes were estimated to be 0.0054 Å for the Sn–Cl and 0.0033 Å for the Cl···Cl.[*2] The stretchings, δr, were estimated by Iwasaki and Hedberg's method[23] to be 0.0005 Å for the Sn–Cl and 0.0008 Å for the Cl···Cl. The r_α values thus obtained are also listed in Table 4. The ratio of r_α(Cl···Cl) to r_α(Sn–Cl) is 1.6320±0.0026, a value which is in perfect agreement with the corresponding ratio, 1.6330, for a regular tetrahedral structure.

The mean amplitude for the Sn–Cl atom pair is $0.049_9 \pm 0.003_3$ Å, which is much smaller than the value of 0.08 Å reported by Livingston and Rao.[7] Such a large discrepancy between the two results cannot have been produced simply by employing different methods of measurement, *i.e.*, the microphotometer method and the visual method. The ignorance of the phase shift in the previous study certainly led to an inaccurate mean amplitude for the Sn–Cl pair. The mean amplitudes for $SnCl_4$ were calculated by Long and Seibold[24] and also by Müller and Cyvin.[25] The former authors used the Urey-Bradley force field with the assumption that $H'=0$ and gave the values of 0.046 Å for the Sn–Cl and 0.119 Å for the Cl···Cl at 298°K, while the latter used symmetry force constants which had been calculated by the method of the "Verfahren der nächsten Lösung"[26] and gave the values of 0.046 and 0.120 Å for the respective

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[21] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, New York (1960), pp. 228, 311.

[22] W. Gordy, W. W. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley & Sons, Inc., London (1953), p. 318.

[*2] If another set of the force constants is used, there is no significant change in the values of the perpendicular mean-amplitudes.

[23] M. Iwasaki and K. Hedberg, *J. Chem. Phys.*, **36**, 2961 (1962).

[24] D. A. Long and E. A. Seibold, *Trans. Faraday Soc.*, **56**, 1105 (1960).

[25] A. Müller and S. J. Cyvin, *J. Mol. Spectry.*, **26**, 315 (1968).

[26] A. Fadini, *Z. Naturforsch.*, **21a**, 426 (1966).

bonds at the same temperature. These calculated values are fairly close to the experimental values. The slight differences must be connected with the force constants used in the mean-amplitude calculations, and originally with the assumptions on which the force constants were given. The mean amplitudes determined in the present study will be helpful in assigning a reasonable set of force constants for tin tetrachloride. The determination and discussion of the force constants for tin tetrachloride will be described in a separate paper.

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