BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1693—1703 (1970)

Determination of the Molecular Structures of AsF_3 and $AsCl_3$ by Gas Electron Diffraction[*1]

Shigehiro KONAKA and Masao KIMURA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received January 8, 1970)

The thermal-average distances and mean amplitudes of $AsCl_3$ and AsF_3 have been determined by gas electron diffraction. The sources of experimental errors have been discussed in detail. The observed molecular parameters are $r_g(\text{As–Cl})=2.1621\pm0.0033$ Å, $\theta_g(\text{ClAsCl})=98°\ 34'\pm34'$, $l(\text{As–Cl})=0.0470\pm0.0024$ Å, $l(\text{Cl–Cl})=0.0945\pm0.0063$ Å, $r_g(\text{As–F})=1.7089\pm0.0016$ Å, $\theta_g(\text{FAsF})=95°53'\pm22'$, $l(\text{As–F})=0.0433\pm0.0022$ Å, and $l(\text{F–F})=0.0689\pm0.0044$ Å. The results have been compared with the structures of other trihalides of the Vb-group elements.

The interatomic distances of AsF_3 and $AsCl_3$ were first observed by the visual method of electron diffraction. Those previous results are summarized in Table 1. The bond angle of AsF_3 was not determined. Kisliuk and Townes[4] measured the rotational constants of $As^{35}Cl_3$ and $As^{37}Cl_3$ by microwave spectroscopy and obtained the $r_s(\text{As–Cl})$ distance of 2.161 ± 0.004 Å and the bond angle of 98°25′±30′.

TABLE 1. MOLECULAR STRUCTURES OF $AsCl_3$ AND AsF_3 DETERMINED BY THE VISUAL METHOD OF ELECTRON DIFFRACTION

r (As–Cl)	∠ ClAsCl	r (As–F)	Ref.
2.18±0.03 Å	101°±40′		1
2.16±0.03 Å	103°±3°	1.72±0.02 Å	2
2.17±0.02 Å	99°±2°		3

The molecular structure of AsF_3, however, could not be determined uniquely from the rotational constant observed in the microwave study of Kisliuk and Geschwind,[5] for no isotope of the fluorine atom was present. They estimated the bond angle of AsF_3 to be 102±2° by a comparison of the observed quadrupole interaction constant of AsF_3 with that of $AsCl_3$, and determined the $r_0(\text{As–F})$ distance to be 1.712 ± 0.005 Å.

Recently, Mirri[6] obtained the centrifugal distortion constants, D_J and D_{JK}, as well as the rotational constant, B_0, his values agreeing with the results of Kisliuk and Geschwind, by an analysis of the millimeter-wave rotational spectrum of AsF_3. She determined the quadratic potential constants of AsF_3 from the observed centrifugal distortion constants and the four observed vibrational frequencies. Then, she calculated the Coriolis coupling constant, ζ_4, from the potential constants and compared it with those determined by studies of the band envelope of infrared spectra.[7,8] It was found that the calculated and the observed values of ζ_4 did not agree well unless the bond angle of AsF_3 was in the range of 99±1°. Mirri assumed the angle to be 98° by referring to the 98.5° of $AsCl_3$,[4] and she obtained 1.708 Å for the As–F distance. However, it is most desirable to determine the molecular structure of AsF_3 directly; her method is still indirect.

The molecular structures derived directly from the observed rotational constants, B_0, include the effect of the interaction of the vibration and the rotation, so they have no definite physical meaning. Although this effect is not large, it can not be neglected in determining molecular structures in the order of one-thousandth of an Angstrom. On the other hand, the interatomic distances obtained by gas electron diffraction are the thermal averages of instantaneous interatomic distances. It is the principal purpose of the present study to determine the accurate structures of AsF_3 and $AsCl_3$ by gas electron diffraction.

[*1] Part of this report was included in the doctoral thesis presented by one of the authors (S. K.) to the Faculty of Science, Hokkaido University.

1) L. O. Brockway and F. T. Wall, *J. Amer. Chem. Soc.*, **56**, 2373 (1934).

2) L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

3) S. M. Swingle, quoted by P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3**, pt. 1, 46 (1950).

4) P. Kisliuk and C. H. Townes, *J. Chem. Phys.*, **18**, 1109 (1950).

5) P. Kisliuk and S. Geschwind, *ibid.*, **21**, 828 (1953).

6) A. M. Mirri, *ibid.*, **47**, 2823 (1967).

7) I. W. Levin and S. Abramowitz, *ibid.*, **44**, 2562 (1966).

8) L. C. Hoskins, *ibid.*, **45**, 4594 (1966).

Experimental

The diffraction apparatus used in the present study was designed and constructed by Murata, Kuchitsu, and Kimura.[9] The camera length was fixed at 10.930 cm. In order to measure the accurate value of the scale factor, the diffraction patterns of CS_2 molecules, the precise structure of which had been given by spectroscopy,[10,11] were taken just before or after those of the samples.

Research-grade arsenic trichloride (above 99% pure) obtained from the Yamanaka Chemical Industry, Inc., was used as the sample. The experimental conditions were as follows: accelerating voltage, about 45 kV; sample pressure, about 4 mmHg; exposure time, 3—4 minutes; electron-beam current, about 0.15 μA, and nozzle temperature, about 18°C. The vacuum in the diffraction chamber was about 6×10^{-5} mmHg during exposures.

A sample of arsenic trifluoride in a polyethylene bottle was obtained from the K and K Laboratories, Inc., of the United States. It was transferred into a sample holder made of glass just before taking photographs. Since arsenic trifluoride (mp −6°C) reacts to some extent with glass, the sample was solidified at about −10°C and evacuated by a rotary pump to eliminate any possible impurities such as SiF_4 (mp −90°C). The experimental conditions were as follows; accelerating voltage, about 52.5 kV; sample pressure, about 10mmHg; exposure time, 70—100 sec; electron-beam current, about 0.15 μA, and nozzle temperature, about 19°C. The vacuum pressure was about 8×10^{-5} mmHg during exposures.

Photographs taken on Fuji-Process Hard plates were developed at 20°C for five minutes with an FD-131 developer diluted twice in volume.

The plates were spun rapidly about the centers of the diffraction patterns, while optical densities were measured with an NLM-VII microphotometer. In the case of $AsCl_3$, the densities were read out at integral q values from 20 to 130 from the density curves recorded on charts. A value taken from one side and the corresponding value from the other side were averaged, point by point, in order to diminish the errors due to the uncertainty as to the center position of the chart.

In the case of AsF_3, the densities were measured with a digital microphotometer*[2] at intervals of $\Delta R=1/3$ mm along the diameters of the concentric patterns. The q value corresponding to the distance, R, on a plate from its center was calculated as:

$$q = \left(\frac{40}{\lambda}\right)\sin\left(\frac{1}{2}\tan^{-1}\left(\frac{R}{L}\right)\right) \tag{1}$$

where λ is the wavelength of the incident electron beam and where L is the camera length. The two sides of the photometer curve were analyzed independently.

The relation between the optical densities and the scattering intensities of the electrons was investigated by the use of two selected plates of AsF_3. The ratio of the densities for the same q value of the two plates was about 1.5. The density-intensity curve obtained by Karle's method[13] fit the $E=D\,(1+0.03D)$ relation with a good approximation. A linear relation between the density and the intensity was assumed for the case of $AsCl_3$. The systematic errors caused by this assumption will be discussed in a later section.

The intensities were corrected for the deviation of the rotating sector from the ideal r^3-shape.

Five plates for $AsCl_3$ and six plates for AsF_3 were selected for analysis. The number of CS_2 plates used for determination of the scale factors were four and five for $AsCl_3$ and AsF_3 respectively.

Analysis of Data

The intensities were levelled by smooth functions based on the theoretical backgrounds. Smooth background curves, I_B, were first drawn arbitrarily through the total intensity curves, I_T, thus obtained. The molecular intensities, $qM(q)$, were calculated as $q(I_T-I_B)/I_B$. The theoretical expression of $qM(q)$ may be written, with notations of the usual significance,[14] as follows:

$$\begin{aligned} qM(q) &= k\sum_{i\neq j} A_{ij}\mu_{ij}\cos\Delta\eta_{ij} \\ &\times\sin\left\{\frac{\pi}{10}q\left(r_{aij}-\left(\frac{\pi}{10}q\right)^2\kappa_{ij}\right)\right\} \\ &\times\exp\left\{-\frac{1}{2}\left(\frac{\pi}{10}q\right)^2 l_{ij}^2\right\}. \end{aligned} \tag{2}$$

The r_a distance is an apparent interatomic distance; it can easily be converted into the thermal-average distance, r_g, as follows:[15]

$$r_g = r_a + \frac{l^2}{r_a}. \tag{3}$$

The elastic scattering factors were calculated by the partial-waves method from the Hartree-Fock potentials.[16] The inelastic scattering factors, also based on the Hartree-Fock potentials, were taken from the table presented by Tavard *et al.*[17] They were used to compute $\mu_{ij}\cos\Delta\eta_{ij}$ and the theoretical

---

[9] Y. Murata, K. Kuchitsu and M. Kimura, *Japan. J. Appl. Phys.*, to be published.

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

[11] Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).

*[2] Recently, an integrating digital voltmeter (TR-65A15) has been combined with the microphotometer in order to speed up the measurement of the densities and to improve the precision. The intensities of light passing through a plate are recorded on a tape and easily converted to optical densities by using a FACOM 270-20 electronic computer.[12]

[12] T. Iijima, H. Fujii and M. Kimura, unpublished.

[13] J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).

[14] S. Konaka, Y. Murata, K. Kuchitsu and Y. Morino, This Bulletin, **39**, 1134 (1966).

[15] K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **35**, 1945 (1961).

[16] M. Kimura, S. Konaka and M. Ogasawara, *ibid.*, **46**, 2599 (1967).

[17] C. Tavard, D. Nicolas and M. Rouault, *J. Chim. Phys.*, **64**, 540 (1967).

backgrounds. In order to revise the background curves, radial distribution curves (RD curves) were calculated as the following Fourier integral:

$$f(r) = \int_0^{q_{\max}} (qM(q)_{\text{obs}} + \Delta qM(q)) \sin\left(\frac{\pi}{10} qr\right) \times \exp(-bq^2)\, \mathrm{d}q. \tag{4}$$

The correction, $\Delta qM(q)$, was added to use the non-negativity criterion of the RD curves as:[13,18]

$$\Delta qM(q) = k \sum_{i \neq j} A_{ij}(g_{ij} - \mu_{ij} \cos \Delta\eta_{ij}) \times \sin\left\{\frac{\pi}{10} q \left(r_{aij} - \left(\frac{\pi}{10} q\right)^2 \kappa_{ij}\right)\right\} \times \exp\left\{-\frac{1}{2}\left(\frac{\pi}{10} q\right)^2 l_{ij}^2\right\}, \tag{5}$$

$$\begin{aligned} g_{\text{As-Cl}} &= \cos(0.0072\, q), \\ g_{\text{Cl-Cl}} &= 1.11, \\ g_{\text{As-F}} &= 0.7 \cos(0.0095q) + 0.5 \exp(-5 \times 10^{-4} q^2), \\ g_{\text{F-F}} &= 1.25 \exp(-3 \times 10^{-6} q^2) + 0.65 \exp(-10^{-3} q^2). \end{aligned} \tag{6}$$

The g functions were so chosen that the correction terms, $\Delta qM(q)$, were small compared with $qM(q)_{\text{obs}}$. In practice, the background curves were revised by the inverse Fourier transformation of $f(r)$ in the range of $r (r \leqq 1\ \text{Å})$. At small q values where $qM(q)$ could not be observed, theoretical values were used. The artificial damping factor, b, was so chosen as to reduce the molecular intensity to one-tenth of the original value at $q_{\max}$.

One of the I_T curves and its I_B curve thus obtained are shown in Fig. 1 for both $AsCl_3$ and AsF_3. The values of I_B express approximately the ratio between the observed and the theoretical background intensities. At small scattering angles, the ratio is smaller than unity. This is mainly due to the errors in the sector correction curve, and it has no effect on the molecular parameters. The gradual increase in the ratio at large scattering angles ($q \geqq 90$) is due to extraneous scattering. This may cause a slight increase in the observed values of mean amplitudes. The molecular intensities, $qM(q)_{\text{obs}}$, were then multiplied by the ratio in order to eliminate errors caused by the extraneous scattering.

The index of resolution, k, and the molecular parameters, r_{ij} and l_{ij}, were determined by the least-squares fitting of the observed $qM(q)$ to its theoretical expression. The anharmonicity parameters were fixed. The anharmonicity parameters for bonded pairs were estimated in the diatomic approximation as;[19]

$$\kappa_{\text{As-Y}} = \left(\frac{1}{6}\right) a_3 \left(1 + \frac{8\kappa}{(1+\kappa)^2}\right) l^4_{\text{As-Y}}, \tag{7}$$

where:

$$\chi = \exp\left(\frac{h\nu_{\text{As-Y}}}{kT}\right). \tag{8}$$

Here, the anharmonicity parameter of the Morse function, a_3, was assumed to be 2.0 Å^{-1} and the characteristic frequencies, $\nu_{\text{As-Y}}$, were taken to be 400 and 721 cm^{-1} for $AsCl_3$ and AsF_3 respectively.[20,7] The estimated values were 3.6×10^{-6}

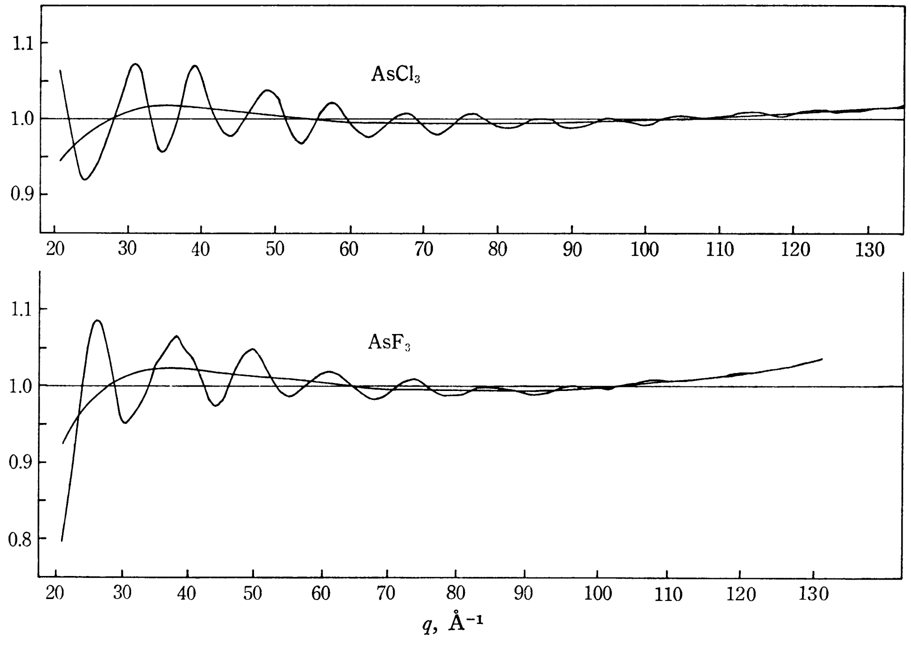

Fig. 1. Levelled intensities and backgrounds.

---

[18] R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

[19] K. Kuchitsu, This Bulletin, **40**, 505 (1967).

[20] P. W. Davis and R. A. Oetjen, *J. Mol. Spectrosc.*, **2**, 253 (1958); *ibid.*, **3**, 581 (1959).

and 1.2×10^{-6} Å^3 for $\kappa_{\mathrm{As-Cl}}$ and $\kappa_{\mathrm{As-F}}$ respectively. The anharmonicity parameters, $\kappa_{\mathrm{Y-Y}}$, for nonbonded paris were assumed to be zero, since no simple method of estimating them was available and since their values could be expected to be of the same order as $\kappa_{\mathrm{As-Y}}$ or less.

The weights of the observed values for least-squares fitting were reduced at small scattering angles because of the uncertainty in the correction curve for the sector shape; those at large scattering angles were also taken to be small because of extraneous scattering. The following from was assumed for AsF_3:

$$\begin{aligned} P(N) &= \exp\left(-a(N-N_1)^2\right), & 1\leqq N\leqq N_1 \\ P(N) &= 1.0, & N_1\leqq N\leqq N_2 \\ P(N) &= \exp\left(-b(N-N_2)^2\right), & N_2\leqq N \end{aligned} \qquad (9)$$

where N shows the numbering of the observed data.

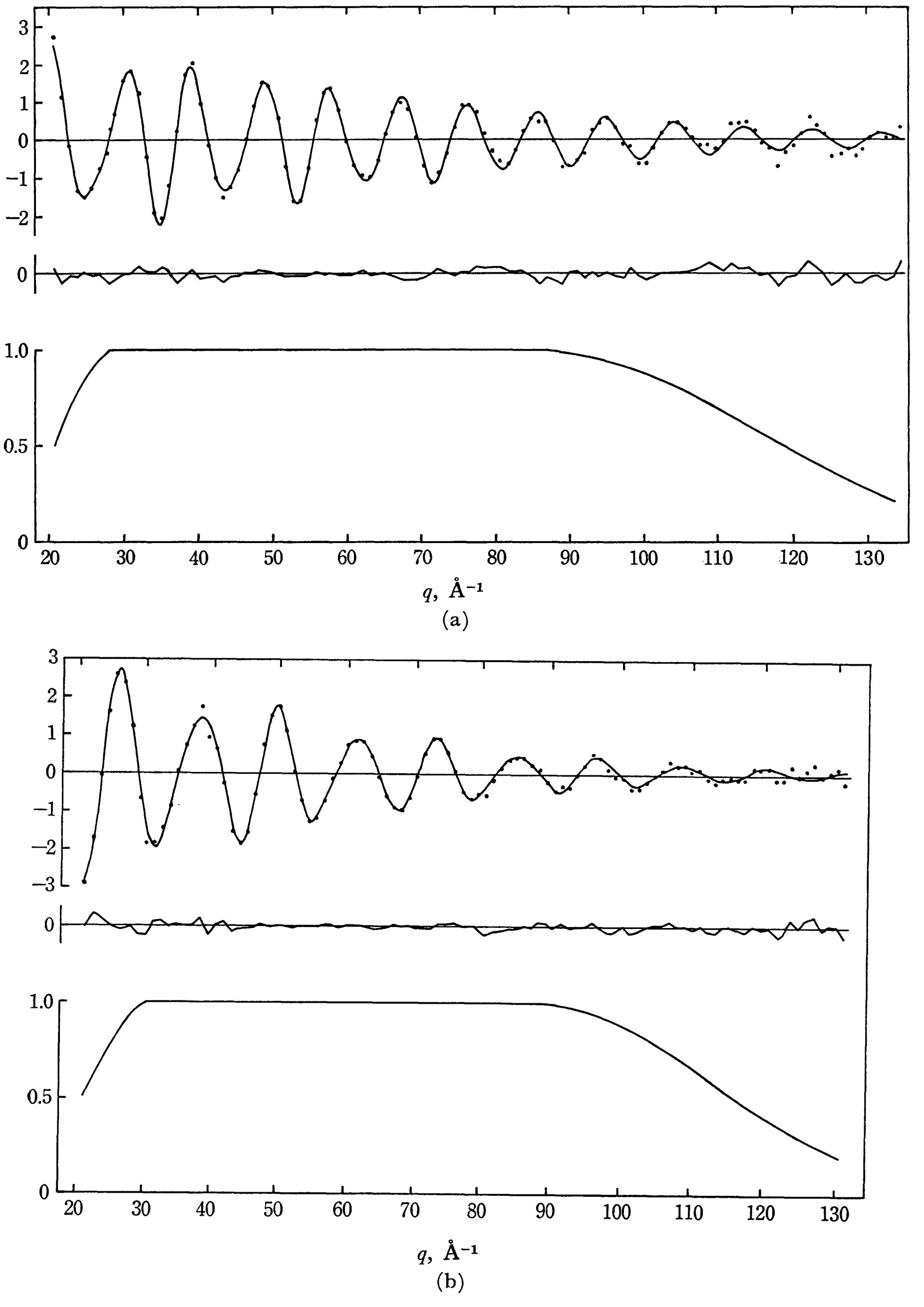

Fig. 2. Molecular intensities (dots for observed values and the solid curve for the best-fit theoretical intensity), the residuals and the weight function used.
(a) $AsCl_3$ and (b) AsF_3.

Errors due to the arbitrariness of the weights were estimated by using several sets of weight functions which had been obtained by changing the parameters, a, b, N_1, and N_2, in the least-squares treatment.

In the case of AsF_3, the analysis was repeated by correcting the positions of the centers of the photometer curves until the interatomic distances obtained from the two sides of each curve showed satisfactory agreement.

A program for the HITAC 5020E electronic computer was written which allowed for automatic computation from the density-intensity transformation to the least-squares fittings. The analysis for AsF_3 was made by using this program. The average time needed for one computation was about 7 sec. The theoretical values of the μ factors and the levelling function were calculated for the observed points by interpolation of the input data, which had been calculated beforehand for the integral values of q by another program.

Examples of the observed molecular intensities and their best-fit curves are shown in Fig. 2, along with the weight function used.

The analysis of the diffraction patterns for CS_2 was made according to the same procedure as that employed for the samples. Five plates for $AsCl_3$ were numbered from I to V, and six plates for AsF_3 were numbered from I to VI. The wavelength for each plate and the number of CS_2 plates employed were as follows: 0.05539±0.00007 Å for the $AsCl_3$ plates I and II, two CS_2 plates; 0.05626±0.00005 Å for the $AsCl_3$ plates from III to V, two CS_2 plates; 0.05217±0.00003 Å for the AsF_3 plates from I to III, three CS_2 plates; 0.05214±0.00004 Å for the AsF_3 plates from IV to VI, two CS_2 plates.

The above values of the wavelengths for the sample plates had, however, to be corrected if the accelerating voltage had drifted during the experimental sequence. The drift of the accelerating voltage was monitored throughout the experiment. Such corrections for the wavelengths were found unnecessary for the $AsCl_3$ plates I, II and IV, but those of about 0.26% and −0.05% were found necessary for the plates III and V respectively by measuring the load current of the high-voltage source. The drift for AsF_3 was confirmed to be less than 0.01% by measuring the voltage drops of the standard resistance in the high-voltage source by the use of a digital voltmeter. The results of the least-squares analyses, corrected for scale factors, are shown in Table 2, along with the averages of standard deviations, $\bar{\sigma}$.

The mean amplitudes and the shrinkage, δ_g, which is defined as $\delta_g=2r_g(\text{C–S})-r_g(\text{S–S})$,[21] observed for CS_2 are shown in Table 3, along with the errors. The method of estimating the errors will be described in a later section. The observed values are close to those calculated from the spectroscopic data.[11]

TABLE 2. LEAST-SQUARES RESULTS (r and l in Å unit)

(a) $AsCl_3$

plate	r_a (As-Cl)	r_a (Cl-Cl)	l (As-Cl)	l (Cl-Cl)	k
I	2.1612	3.2822	0.0478	0.0930	0.890
II	2.1611	3.2729	0.0474	0.0901	0.915
III	2.1631	3.2797	0.0452	0.0993	0.818
IV	2.1601	3.2662	0.0478	0.0957	0.863
V	2.1598	3.2685	0.0486	0.0975	0.862
Average	2.1611	3.2739	0.0474	0.0951	0.870
$\bar{\sigma}$	0.0011	0.0069	0.0017	0.0054	0.023
σ_1	0.0005	0.0031	0.0008	0.0024	0.011
σ_2	0.0006	0.0031	0.0006	0.0016	0.016

(b) AsF_3

plate	r_a (As-F)	r_a (F-F)	l (As-F)	l (F-F)	k
I	1.7078	2.5370	0.0457	0.0685	0.963
II	1.7084	2.5361	0.0431	0.0710	0.932
III	1.7077	2.5315	0.0436	0.0689	0.908
IV	1.7094	2.5371	0.0439	0.0711	0.919
V	1.7082	2.5343	0.0437	0.0699	0.913
VI	1.7060	2.5353	0.0431	0.0696	0.920
Average	1.7079	2.5352	0.0439	0.0698	0.926
$\bar{\sigma}$	0.0009	0.0045	0.0017	0.0037	0.022
σ_1	0.0004	0.0018	0.0007	0.0015	0.009
σ_2	0.0005	0.0009	0.0004	0.0004	0.008

TABLE 3. MEAN AMPLITUDES, SHRINKAGE, AND INDEX OF CS_2 (l and δ_g in Å unit)

	Obsd[a]	Obsd[b]	Calcd[c]
l (C-S)	0.0378±0.0030	0.0366±0.0026	0.0391
l (S-S)	0.0426±0.0036	0.0403±0.0030	0.0421
δ_g	0.0061±0.0049	0.0073±0.0031	0.0070
k	0.90 ±0.05	0.92 ±0.05	

a) Results of four CS_2 plates used for determining the scale factors for $AsCl_3$.

b) Results of five CS_2 plates used for determining the scale factors for AsF_3.

c) Ref. 11.

Error Analysis

1) Estimation of Random Errors. Experimental random errors are introduced mainly in the process of photographing, development, and photometry. Random errors can be estimated from the standard deviations in the least-squares treatment (σ_1) and from the fluctuation among the results on several plates (σ_2).[22] The standard deviations, σ_1,

---

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

[22] Y. Morino, K. Kuchitsu and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

associated with the average values in Table 2 were estimated to be $\bar{\sigma}/\sqrt{N}$, where N is the number of plates, since the individual standard deviations for all the plates were nearly equal. The standard deviations, σ_2, are defined by $\sqrt{\sum_{i=1}^{N}(x_i-\bar{x})^2/N(N-1)}$. Random errors corresponding to a 99% confidence interval have so far been taken to be 2.5 times the larger of σ_1 and σ_2.[14,22] It seems, however, more reasonable to estimate them from either 2.58 times σ_1, or 4.60 ($N=5$) or 4.03 ($N=6$) times σ_2, according to Student's t-distribution.[23] If σ_1 and σ_2 are of nearly equal magnitude, 2.58 σ_1 can be taken as the confidence interval, because all the observations on N plates are considered to belong to a single statistical population, as has been discussed by Morino *et al.*[22] When σ_2 is considerably larger than σ_1, the confidence interval should be estimated from σ_2 and the t-value depending on N. Since σ_2 is equal to, or slightly smaller than, σ_1 for almost all the parameters in the present analysis, 2.58 σ_1 was chosen as the random error corresponding to the 99% confidence interval.

2) Estimation of Systematic Errors for Interatomic Distances. The sources of systematic errors taken into consideration were as follows:

a) The Uncertainty in the Camera Length.

b) The Uncertainty in the Scale-magnification Ratio on the Microphotometer Trace.[24] The above two errors are, however, negligible because of the use of the reference sample (CS_2).

c) Errors in the Determination of the Center of the Microphotometer Trace. These errors are also negligible since, in the case of AsF_3, both sides of the photometer trace were analyzed and the results from both sides averaged, and in the case of $AsCl_3$ the corresponding densities of both sides were averaged.

d) The Finite Size of the Light Beam on Microphotometry. This effect was discussed by Kuchitsu.[24] In the present experiment, the size of the light beam was 0.03 mm × 0.1 mm. The inward shift of the halo of the radius, R (mm), is about $(0.1)^2/24R$ in mm units, which is about 0.001% of R even at $R=6$ mm. Thus, this effect is completely negligible.

e) Errors Due to Averaging Densities over a Scanning Length of About 0.1 mm on the Plate on Microphotometry. In the case of AsF_3, the optical density obtained on microphotometry is the average of densities over a range of about 0.1mm on the plate.*[3] The effect of such an averaging process on molecular-parameter values may be estimated as follows. The average of the molecular intensity is given by the following integration:

$$M=\frac{1}{2\Delta R}\int_{R_0-\Delta R}^{R_0+\Delta R}\exp\left(-\frac{1}{2}l^2s^2\right)\frac{\sin sr}{sr}\,\mathrm{d}R \tag{10}$$

Here s is a function of the scanning length, R, measured from the center of the photographic plate and ΔR is half of the range over which the average is taken. By noting that s is proportional to R in a good approximation, *E*q. (10) can be transformed into the following equation by neglecting higher-order terms than $(\Delta R/R_0)^2$:

$$M=\exp\left(-\frac{1}{2}l^2s_0^2\right)\frac{\sin s_0r}{s_0r}\left[1+\frac{1}{6}\left(\frac{\Delta R}{R_0}\right)^2\right.$$
$$\left.\times\{(ls_0)^4-(rs_0)^2-2(l^2s_0^2+1)s_0r\cot s_0r\}\right] \tag{11}$$

This can be rewritten in the same order of approximation as follows:

$$M=(1+\Delta k)\exp\left\{-\frac{1}{2}(l+\Delta l)^2s_0^2\right\}\frac{\sin s_0(r+\Delta r)}{s_0(r+\Delta r)} \tag{12}$$

where:

$$\Delta k=-\frac{1}{6}\left(\frac{\Delta R}{R_0}\right)^2(s_0r)^2, \tag{13}$$

$$\frac{\Delta l}{l}=\frac{1}{6}\left(\frac{\Delta R}{R_0}\right)^2(s_0l)^2, \tag{14}$$

and:

$$\frac{\Delta r}{r}=-\frac{1}{3}\left(\frac{\Delta R}{R_0}\right)^2((s_0l)^2+1). \tag{15}$$

Since the value of $\Delta Rs_0/R_0(=\Delta s)$ is about 0.05 Å^{-1} for the accelerating voltage of 52.5 kV, the apparent decreases of interatomic distances are about 0.001% for both As–F and F–F distances; both are negligible.

f) Errors Involved in the Determination of the Scale Factors. They were estimated to be 0.14% and 0.07% for $AsCl_3$ and AsF_3 respectively from the standard errors corresponding to the 99% confidence interval of the C–S and S–S distances in the least-squares treatment of CS_2 and from the drift of the accelerating voltage while taking photographs of CS_2 and the samples.

g) Errors Due to Uncertainty in the Parameter, κ. The uncertainties for the κ values were estimated to be 1, 8, 0.6, and 4×10^{-6} Å^3 for As–Cl, Cl–Cl, As–F, and F–F respectively, values which correspond to uncertainties of 0.0004, 0.0016, 0.0002, and 0.0014 Å in the respective distances.

h) Errors Due to Uncertainty in the Correction Curve for the Sector Shape. They include errors due to small pieces of dust which might have been at the edge of the sector during the experiment. They were estimated by changing the sector correction curve over the range of small scattering angles ($q\leqq40$).

i) Errors Due to the Delocalization of the Sample

---

23) J. Bass, "Elements of Probability Theory," Academic Press Inc., New York (1966), p. 214.

24) K. Kuchitsu, This Bulletin, **32**, 748 (1959).

*[3] In the microphotometry of AsF_3, photographing plates were moved at the speed of about 0.025 mm/sec, while the intensities of light passing through the plates were integrated for 4 seconds by using a digital voltmeter.[12]

Gas. Scattering from unlocalized gas causes an apparent increase in the interatomic distances.[25] If the decrease in the index of resolution from unity is assumed to be due completely to the samlpe delocalization in the diffraction chamber, the apparent increase in interatomic distances can be estimated as follows:[25]

$$\frac{\Delta r}{r}=\frac{[3(1-k)/k]}{[20+(sr)^2]} \tag{16}$$

By taking the effective value of s to be 15 Å^{-1}, the values listed in Table 4 were obtained for $AsCl_3$ and CS_2, and for AsF_3 and CS_2. The corrections for r_a distrances were estimated to be as shown in Table 9. The errors associated with this correction were taken to be 0.02%.

Table 4. Apparent increases of the interatomic distances ($\Delta r/r$) due to the delocalization of sample gas for $AsCl_3$ and CS_2, and AsF_3 and CS_2

r(As-Cl)	r(Cl-Cl)	r(C-S)	r(S-S)
0.04%	0.02%	0.06%	0.02%

r(As-F)	r(F-F)	r(C-S)	r(S-S)
0.04%	0.02%	0.05%	0.01%

Table 5. Estimation of errors for r_a distances (in 10^{-4} Å unit)

Source of errors	As-Cl	Cl-Cl	As-F	F-F
Random errors (2.58 σ_1)	13	80	10	47
Scale factor	30	46	12	18
Uncertainty of κ	4	16	2	14
Sector correction curve	2	8	1	10
Delocalization of sample gas	4	6	3	5
Arbitrariness of background	2	3	2	2
Arbitrariness of weight	3	4	2	13
Total errors	33	94	16	55

j) Errors Due to Arbitrariness of the Background Curves. The errors were estimated by changing the artificial damping factor and the range of the inverse Fourier transformation.

k) Errors Due to Arbitrariness of the Weight Function. They were estimated by changing weight functions.

The errors for interatomic distances are summarized, along with the total errors, in Table 5.

3) Estimation of Systematic Errors for Mean Amplitudes. *a) Effect of the Finite Sample Size.* The finite sample size causes an apparent increase in the mean amplitudes.[26] The distribution of gaseous molecules spouted from the nozzle depends mainly on the distance, a, from the top of the nozzle to the main beam, the diameter, b, of the nozzle aperture and the viscosity of the gas.

The distribution of silicon tetrachloride molecules jetted from the needle-type nozzle ($a=0.41$ mm and $b=0.55$ mm) was investigated by Morino and Murata.[26] The distribution function obtained by their experiments was:

$$f(x)=\left(\frac{2.74}{2}\right)\exp(-2.74\,|x|) \tag{17a}$$

for $|x|\leqq 0.7$, and:

$$f(x)=0.356\exp(-1.59x) \tag{17b}$$

for $|x|\geqq 0.7$, where x is the distance in millimeters measured from the center of the nozzle inlet along the direction of the beam. Since the nozzle type with a diameter of 0.2 mm was used at $a=0.4$ mm in the present experiment, more localization of gas molecules may be expected than in their experiment. The following distribution function was, therefore, tentatively assumed:

$$f(x)=1.5\exp(-3\,|x|). \tag{18}$$

The apparent increase in the mean amplitudes estimated from this distribution is:

$$\Delta l_{ij}=\frac{r_{ij}^2}{l_{ij}}\frac{1}{(3L)^2} \tag{19}$$

where L is the camera distance in millimeters. Numerical values of Δl_{ij} for $AsCl_3$, AsF_3, and CS_2 are tabulated in Table 6. The errors associated with this correction were taken to be 70% of the correction. The values of CS_2 corrected for this effect are shown in Table 3.

b) Errors for Density-Intensity Calibration. For AsF_3, they were estimated by changing the parameter c from 0 to 0.5 in the relation, $E/D=(1+cD)$.

Table 6. Apparent increases in the mean amplitudes caused by the finite sample size (in Å unit)

l(As-Cl)	l(Cl-Cl)	l(As-F)	l(F-F)	l(C-S)	l(S-S)
0.0009	0.0010	0.0006	0.0009	0.0006	0.0021

Table 7. Estimation of errors for mean ampitudes (in 10^{-4} Å unit)

Source of errors	As-Cl	Cl-Cl	As-F	F-F
Random errors (2.58 σ_1)	21	62	18	39
Sample size	6	7	4	6
E-D calibration	2	1	4	3
Extraneous scattering	2	2	2	2
Atomic scattering factors	5	9	8	14
Sector correction curve	4	6	6	11
Arbitrariness of background	2	2	1	2
Arbitrariness of weight	6	4	1	7
Total errors	24	63	22	44

---

[25] L. S. Bartell, *J. Appl. Phys.*, **31**, 252 (1960).

[26] Y. Morino and Y. Murata, This Bulletin, **38**, 114 (1965).

Because a linear relation ($c=0$) was assumed in the analysis of the $AsCl_3$ data, the effect of the parameter c on the mean amplitudes was examined by the reanalysis of the densest plate ($D_{max}=0.8$) of $AsCl_3$. By taking 70% of the correction for this plate as the average values of the mean amplitudes, they were estimated to be 0.0002 Å and 0.0001 Å for As–Cl and Cl–Cl respectively. The uncertainties of this correction were estimated to be as is shown in Table 7.

c) Errors for Averaging Densities over a Scanning Length of About 0.1 mm on the Plate on Microphotometry. This effect was considered in the previous section. The apparent increase in the mean amplitudes of AsF_3 is smaller than 0.0005%; this effect is thus found to be completely negligible.

d) Corrections for Extraneous Scattering. The correction was made in the analysis. The errors for this correction were estimated to be 70% of the correction.

e) Errors Due to the Uncertainty of the Atomic Scattering Factors. Since the complex scattering factors based on the Hartree-Fock atomic potentials were used, these errors would be small. Their estimated values are shown in Table 7.

f) The Drift of the Wavelength of the Incident Electron during Exposure for One Plate. For the plates III, IV, and V of $AsCl_3$, a slight drift of accelerating voltage was observed; its effect on the molecular parameters must be investigated. If the wavelength is assumed to have drifted from $\lambda_0-\Delta\lambda$ to $\lambda_0+\Delta\lambda$ during one exposure, the observed molecular intensity is given by;

$$M=\frac{1}{2\Delta\lambda}\int_{\lambda_0-\Delta\lambda}^{\lambda_0+\Delta\lambda}\exp\left(-\frac{1}{2}l^2s^2\right)\frac{\sin sr}{sr}\,d\lambda \tag{20}$$

where s is a function of λ. By expanding this equation into the power series of $(\Delta\lambda/\lambda_0)$ and by neglecting the higher order terms than $(\Delta\lambda/\lambda_0)^2$, it can be rewritten in the following form;

TABLE 8. ESTIMATION OF ERRORS FOR INDICES

Source of errors	$AsCl_3$	AsF_3
Random errors (2.58 σ_1)	0.02_8	0.02_3
E-D calibration	0.02	0.02
Atomic scattering factors	0.03	0.03
Sector correction curve	0.02	0.02
Arbitrariness of background curve	0.00_5	0.00_5
Arbitrariness of weight	0.02	0.02
Total errors	0.05	0.05

TABLE 9. CORRECTIONS FOR INTERATOMIC DISTANCES (in 10^{-4} Å unit)

	As–Cl	Cl–Cl	As–F	F–F
Delocalization of sample gas	0	6	−1	3
r_g-r_a	10	28	11	19

TABLE 10. FINAL RESULTS FOR $AsCl_3$ AND AsF_3

	$AsCl_3$	AsF_3
r_g(As–Y)	2.1621±0.0033	1.7089±0.0016
r_g(Y–Y)	3.2773±0.0094	2.5374±0.0055
θ_g(YAsY)	98°34′ ±34′	95°53′ ±22′
l(As–Y)	0.0470±0.0024	0.0433±0.0022
l(Y–Y)	0.0945±0.0063	0.0689±0.0044
k	0.87 ±0.05	0.93 ±0.05

TABLE 11. MOLECULAR STRUCTURES OF GROUP Vb TRIHALIDES

(a) Bond distances (in Å unit)

	F	Cl	Br	I
N	1.365 ±0.002 a)			
p	$1.570_0\pm0.001_2$ b)	2.039 ±0.0014 c) 2.043 ±0.003 d)	2.18 ±0.03 e)	2.43 ±0.04 e)
As	$1.708_9\pm0.001_6$ f)	$2.162_1\pm0.003_3$ f)	2.329±0.002 g)	2.557±0.005 h)
Sb	1.876 ±0.005 i) 1.879 ±0.004 j)	2.325 ±0.005 k) (2.37 ±0.02 e))	2.51 ±0.02 e)	2.719±0.0015 l)

(b) Bond angles (in degrees)

	F	Cl	Br	I
N	102.37±0.04 a)			
P	97.8 ±0.2 b)	100.27±0.09 c) 100.1 ±0.3 d)	101.5±1.5 e)	102 ±2 e)
As	95.9 ±0.4 f)	98.6 ±0.6 f)	99.7±0.3 g)	100.2±0.4 h)
Sb	94 ±2.5 i) 95.0 ±0.8 j)	99.5 ±1.5 k) 96 ±4 e)	97 ±2 e)	99.1 l)

a) Ref. 28 b) Ref. 29 c) Ref. 30 d) Ref. 4 e) Ref. 3 f) Present results
g) Ref. 31 h) Ref. 32 i) Ref. 33 j) Ref. 34 k) Ref. 35 l) Ref. 36

$$M = \exp\left(-\frac{1}{2}l^2{s_0}^2\right)\frac{\sin s_0r}{s_0r}\left[1-\frac{1}{6}\left(\frac{\Delta\lambda}{\lambda_0}\right)^2 \times \{(s_0l)^2+(s_0l)^2\cot s_0r+(s_0r)^2-(s_0l)^4\}\right] \tag{21}$$

Therefore, an apparent increase in the mean amplitude is given approximately as:

$$\Delta l = \frac{1}{6}\left(\frac{\Delta\lambda}{\lambda_0}\right)^2\frac{r^2}{l}. \tag{22}$$

Since the value of $\Delta\lambda/\lambda_0$ was 0.2% at most, the corrections for the mean amplitudes of $AsCl_3$ are 0.0001 Å or less. The effects on interatomic distances can also be completely ignored.

The following three kinds of systematic errors were estimated in the same way as has been described for the case of interatomic distances:

g) Errors Due to the imperfection of the correction curve for the sector shape.

h) Errors Due to the arbitrariness of the backgrounds.

i) Errors Due to the arbitrariness of the weight func-

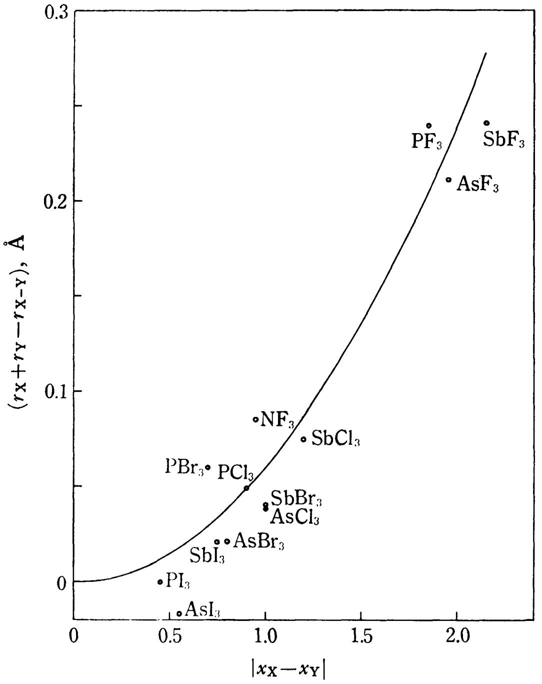

Fig. 3. Plot of the shortenings of bond distances from the sum of the covalent radii *versus* the differences of electronegativities. The solid curve represents a relation $(r_X+r_Y-r_{X\text{-}Y})=0.06\ (x_X-x_Y)^2$.

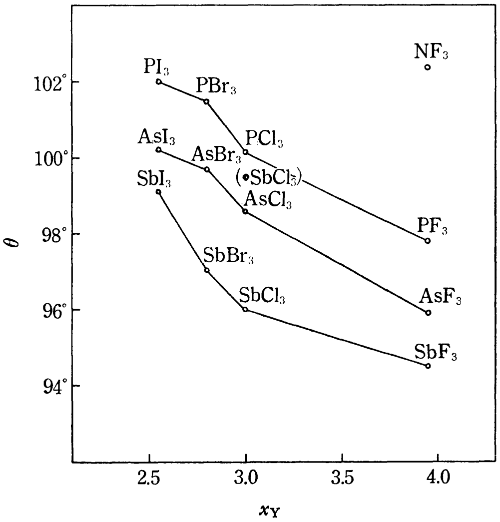

Fig. 4. Variation of bond angles θ with the electronegativities of halogens x_Y.

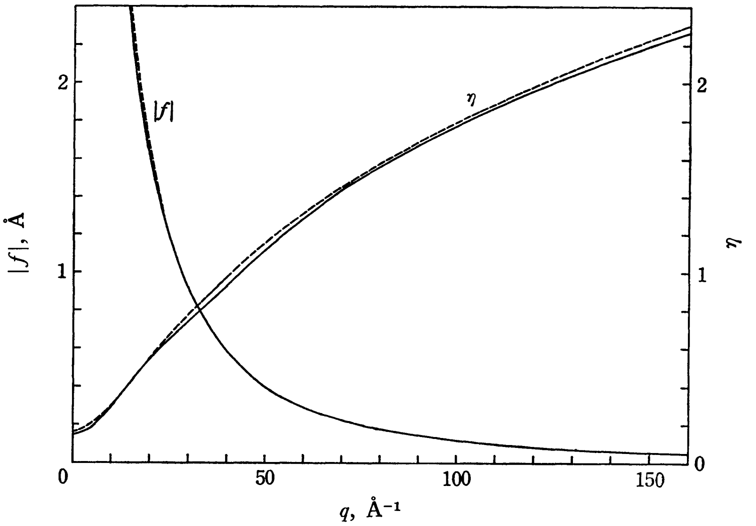

Fig. 5. Scattering factors of arsenic calculated from the H. F. and T. F. D. potentials for 52.5 keV electrons.
—— H. F., ------ T. F. D.

tion. The systematic errors for the mean amplitudes are summarized in Table 7, together with the total errors.

The systematic errors for the index of resolution were estimated to be as shown in Table 8. The deviation of the indices of resolution from unity is considered to be due mainly to the extraneous scattering, which raises the background intensities uniformly over the whole observed range of scattering angles. This extraneous scattering is certainly caused partly by the delocalization of the sample gas in the diffraction chamber and partly by the reflection of scattered electrons by the chamber walls.

Results and Discussion

The corrections necessary for obtaining thermal average distances from the interatomic distances given in Table 2 are listed in Table 9. The final values of the r_g distances, the mean amplitudes, and the indices of resolution are tabulated in Table 10. The θ_g(YAsY) bond angles were calculated by the relation:[*4]

$$\sin\left(\frac{\theta_g}{2}\right)=\frac{r_g(\text{Y-Y})}{2r_g(\text{As-Y})} \tag{23}$$

The bond angle of $AsCl_3$ is close to the microwave value, but that of AsF_3 is about 6° smaller than Kisliuk's value and 2° smaller than Mirri's value.[*5] The molecular structures are compared with those of other arsenic trihalides in Table 11.[28–36] They vary gradually with the atomic numbers of halogens. The molecular structures of the other trihalides of the Vb-group elements XY_3 are also shown in Table 11. The bond distances, r_{X-Y}, are shorter than the sum of the covalent radii[*6] (r_X+r_Y) in almost all cases. Figure 3 shows the shortenings $(r_X+r_Y-r_{X-Y})$ plotted against the differences in electronegativities $|x_X-x_Y|$ taken from the literature.[38] The curve can be roughly expressed by the $(r_X+r_Y-r_{X-Y})=0.06\,(x_X-x_Y)^2$ relation. Aside from the causes of these bond shortenings, this relation shows that the bond shortening varies rather regularly with the difference in electronegativity.

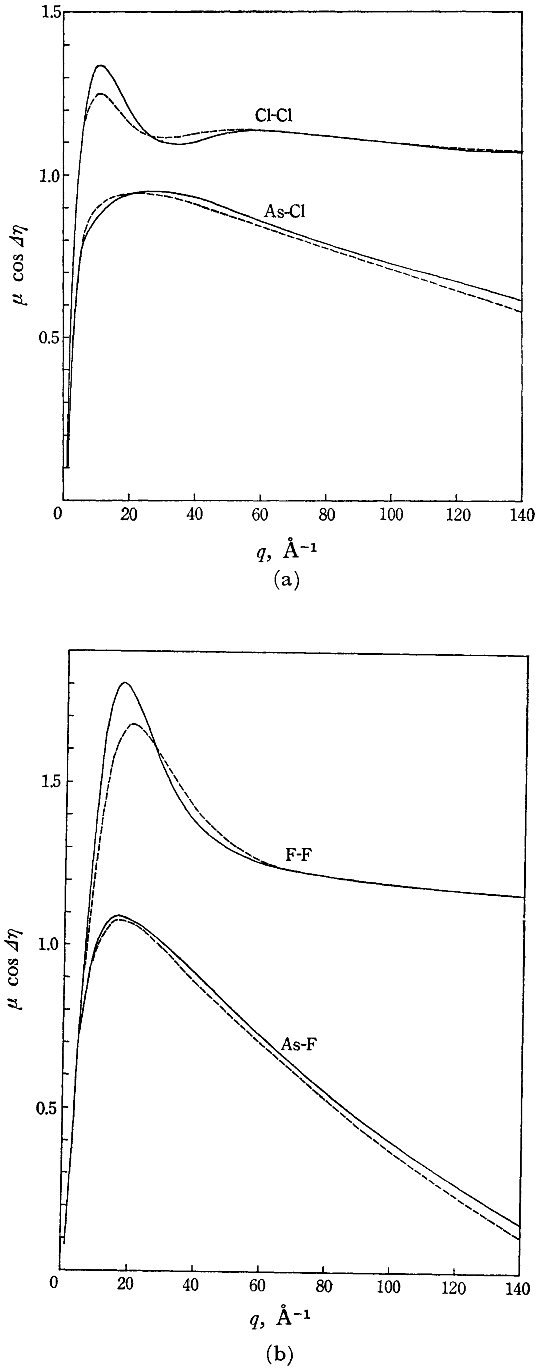

Fig. 6. The μ factors calculated by using the H. F. scattering factors (——) and those obtained by replacing the elastic scattering factors for arsenic by the T. F. D. scattering factors (------).
(a) $AsCl_3$ 45 keV and (b) AsF_3 52.5 keV.

[*4] Strictly speaking, the bond angles thus obtained are not necessarily equal to the thermal average of the bond angles. It is likely, however, that the difference is, in the present case, much smaller than the experimental uncertainty. K. Kuchitsu, private communication.

[*5] The present finding for the structure of AsF_3 is consistent with the recent gas electron diffraction finding obtained independently by Clippard and Bartell.[27]

27) F. B. Clippard and L. S. Bartell, "Symposium on Molecular Structure and Spectroscopy," Columbus, Ohio, September, 1968, E9.

[*6] The covalent radii were taken from the literature.[37]

28) M. Otake, C. Matsumura and Y. Morino, *J. Mol. Spectrosc.*, **28**, 316 (1968).

29) Y. Morino, K. Kuchitsu and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).

Table 12. Change of parameters (X) and standard deviations ($\bar{\sigma}$) in the least-squares fitting when $f_{\mathrm{T.F.D.}}$ is used for arsenic (r and l in 10^{-4} Å unit)

X	AsCl$_3$		AsF$_3$	
	ΔX	$\Delta\bar{\sigma}$	ΔX	$\Delta\bar{\sigma}$
r_a(As–Y)	2	0	−5	1
r_a(Y–Y)	−6	1	−5	5
l(As–Y)	−5	0	3	1
l(Y–Y)	16	2	27	4
k	0.014	0.001	0.036	0.003

The bond angles decrease with the increase in the electronegativity of halogens relative to Vb-group atoms as is shown in Fig. 4. This is in accordance with the valence-shell electron-pair repulsion theory of Gillespie,[39] as discussed by Morino *et al.*[29]

The values of the parameters listed in Table 10 were obtained by using the Hartree-Fock scattering factors ($f_{\mathrm{H.F.}}$), which are better than the Thomas-Fermi-Dirac scattering factors ($f_{\mathrm{T.F.D}}$).[16] Since $f_{\mathrm{H.F.}}$ factors are not available for atoms heavier than krypton, it is worthwhile looking at the changes in the results given rise to by the use of $f_{\mathrm{T.F.D}}$ factors instead of $f_{\mathrm{H.F.}}$ factors for arsenic. The two scattering factors are compared in Fig. 5, while the corresponding μ factors are shown in Fig. 6. Table 12 shows that, although the changes in parameter values are apparent, they are smaller than the experimental errors. Slight increases in the standard deviations were found, as was expected.

The molecular structures and mean amplitudes obtained here will be combined with the spectroscopic data to determine harmonic potential constants and more accurate molecular structures in a succeeding paper.[40]

We wish to thank the Computing Center of the University of Tokyo for providing their facilities. Our thanks are also due to Dr. Takao Iijima for his helpful discussions.

---

30) K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, **36**, 589 (1962).

31) K. Hedberg, *Trans. Amer. Cryst. Association*, **2**, 79 (1966).

32) Y. Morino, T. Ukaji and T. Ito, This Bulletin, **39**, 71 (1966).

33) T. Ukaji and H. Uchimura, presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1969.

34) C. Matsumura and H. Takeo, "Symposium on Molecular Structure," Fukuoka, Oct., 15, 1969.

35) P. Kisliuk and C. H. Townes, *Phys. Rev.*, **83**, 210 (1951).

36) A. Almenningen and T. Bjorvatten, *Acta Chem. Scand.*, **17**, 2573 (1963).

37) W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley & Sons, Inc., New York (1953), p. 309.

38) W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

39) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

40) S. Konaka, This Bulletin, to be published.