*Accurate Determination of Interatomic Distances of Carbon Disulfide**

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In some recent studies[1,2] of molecular structure by gas electron diffraction, attentions have been paid to the physical meanings of various distance-parameters for comparing the results obtained by different techniques. In almost all cases, however, it has been impossible to show the consistency of the results of electron diffraction with those of spectroscopy because of the limited knowledge on the anharmonicity of molecular vibration.

The interatomic distances in a molecule are not constant but vary periodically because of the molecular vibrations. The distance averaged over the vibration is denoted by r_g in the sense that r_g is the center of gravity of the distribution function. In the studies of electron diffraction by gas molecules, we obtain r_g from the experimental data by a simple analytical procedure. In the spectroscopy, however, it is r_0 that is usually obtained from the rotational constant of the ground vibrational state. The r_g can be calculated if the equilibrium distance r_e and the anharmonic potential constants, especially the cubic constants, are known. Carbon disulfide is one of the simple molecules of which detailed spectroscopic data are available. The purpose of the present work is to examine if the results of the electron diffraction experiment are consistent with those of the spectroscopy by taking carbon disulfide as an example.

Among a number of spectroscopic studies for carbon disulfide, a high resolution Raman spectrum by Stoicheff[3], and an analysis of infrared rotation-vibration spectra by Guenther, Wiggins, and Rank[4], combined with another infrared study by Allen, Plyler and Blaine[5], provide us with information necessary for this work.

Calculation of r_g from Spectroscopic Data

An instantaneous distance of the C–S atom pair is expressed by

$$r=r_e+\varDelta z+\frac{\varDelta\rho^2}{2r_e} \tag{1}$$

in terms of internal coordinates, $\varDelta z$ and $\varDelta\rho$, where $\varDelta z$ denotes the relative displacement of the atoms C and S along the molecular axis and $\varDelta\rho$ is the relative displacement perpendicular to the axis. $\varDelta\rho^2$ is sometimes written as $\varDelta x^2+\varDelta y^2$. By taking an average of Eq. 1 with respect to the distribution function, the average C–S distance r_q(C–S) is expressed by

$$r_g=r_e+\langle\varDelta z\rangle+\frac{\langle\varDelta\rho^2\rangle}{2r_e} \tag{2}$$

The internal coordinates $\varDelta z$ and $\varDelta\rho$ are related to the normal coordinates by the following relations,

$$\varDelta z_1=b_1q_1+b_3q_3 \tag{3a}$$

$$\varDelta z_2=b_1q_1-b_3q_3 \tag{3b}$$

and

$$\varDelta\rho^2=b_{22}(q_{2a}^2+q_{2b}^2) \tag{3c}$$

where $\varDelta z_1$ and $\varDelta z_2$ denote the displacements of the two C–S atompairs, respectively, and q's are the dimensionless normal coordinates which are related to the normal coordinate Q's as $q_i=2\pi(c\omega_i/h)^{1/2}Q_i$. The coefficients b's are given by the standard treatment of normal vibrations, as

$$b_1=\left(\frac{h\mu_s}{8\pi^2c\omega_1}\right)^{1/2} \tag{4a}$$

$$b_3=\left[\frac{h}{8\pi^2c\omega_3}(\mu_s+2\mu_c)\right]^{1/2} \tag{4b}$$

$$b_{22}=\frac{h}{8\pi^2c\omega_2}(\mu_s+2\mu_c) \tag{4c}$$

μ_s and μ_c are the inverse masses of S-atom and C-atom, respectively.

The $<\varDelta z>$ is thus calculated as,

$$\langle\varDelta z\rangle=b_1\langle q_1\rangle \tag{5}$$

in terms of the average of the totally symmetric normal coordinate q_1, because the averages of all the linear terms of normal coordinates vanish except for the term of q_1. The general expression of $\langle q_1\rangle$ has been derived by Morino, Toyama and Oka[6], and it is reduced to the following equation for the case of a linear symmetric triatomic molecule,

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* A part of this work was reported at the International Conference on Magnetism and Crystallography, Kyoto, September, 1961.

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[2] L. S. Bartell and R. C. Hirst, ibid., **31**, 449 (1959).

[3] B. P. Stoicheff, *Can. J. Phys.*, **36**, 218 (1958).

[4] A. H. Guenther, T. A. Wiggins and D. H. Rank, *J. Chem. Phys.*, **28**, 682 (1958).

[5] H. C. Allen, E. K. Plyler and L. R. Blaine, *J. Am. Chem. Soc.*, **78**, 4843 (1956).

[6] Y. Morino, M. Toyama and T. Oka, to be published.

TABLE I. MOLECULAR CONSTANTS OF CS_2

ω_1^e	671.36 cm^{-1}	α_1	0.000156 cm^{-1}	k_{111}	−14.90 cm^{-1}	B_0	0.10910 cm^{-1}
ω_2^e	398.62 cm^{-1}	α_2	−0.000256 cm^{-1}	k_{122}	50.10 cm^{-1}	B_e	0.10928 cm^{-1}
ω_3^e	1551.92 cm^{-1}	α_3	0.000711 cm^{-1}	k_{133}	−129.56 cm^{-1}	r_e	1.5532 Å

$$\langle q_1\rangle = -\frac{1}{2\,\omega_1}\left[3\,k_{111}\coth\frac{hc\omega_1}{2\,kT} + 2\,k_{122}\coth\frac{hc\omega_2}{2\,kT} + k_{133}\coth\frac{hc\omega_3}{2\,kT}\right] + \left(\frac{8\,\pi^2 c\omega_1}{h\,\mu_s}\right)^{1/2}\frac{kT}{f_{11}r_e} \qquad (6)$$

when the potential energy expression for a CS_2 type molecule is given by,

$$V = \frac{hc}{2}\left[\omega_1 q_1^2 + \omega_2(q_{2a}^2 + q_{2b}^2) + \omega_3 q_3^2\right] + hc\left[k_{111}\,q_1^3 + k_{122}\,q_1(q_{2a}^2 + q_{2b}^2) + k_{133}\,q_1 q_3^2\right] \qquad (7)$$

The quartic and higher-order terms are neglected in this work, because the average interatomic distances are strongly affected by the asymmetric deformation of the distribution function which is mainly dependent on the cubic terms of the potential function. The first term of Eq. 6 is due to the anharmonicity of vibrations and the second term to the centrifugal stretching for which the mean rotational energy is approximated by kT. The f_{11} is the force constant of the totally symmetric stretching vibration. The $\langle \Delta\rho^2\rangle$ is simply calculated by inserting the relation $\langle q_i^2\rangle = (1/2)\coth(hc\omega_i/2\,kT)$, into Eq. 3c.

The cubic potential constants k_{ijk}'s are calculated from α_i's, the variation of the rotational constants which have been obtained through the relations⁷⁾,

$$\alpha_1 = -\frac{6\,B_e^2}{\omega_1} - 6\sqrt{2}\left(\frac{B_e}{\omega_1}\right)^{3/2} k_{111} \qquad (8a)$$

$$\alpha_2 = -\frac{B_e^2}{\omega_2}\cdot\frac{3\,\omega_2^2 + \omega_3^2}{\omega_2^2 - \omega_3^2} - 2\sqrt{2}\left(\frac{B_e}{\omega_1}\right)^{3/2} k_{122} \qquad (8b)$$

and $$\alpha_3 = -\frac{2\,B_e^2}{\omega_3}\cdot\frac{3\,\omega_3^2 + \omega_2^2}{\omega_3^2 - \omega_2^2} - 2\sqrt{2}\left(\frac{B_e}{\omega_1}\right)^{3/2} k_{133} \qquad (8c)$$

The values of α_i's used and those of k_{ijk}'s obtained from them are listed in Table I.

As the result of numerical computation, $\langle \Delta z\rangle$ was found to be 0.0013 Å, which included the contribution of the centrifugal stretching 0.0003 Å, and $\langle \Delta\rho^2\rangle/2\,r_e = 0.0035$ Å was obtained for $T = 288$°K. Accordingly, r_g(C–S) is calculated to be

$$r_g(\text{C–S}) = r_e + \langle \Delta z\rangle + \frac{\langle \Delta\rho^2\rangle}{2\,r_e} = 1.5532 + 0.0013 + 0.0035 = 1.5580\,\text{Å}$$

Similarly for the S–S distance,

$$r_g(\text{S–S}) = r_e + \langle \Delta z_1 + \Delta z_2\rangle = r_e + 2\langle \Delta z\rangle = 3.1064 + 0.0026 = 3.1090\,\text{Å}$$

where it is noted that $\Delta\rho$ is zero for the S–S distance.

The apparent non-linearity or the shrinkage⁸⁾ $\delta_g = 2\,r_g(\text{C–S}) - r_g(\text{S–S})$ is equal to $\langle \Delta\rho^2\rangle/r_e$, and it was found to be 0.0070 Å by the calculation.

According to Stoicheff³⁾, $\alpha_1 = 0.00018$ cm^{-1} may be preferable when the effect of Fermi resonance is considered. This alternative value of α_1 leads to $k_{111} = -16.27$ cm^{-1} and $\langle \Delta z\rangle = 0.0011$ Å. The equilibrium distance r_e is also affected by this change: it becomes 1.5530 Å. However, the average distance r_g is little altered: it was found to be 1.5579 Å. Therefore, the uncertainty in the value of α_1 due to Fermi resonance gives no serious error in the present study.

Measurement of r_g by Electron Diffraction

Experimental.—The diffraction photographs were taken by the apparatus⁹,¹⁰⁾ equipped with an r^3-sector, with the camera length of 12 cm. and the accelerating voltage of about 45 kv which was calibrated by the transmission pattern of a gold-foil. The beam current was about 0.025 μamp., and the exposure time was about 3 min. Fuji Process Plates were used to record the diffraction patterns and developed by the FD-131 developer at 20°C.

Three photographic plates were mounted in the camera at one time, fixed on a disk which was held nearly perpendicular to the main beam. Each plate was set at the exposure position one by one, by rotating the disk from outside. Photographic plates in the unit are, therefore, not exactly but only nearly perpendicular to the beam, so that the value of $L\lambda$ obtained by measuring the diameter of the gold-foil pattern recorded along the edge of the plate may differ from that of the diffraction pattern recorded on the center of the plate. The correction factor for $L\lambda$ was obtained by taking the photographs of gold-foil patterns both on the edge and on the center of the plate. The measurement was repeated

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7) H. H. Nielsen, *Revs. Modern Phys.*, **23**, 90 (1951).

8) Y. Morino, J. Nakamura and P. W. Moore, *J. Chem. Phys.*, **36**, 1050 (1962).

9) T. Ino, *J. Phys. Soc. Japan*, **8**, 92 (1953).

10) Y. Morino et al., "Jikken Kagaku Koza", Vol. 3, Maruzen Co. Ltd., Tokyo (1957), p. 253.

four times, that is, for twelve (4×3) plates and two gold-foil patterns on each, the corrections of $L\lambda$ were found to be,

A	$-0.3\pm0.03\%$
B	$0.0\pm0.05\%$
C	$0.0\pm0.03\%$

for the three positions, A, B and C, of the plate on the disk, with the standard deviations among the four measurements.

In order to get the exact value of the camera length for the photograph of the gas electron diffraction, the reference gold-foil should be put at the same place as the center of the gas distribution at the nozzle. It was confirmed by an examination with a microscope that there was no considerable deficiency in the geometrical design and in the screwing mechanism of the nozzle. There is, however, an anxiety pointed out by Murata[11], that the center of the gas distribution might deviate slightly backwards, because the nozzle aperture has an asymmetric form along the beam axis, i. e., it is widened at the front side by a cone-shape cut to avoid the shielding of the scattered beam by the edge. The effect was examined by taking diffraction photographs with the nozzle turned around by 180°. The result showed no significant deviation as compared with the results of the ordinary nozzle orientation. This is in contrast to the case of $SiCl_4$[11] for which a slight deviation was really observed. The difference might be caused by the different rates of flow of gas samples.

The photographs were traced with a Rigaku-Denki MP-3 microphotometer. The full scale of the transmittancy axis on the recording chart is 24 cm. As it is not wide enough to record minute feature of diffraction patterns, an expanding device was attached to the unit to facilitate expanded recordings along the transmittancy axis, in the scale five times as large as the ordinary one.

During the tracing, the plate was rotated around the center of the pattern to average out irregularities. The recorded photometer curve became narrower as the plate was rotated more rapidly. It was observed, however, that when the pen of the recorder showed no high-frequency vibration due to the irregularities as the result of a rapid rotation, a remarkable retardation of the recording took place, presumably because of the inertia of the recording system. Accordingly, the speed of rotation was kept rather slow, about 150∼500 r. p. m., and varied during the scanning so as to maintain a high-frequency vibration of the pen in an appreciable amplitude. (The width is 0.5∼1 mm.)

To avoid ambiguity caused by the calibration of density into intensity of scattered electrons, the exposure was kept in the range where the linearity held between density and intensity. The linearity was shown to be valid in the range of density less than 0.6, by an application of the pair method[12] to the diffraction patterns of a gold-foil. It was confirmed for FD-131 (diluted twice in volume and developed for 5 min. at 20°C) and for D72 (diluted twice in volume, developed for 3 min. at 20°C), but the linearity was found rather poor for D76.

The nozzle was covered with a liquid-air trap though not in contact with it. The temperature decrease of the nozzle was tested with a thermocouple inserted in place of the nozzle-head. Even after the trap was charged with liquid-air, no temperature decrease was observed unless the gas was led into the apparatus. By the same rate of gas flow as in the experiment, a decrease of 5°C was observed. The temperature decrease due to adiabatic expansion of the gas was estimated to be negligibly small. Therefore it seems reasonable to assume that the temperature of gas molecules is nearly equal to the room temperature.

The lattice constant of the gold-foil used in the present study was examined by two methods. By an X-ray diffractometer, Geigerflex, the lattice constant was determined to be $a_0=4.072\pm0.003$ Å, from four diffraction peaks, (400), (331), (420) and (422), obtained by Cu-$K\alpha$. On the other hand, the lattice constant was also confirmed by the comparison of electron diffraction rings of the foil with those of thallium chloride which was proved by H. Reather* to be suitable for the use as a standard substance of wavelength measurement. An evaporated film of TlCl was deposited on a thinned gold-foil and diffraction rings of gold and TlCl were recorded simultaneously on a photographic plate by 45 kv electron beam. By taking the value of the lattice constant of TlCl, 3.8424 Å, (or 3.8347 kX[13]), the lattice constant of the gold foil was determined to be $a_0=4.067\pm0.003$ Å.

A mean of this value and that obtained by the X-ray diffraction leads to the value $a_0=4.070\pm0.002$ Å. This is 0.2% smaller than the value for pure gold, 4.078 Å**, probably became copper was contained by an amount of ca. 0.55% by weight. Chemical analysis revealed that the amount of copper in the gold-foil used in the present study was 0.47% by weight.

Analysis.—The analysis of the intensity curves to obtain molecular intensity and radial distribution curve was carried out by the same procedure as that usually applied. Elastic scattering factors given by several authors are compared in Fig. 1, and the values on the full line, those by McWeeny[16] and Berghuis et al.[15] for C-atom, and those by Tomiie and Stam[17] for S-atom, were used in the present analysis. The phase factors due to the failure of the Born approximation were obtained from the table calculated by Ibers and Hoerni[19].

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** The X-ray value of the lattice constant of gold usually adopted is 4.070[14], but it is to be noted that this is expressed in kX unit, not in Å. (1 kX=1.0020 Å)

[15] J. Berghuis and C. H. MacGillavry et al., *Acta Cryst.*, **8**, 478 (1955).

[16] R. McWeeny, ibid., **4**, 513 (1951).

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[19] J. A. Ibers and J. A. Hoerni, ibid., **7**, 405 (1954).

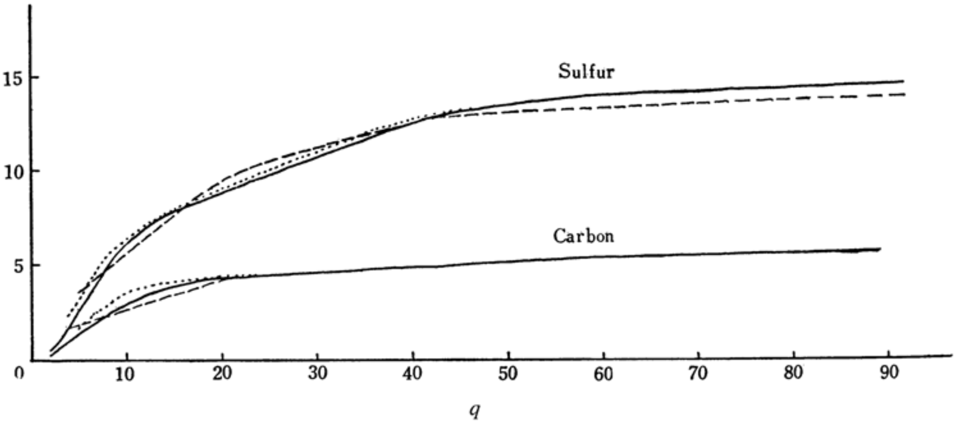

Fig. 1. The atomic scattering factors of carbon and sulfur.
—— Refs. 15 and 16 for carbon, and Ref. 17 for sulfur
······ Ref. 18
- - - Ref. 19

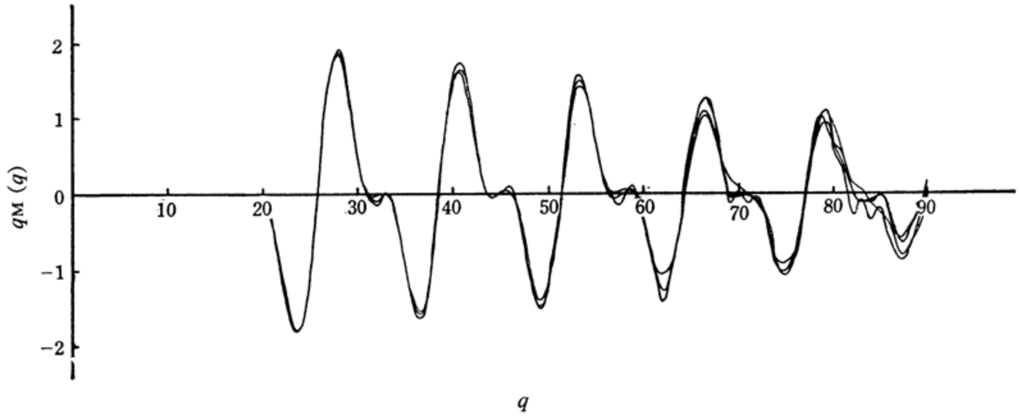

Fig. 2. The four observed molecular intensity curves of CS_2.

Inelastic scattering factors were calculated by the function given by Bewilogua[20].

Least-Squares Analysis[21,22].—Four molecular intensity curves were separately analyzed by the least-squares method described in the previous paper[21]. Each molecular intensity curve was fitted to the following equation,

$$F=i\{C_1(1/r_a{}'_1)\exp(-a_1s^2)\sin r_a{}'_1s + C_2(1/r_a{}'_2)\exp(-a_2s^2)\sin r_a{}'_2s\} \tag{9}$$

where the subscript 1 denotes the atom pair of C–S, and 2 the atom pair of S–S, and $r_a{}'$ stands for $r_a - \kappa s^2$. Rigorously speaking, the $r_a{}'$ in the denominators should be r_e, but it can be approximated by $r_a{}'$, as adopted in the present treatment. The coefficients C's are,

$$C_1=\frac{4\,|F_c{}^e(s)\,\|\,F_s{}^e(s)|\cos\Delta\eta}{\sum\limits_i |\,F_i{}^e(s)|^2+\sum\limits_i s_i(s)} \tag{10a}$$

$$C_2=\frac{2\,|\,F_i{}^e(s)|^2}{\sum\limits_i |\,F_i{}^e(s)|^2+\sum\limits_i S_i(s)} \tag{10b}$$

$F_i{}^e$ and S_i denote the elastic and the inelastic scattering factors of atom i, respectively.

The distance-parameter $r_a{}'$ to be determined by this method should be interpreted as the weighted mean of $r_a - \kappa s^2$, averaged over the observed range of s. It is not successful to attempt to determine κ as one of the parameters of the least-squares treatment, except for the case when κ is sufficiently large. The magnitude of κ theoretically expected is of the order of 10^{-6} A^3, and it was shown in the study of $GeCl_4$ that the magnitude of the standard deviation of κ was equal to or ten times as large as κ itself[21]. Therefore no significant value of κ can be expected to be determined.

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

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

[22] O. Bastiansen, K. Hedberg and L. Hedberg, ibid., 27, 1311 (1957).

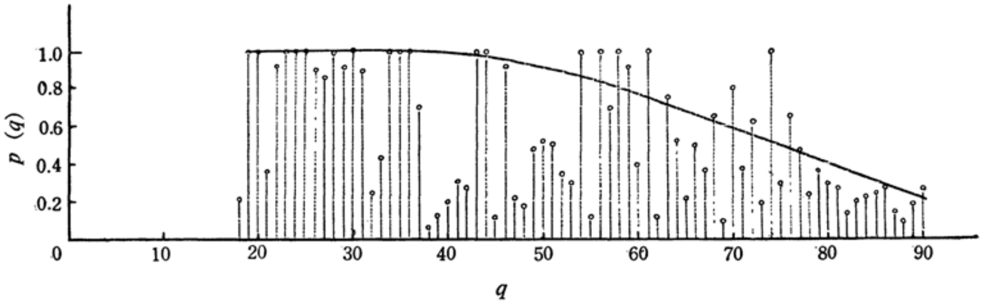

Fig. 3. The weight function: The weight determined as inversely proportional to σ^2 at each q. The smooth curve shows the general tendency.

Moreover the value of r_a may be strongly affected by the correlation between r_a and κ. Accordingly, it is more reasonable to determine the value of r_a from r_a' by the use of κ calculated from the cubic term of the distribution function.

In order to estimate the weight of the observed values of the molecular intensity at each q, ($q=(10/\pi)s$), the standard errors of the molecular intensity were evaluated by the fluctuation among the four molecular intensity curves. The weight function was assumed to be inversely proportional to the square of the standard error at each q. It is graphically shown in Fig. 3. The results of the least squares calculation obtained by the discontinuous weight function coincided with those obtained by taking the smooth function which expresses the general tendency of the observed $1/\sigma^2$. By the second refinement of the least-squares, the convergence of the parameters was found to be sufficiently good. The results are tabulated in Table II. As the standard deviations σ are nearly the same for every intensity curve, the greatest ones are tabulated.

The standard deviations σ_{av} attached to the averaged values were evaluated from the fluctuation among the results of four intensity curves. It is expected that σ_{av} is nearly equal to $1/\sqrt{4}$ of the σ of the parameters determined for an individual curve, if sufficiently large number of plates are analyzed, or it may be somewhat greater because of the possible systematic errors independently included in each plate. The expectation that σ_{av} is almost equal to $(1/\sqrt{4})\sigma$, is nearly realized, and it may accordingly be stated that the systematic error specific to each plate is not a predominant factor.

TABLE II. THE RESULTS OF THE LEAST SQUARES TREATMENT

Plate	Index	r_a'(C–S)	r_a'(S–S)	l(C–S)	l(S–S)
I	0.97	1.5564	3.1085	0.0347	0.0481
II	1.00	1.5590	3.1136	0.0368	0.0484
III	1.01	1.5572	3.1121	0.0419	0.0515
IV	1.02	1.5587	3.1133	0.0368	0.0509
σ	0.02	0.0011	0.0016	0.0020	0.0022
Average	1.00	1.5578	3.1119	0.0376	0.0497
σ_{av}	0.01	0.0006	0.0012	0.0015	0.0008

Corrections.—As was stated in the preceding section, the distance r_a' is related to the r_a as,

$$r_a' \cong \langle r_a - \kappa s^2 \rangle_s = r_a - \kappa \langle s^2 \rangle_s \tag{11}$$

where κ is related to the cubic coefficient β_3 of the distribution function as[21],

$$\kappa = l^6 \cdot \beta_3 \tag{12}$$

and
$$\langle s^2 \rangle_s = \sum_s p(s) s^2 / \sum_s p(s) \tag{13}$$

Thus κ for C–S was estimated to be 1.0×10^{-6} Å^3, and similarly 0.6×10^{-6} Å^3 for S–S. The weighted mean of s^2 was roughly estimated to be 250 Å^{-2}, and therefore $\kappa\langle s^2 \rangle$ is 0.3×10^{-3} Å for C–S and 0.2×10^{-3} Å for S–S, respectively*. Accordingly, we have,

r_a(C–S) : 1.5581 Å

and r_a(S–S) : 3.1121 Å

The average interatomic distances r_g are easily obtained from r_a by the relation[21],

$$r_g = r_a + \frac{l^2}{r_e} \tag{14}$$

With values of l^2/r_e, 0.0011 Å for C–S, and 0.0005 Å for S–S, the final results were obtained as follows,

r_g(C–S) : 1.5592 Å

and r_g(S–S) : 3.1126 Å

The root mean square amplitudes were corrected for the finite sample size around the

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* Rigorously speaking,

$$\frac{\sum_s p(s) s^4 \exp(-2as^2) \cos^2 r_a s}{\sum_s p(s) s^2 \exp(-2as^2) \cos^2 r_a s}$$

should be taken in place of $\langle s^2 \rangle_s$, if the correlation is assumed to be considerable only between r_a and κ. This expression was estimated to be nearly 300 Å^{-2}. Therefore the approximation by $\langle s^2 \rangle_s$ is practically acceptable.

nozzle, by -0.0012 Å for C–S and -0.0049 Å for S–S, respectively. These corrections were calculated from the distribution of the gas molecule, which was estimated by the discrepancy of the observed background intensity from the theoretical one in the region of q larger than 70[23]. Thus the corrected values of l's are,

l(C–S) : 0.0364 Å

and l(S–S) : 0.0448 Å

Estimation of Reliabilities.—The reliabilities of the results of the present work are indicated by *the 99 per cent confidence intervals*, where both random and systematic errors were taken into consideration. The greater of the σ_{av} and $(1/\sqrt{4})\sigma$ of each parameter was regarded as the standard deviation originating from the random error, and 2.5 times that amount was considered to specify the 99 per cent confidence interval in the sense that the probability of finding the result of any observation outside this interval would be less than 1%[24].

The sources and the amounts of several systematic errors for both interatomic distances and root mean square amplitudes were thoroughly examined by Kuchitsu[23]. Although most of his estimates remain valid in the present work, there are required slight modifications due to some differences in experimental and analytical procedures. The systematic errors not negligible were estimated as follows corresponding to the 99 per cent confidence intervals, although there was no statistical evidence available to show that they were really so.

i) For atomic distances.

The drift of the wavelength of the primary electron beam ; 0.05%. (The accelerating voltage was regulated constant within 0.1%.)

Uncertainty of the lattice constant of the gold-foil ; 0.05%.

Errors associated with the corrections for the inclination of plates ; 0.075%. (From the standard deviations σ_A, σ_B and σ_C of the correction factors for the three plate-positions A, B and C, the standard deviation σ_P due to this correction was estimated for the average value obtained from four plates by

$$\sigma_P=\frac{1}{4}\left[\sigma_A{}^2+(2\,\sigma_B)^2+\sigma_C{}^2\right]^{1/2}$$

because these four consisted of one photographed at A, two at B and one at C. The 2.5 times σ_P was found to be 0.075%.)

Thus the total amounts to 0.10%, because these systematic errors are independent of each other.

ii) For root mean square amplitudes.

Errors associated with the correction for the distribution of gas molecules ; 1% for C–S, 4% for S–S. (They were tentatively taken as 50% of the correction.)

Uncertainty of the values of η in the correction for the Born approximation ; 2% for C–S.

Errors due to the arbitrary choice of the weight function[11] ; 2%.

Thus the total amounts 3% for C–S and 5% for S–S, respectively.

The confidence intervals were estimated from the square root of the sum of $(2.5\,\sigma)^2$ and (systematic error)^2, as summarized in Table III, and the final results of the present work are listed in Table IV, in comparison with the values calculated from the spectroscopic data.

TABLE III. ESTIMATION OF THE 99 PER CENT CONFIDENCE INTERVALS

	σ (random)	System. error	2.5σ (random)	Confidence interval
i	0.01		0.025	0.029
r_g(C–S)	0.0006	0.0016	0.0015	0.0022
r_g(S–S)	0.0012	0.0031	0.0030	0.0044
l(C–S)	0.0015	0.0012	0.0038	0.0040
l(S–S)	0.0011	0.0025	0.0028	0.0038

TABLE IV. INTERATOMIC DISTANCES, ROOT-MEAN-SQUARE AMPLITUDES AND SHRINKAGE OF CS_2 AT 15°C, WITH THE 99 PER CENT CONFIDENCE INTERVALS

	E. D.	Spectr.
Index i	1.00 $\pm$0.03	
r_g(C–S)	1.5592$\pm$0.0022 Å	1.5580$\pm$0.0005 Å
r_g(S–S)	3.1126$\pm$0.0044 Å	3.1090$\pm$0.0010 Å
l(C–S)	0.0364$\pm$0.0040 Å	0.0391 Å
l(S–S)	0.0448$\pm$0.0038 Å	0.0412 Å
δ_g	0.0058$\pm$0.0042 Å	0.0070 Å

Conclusion

As shown in Table IV, the results obtained by electron diffraction are in good agreement with those obtained from spectroscopic data. Thus the consistency between electron diffraction and spectroscopy has been well confirmed : it gives a support to the present interpretation of the distance-parameters and the effect of molecular vibrations upon them. Moreover, it should be noted that the r_0 of the C–S distance obtained by spectroscopy is 1.5545$\pm$0.0003 Å, and r_e is 1.5532$\pm$0.0005 Å[3], and they are significantly shorter than the r_g obtained by electron diffraction. This fact clearly shows that it is important to take accurately the physical meanings of various distance-parameters

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[24] W. A. Wallis and H. V. Roberts, "Statistics", The Free Press, Glencoe, Illinois (1956), p. 456.

into consideration, in comparing them with each other. The shrinkage effect has been confirmed as well.

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