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Force Constants and Average Structures of AsF_3 and $AsCl_3$ as Determined by Electron Diffraction and Spectroscopy[*1]

Shigehiro KONAKA

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

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The general quadratic potential constants of $AsCl_3$ have been determined by the use of a combination of the mean amplitudes observed by gas electron diffraction and the vibrational frequencies. Those of AsF_3 have been determined from the mean amplitudes, the centrifugal distortion constants given by microwave spectroscopy and the Coriolis coupling constants and the vibrational frequencies given by infrared spectroscopy on the basis of the molecular structure newly-determined by electron diffraction. By using these potential constants, zero-point average structures have been derived from the r_g structures obtained by electron diffraction. The results have been found to be consistent with the average rotational constants, B_z, derived from the effective rotational constants, B_0, observed by microwave spectroscopy according to the theory of vibration-rotation interactions. The final results, obtained by the use of a combination of the electron diffraction and microwave data, are:

$$r_z(\text{As–Cl}) = 2.1621 \pm 0.0009\,\text{Å}, \quad \theta_z(\text{ClAsCl}) = 98°38' \pm 22'$$

$$r_z(\text{As–F}) = 1.7080 \pm 0.0004\,\text{Å}, \text{ and } \theta_z(\text{FAsF}) = 95°58' \pm 17'.$$

Formulas for calculating the sum of perpendicular mean amplitudes for pyramidal XY_3-type molecules have been derived and used to reduce r_g to r_z.

If the anharmonic as well as the harmonic potential constants are known, the equilibrium structures (r_e-structures) of gaseous molecules can be determined by spectroscopy[1)] and gas electron diffraction (ED).[2)] The r_e-structures derived from ED agreed within the limits of experimental errors with those derived from spectroscopy for CH_4, CD_4,[2-4)] and CS_2.[5,6)]

Since the anharmonic potential constants are, however, not yet available except for a very limited number of molecules, the r_e-structures have not been obtained for most molecules. Even so, the zero-point average structures (r_z-structures) can be derived from the average rotational constants, B_z, which can themselves be reduced from the effective ground-state rotational constants, B_0, by using only the harmonic potential constants.[7-9)] Since the thermal average distances, r_g, observed by ED can also be converted to the r_z distances, it is possible to make an exact comparison between the molecular structures obtained by the two different experimental techniques.[10-15)] Furthermore, it is possible to combine both sets of results so as to obtain more precise structures.[16-21)]

[*1] Main part of this report is included in the doctral thesis presented by the author to the Faculty of Science, Hokkaido University.

1) H. H. Nielsen, *Rev. Mod. Phys.*, **23**, 90 (1951).

2) L. S. Bartell, K. Kuchitsu and R. J. de Neui, *J. Chem. Phys.*, **35**, 1211 (1961).

3) R. A. Olafson, M. A. Thomas and H. L. Welsh, *Can. J. Phys.*, **39**, 419 (1961).

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

7) T. Oka, *J. Phys. Soc. Jap.*, **15**, 2274 (1960).

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10) Y. Morino, K. Kuchitsu and T. Oka, *ibid.*, **36**, 1108 (1962).

11) K. Kuchitsu, *ibid.*, **44**, 906 (1966).

12) K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966).

13) Y. Morino, K. Kuchitsu and S. Yamamoto, *Spectrochim. Acta*, **24A**, 335 (1968).

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

15) M. Tanimoto, K. Kuchitsu and Y. Morino, This Bulletin, **42**, 2519 (1969).

16) K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Structure*, **1**, 463 (1967—1968).

17) Y. Morino, K. Kuchitsu, Y. Hori and M. Tanimoto, This Bulletin, **41**, 2349 (1968).

18) K. Kuchitsu, *J. Chem. Phys.*, **49**, 4456 (1968).

The r_g-structures of AsF_3 and $AsCl_3$ have been determined by the sector-microphotometer method of gas electron diffraction described in a preceding paper.[22] The ground-state rotational constants, B_0, obtained from the microwave spectra (MW) are 2147.2 ± 0.2 and 2044.7 ± 0.3 Mc for $As^{35}Cl_3$ and $As^{37}Cl_3$ respectively,[23] and 5878.971 ± 0.002 Mc for AsF_3.[24] In the present study, both sets of results have been converted to the r_z-structures or the corresponding average rotational constants, and then compared with each other. Furthermore, more accurate molecular structures have been obtained by the use of a combination of the electron-diffraction and the spectroscopic data.

It is necessary to know the quadratic potential constants for the above purpose. For the pyramidal XY_3-type of molecules, the quadratic potential constants can not be determined from only the observed vibrational frequencies. We must use certain additional physical quantities which can be related to the quadratic potential constants. The mean amplitudes of thermal vibration, which are observed by ED, can be used for such a purpose.[25,26]

There is no published work in which the force constants of $AsCl_3$ have been determined experimentally. In the present study, the intramolecular force field of $AsCl_3$ has been determined by using the observed mean amplitudes given in the preceding paper.[22]

Some investigations have already attempted to determine the force constants of AsF_3 by using the centrifugal distortion constants[27] or the Coriolis constants obtained by spectroscopy.[28,29] However, the bond angles of 98° [27] and 102° [28,29] assumed in these previous studies are appreciably larger than the bond angle of 95.9°±0.4° which has been determined by our own recent electron-diffraction study.[22] In the present study, the most probable set of the force constants of AsF_3 has been determined from the mean amplitudes,[22] the centrifugal distortion constants, and the Coriolis constants on the basis of the accurate molecular structure.

Determination of the Force Constants

The general quadratic force field for the pyramidal XY_3 molecule can be expressed in terms of the internal coordinates:

$$\begin{aligned}2V = {} & \sum f_r(\Delta r_i)^2 + 2\sum f_{rr}(\Delta r_i)(\Delta r_j) \\ & + \sum f_\theta(r_e\Delta\theta_{ij})^2 + 2\sum f_{\theta\theta}(r_e\Delta\theta_{ij})(r_e\Delta\theta_{jk}) \\ & + 2\sum f_{r\theta}(\Delta r_i)(r_e\Delta\theta_{ij}) + 2\sum f_{r\theta'}(\Delta r_i)(r_e\Delta\theta_{jk}). \quad (1)\end{aligned}$$

Here all the notations except for the equilibrium bond distance, r_e, are those used in Ref. 26.

The symmetry coordinates used are as follows:

$$\begin{aligned} S_1 &= \frac{1}{\sqrt{3}}(\Delta r_1+\Delta r_2+\Delta r_3), \\ S_2 &= \frac{1}{\sqrt{3}}r_e(\Delta\theta_{12}+\Delta\theta_{23}+\Delta\theta_{31}), \\ S_3 &= \frac{1}{\sqrt{2}}(\Delta r_1-\Delta r_2), \\ S_4 &= \frac{1}{\sqrt{2}}r_e(\Delta\theta_{23}-\Delta\theta_{31}), \\ S_5 &= \frac{1}{\sqrt{6}}(\Delta r_1+\Delta r_2-2\Delta r_3), \\ S_6 &= \frac{1}{\sqrt{6}}r_e(\Delta\theta_{23}+\Delta\theta_{31}-2\Delta\theta_{12}), \qquad (2a)\end{aligned}$$

which may be written in a matrix form as:

$$\boldsymbol{S} = \boldsymbol{UR}. \qquad (2b)$$

The relations between the force constants in the symmetry coordinates and those in the internal coordinates are:

$$\begin{aligned} F_{11} &= f_r + 2f_{rr}, \\ F_{12} &= f_{r\theta'} + 2f_{r\theta}, \\ F_{22} &= f_\theta + 2f_{\theta\theta}, \\ F_{33} &= f_r - f_{rr}, \\ F_{34} &= f_{r\theta'} - f_{r\theta}, \\ F_{44} &= f_\theta - f_{\theta\theta}. \qquad (3)\end{aligned}$$

The elements of the $\boldsymbol{G}$ matrix in the symmetry coordinates are given as follows:

A_1 species:

$$\begin{aligned} G_{11} &= \mu_X(1+2c)+\mu_Y, \\ G_{12} &= -2\mu_X(1-c)(1+2c)/s, \\ G_{22} &= 2(1-c)(1+2c)[2(1-c)\mu_X+\mu_Y]/s^2, \qquad (4)\end{aligned}$$

E species:

$$\begin{aligned} G_{33} = G_{55} &= \mu_X(1-c) + \mu_Y, \\ G_{34} = G_{56} &= \mu_X(1-c)^2/s, \\ G_{44} = G_{66} &= (1-c)[\mu_X(1-c)^2+\mu_Y(2+c)]/s^2. \qquad (5)\end{aligned}$$

Here μ_X and μ_Y are the reciprocals of the atomic masses, m_X and m_Y, respectively, while s and c stand for $\sin\theta$ and $\cos\theta$ respectively.

The formulas for calculating the mean amplitudes of the pyramidal XY_3 molecules, l(X—Y) and

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[19] T. Fukuyama, K. Kuchitsu and Y. Morino, This Bulletin, **42**, 379 (1969).

[20] T. Iijima and M. Kimura, *ibid.*, **42**, 2159 (1969).

[21] T. Iijima, *ibid.*, **43**, 1049 (1970).

[22] S. Konaka and M. Kimura, *ibid.*, **43**, 1693 (1970).

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

[24] P. Kisliuk and S. Geschwind, *ibid.*, **21**, 828 (1953).

[25] Y. Morino, Y. Nakamura and T. Iijima, *ibid.*, **32**, 643 (1960).

[26] M. Iwasaki and K. Hedberg, *ibid.*, **36**, 594 (1962).

[27] A. M. Mirri, *ibid.*, **47**, 2823 (1967).

[28] I. W. Levin and S. Abramowitz, *ibid.*, **44**, 2562 (1966).

[29] L. C. Hoskins, *ibid.*, **45**, 4594 (1966).

l(Y–Y), are given as follows:[26]

$$[l(\text{X-Y})]^2 = \frac{1}{3}(\Sigma_{11}+2\Sigma_{33}), \tag{6}$$

$$[l(\text{Y-Y})]^2 = \frac{2}{3}(2\Sigma_{11}+\Sigma_{33})\sin^2\frac{\theta}{2} + \frac{4}{3}(\Sigma_{12}-\Sigma_{34})\sin\frac{\theta}{2}\cos\frac{\theta}{2} + \frac{1}{3}(\Sigma_{22}+2\Sigma_{44})\cos^2\frac{\theta}{2}. \tag{7}$$

Here Σ_{ij} denotes the thermal average of the product of S_i and S_j. The values of Σ_{ij} can easily be calculated from the force constants.[26]

When the four observed vibrational frequencies are used, the force constants have only two degrees of freedom. For a given value of F_{12}, the other force constants of A_1 species are calculated as:

$$F_{11} = (\gamma\pm\delta)/2G_{11}, \qquad F_{22} = (\gamma\mp\delta)/2G_{22}, \tag{8}$$

where:

$$\gamma = \lambda_1 + \lambda_2 - 2G_{12}F_{12}, \tag{9}$$

$$\delta = [\gamma^2-4G_{11}G_{22}(\lambda_1\lambda_2/(G_{11}G_{22}-G^2_{12})+F^2_{12})]^{1/2}, \tag{10}$$

$$\lambda_k = 4\pi^2c^2\nu_k{}^2. \tag{11}$$

Similar relations hold for the force constants of the E species. The relations in these force constants are shown in Fig. 1. The frequencies used in the calculation are tabulated in Table 1. The bond angles used are 98.5° and 95.9° for $AsCl_3$ and AsF_3 respectively.[22] The solid and dotted curves correspond to the upper sign and the lower sign of Eq. (8) respectively. In the solid curves, the

Table 1. Fundamental frequencies used for the force constant calculation (in cm^{-1} unit)

	ν_1	ν_2	ν_3	ν_4	Ref.
$AsCl_3$	411.8	193.6	386.7	155.3	30
AsF_3	740	336	702	262	28

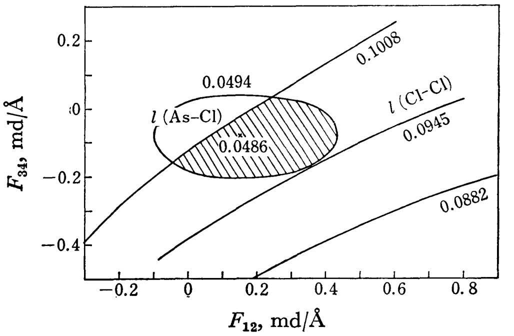

Fig. 2. Force constants of $AsCl_3$ allowed by the observed mean amplitudes at 291°K.

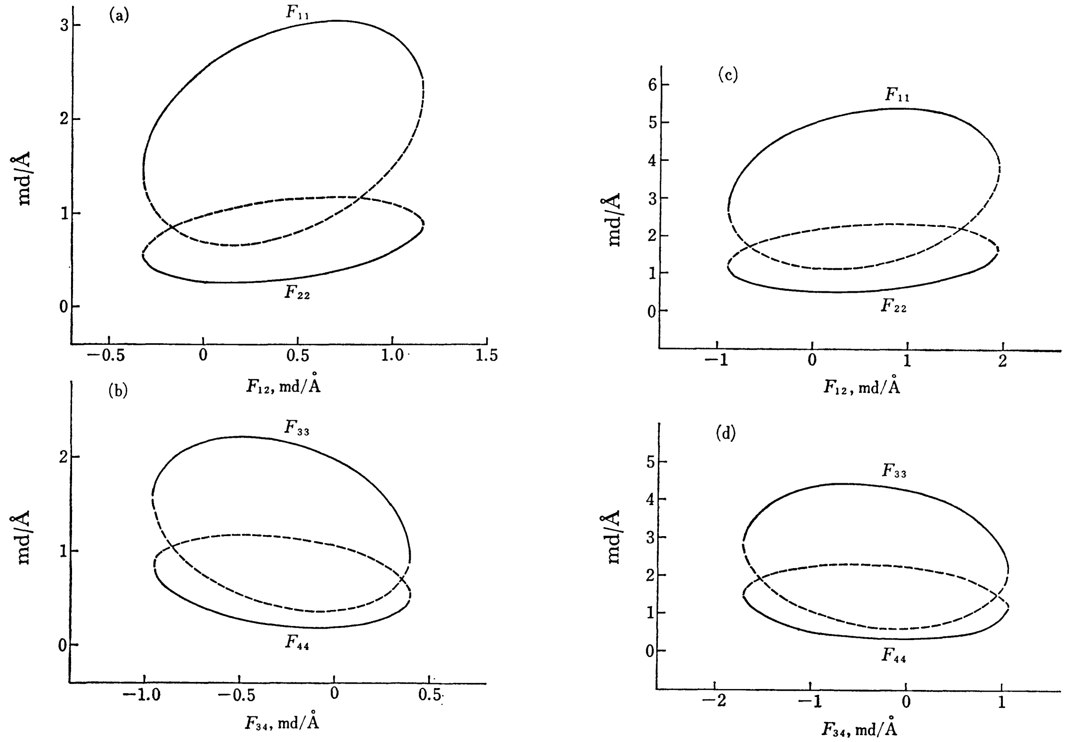

Fig. 1. Correlation curves of force constants (a), (b) $AsCl_3$ and (c), (d) AsF_3.

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30) P. W. Davis and R. A. Oetjen, *J. Mol. Spectry.*, **2**, 253 (1958); *ibid.*, **3**, 581 (1959).

TABLE 2. FORCE CONSTANTS OF $AsCl_3$ DETERMINED BY USING THE OBSERVED MEAN AMPLITUDES AND VIBRATIONAL FREQUENCIES (in md/Å unit)

Symmetry coordinate		Internal coordinate	
F_{11}	2.72 ± 0.27	f_r	2.31 ± 0.08
F_{12}	0.19 ± 0.24	f_{rr}	0.22 ± 0.10
F_{22}	0.28 ± 0.02	f_θ	$0.22 \pm 0.00_5$
F_{33}	2.05 ± 0.10	$f_{\theta\theta}$	0.03 ± 0.01
F_{34}	$-0.08_5 \pm 0.12$	$f_{r\theta}$	0.11 ± 0.07
F_{44}	$0.19_5 \pm 0.00_5$	$f_{r\theta'}$	0.00 ± 0.13

TABLE 3. FORCE CONSTANTS OF AsF_3 DETERMINED BY EARLIER AUTHORS AND THE SPECTROSCOPIC AND STRUCTURAL DATA USED IN THEIR CALCULATIONS (F, D, ν and r are in md/Å, kc, cm^{-1} and Å units, respectively)

	Levin and Abramowitz[28)]	Hoskins[29)]	Mirri[27)]
F_{11}			4.80 ± 0.06
F_{12}			-0.28 ± 0.06
F_{22}			0.57 ± 0.01
F_{33}	4.20 ± 0.05	4.27 ± 0.04	4.34 ± 0.01
F_{34}	0.00 ± 0.05	-0.12 ± 0.06	-0.135 ± 0.006
F_{44}	0.30 ± 0.02	0.29 ± 0.03	0.315 ± 0.001
ζ_3	0.31	0.21	
ζ_4	−0.44	−0.43	
D_J			4.63 ± 0.03
D_{JK}			-6.17 ± 0.05
ν_1	740		740
ν_2	336		336
ν_3	702	702.2	702
ν_4	262	262.3	262
r_e (As–F)	1.712	1.712	1.708
θ	102°	102°	98°

TABLE 4. EXPERIMENTAL PARAMETERS USED FOR THE FORCE CONSTANT CALCULATION OF AsF_3

l (As–F)	0.0433 ± 0.0022 Å[a)]
l (F–F)	0.0689 ± 0.0044 Å[a)]
D_J	4.63 ± 0.03 kc[b)]
D_{JK}	-6.17 ± 0.05 kc[b)]
ζ_4	-0.35 ± 0.02[c)]
r_e	1.708 Å[d)]
θ	95.9°

a) Ref. 22 b) Ref. 27
c) The error was estimated by the present author.
d) Assumed.

stretching force constants, F_{11} and F_{33}, are larger than the bending force constants, F_{22} and F_{44} respectively. Since such is not necessarily the case for the dotted curves, they should be abandoned. Thus, for a given set of F_{12} and F_{34}, all of the other force constants can be determined uniquely.

The mean amplitudes of $AsCl_3$ were calculated for the various values of F_{12} and F_{34}. The force constants allowed by the two observed mean amplitudes, l(As–Cl)$=0.0470 \pm 0.0024$ Å and l(Cl–Cl)$=0.0945 \pm 0.0063$ Å,[22)] and the four vibrational frequencies are shown by the shaded area in Fig. 2. The corresponding values of the other force constants were determined from the solid curves in Figs. 1a and b. The values of the force constants in the symmetry coordinates thus determined are listed in Table 2, along with those in the internal coordinates.

The force constants of AsF_3 reported by earlier authors are listed in Table 3, along with the spectro-

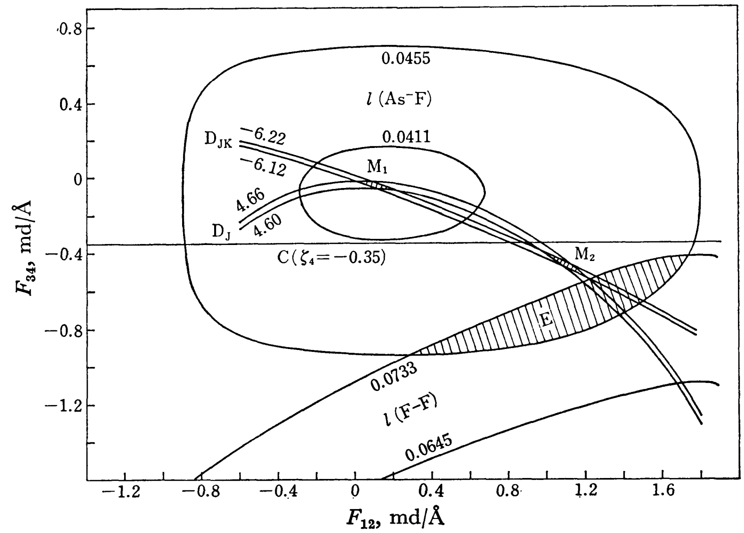

Fig. 3. Comparison of the allowed regions of the force field of AsF_3 which are compatible with the observed values of two mean amplitudes at 292°K (E), two centrifugal distortion constants (M_1 and M_2) and a Coriolis coupling constant (C).

scopic and structural data used in their calculations. The force constants of AsF_3 allowed by the observed mean amplitudes given in Table 4 are shown by the E region of Fig. 3. They are inconsistent with the force constants listed in Table 3.

The force constants reported by Levin and Abramowitz[28] and by Hoskins[29] were obtained by using the Coriolis constants, ζ_3 and ζ_4, which were estimated from the P–R splittings of ν_3 and ν_4 infrared bands respectively. The values of the Coriolis constants thus estimated depend on the assumed values of the bond angles. The value of $(\zeta_3+\zeta_4)$ given by the sum rule[31] also depends on the molecular geometry:

$$\zeta_3 + \zeta_4 = I_c^e/(2I_b^e) - 1. \qquad (12)$$

Here I_c^e and I_b^e are the equilibrium moments of inertia about the symmetry axis and about an axis perpendicular to it respectively. The theoretical values of $(\zeta_3+\zeta_4)$ are -0.22 for the bond angle of 102° and -0.29 for the bond angle of 95.9°.

For the bond angle of 95.9°, the Coriolis constant, ζ_4, was estimated to be -0.35 from the P–R separation of ν_4, 26.7 cm^{-1},[28,29] by the use of the relations given by Edgell and Moynihan.[32] Similarly, the P–R separation of ν_3, 15.4 cm^{-1},[29] led to $\zeta_3=0.32$. However, these values did not satisfy the sum rule. Since the position of the P-branch of the ν_3 band had been very obscure,[29,33] ζ_3 was not included in the present calculation of the force constants. By using the relation between ζ_4 and the force constants,[31] F_{34} was determined to be -0.35 md/Å from the ζ_4 value of -0.35.

The force constants reported by Mirri[27] had been obtained by using the centrifugal distortion constants, D_J and D_{JK}, observed by microwave spectroscopy. Since the bond angle of 98° had been used in her calculation, it was desirable to follow her calculation using the bond angle of 95.9°. The centrifugal constants were calculated from the force constants according to the theory of the semi-rigid rotator.[34,35] The allowed values of the force constants are shown by the two regions, M_1 and M_2, in Fig. 3. It is noticeable that two sets of solutions are present. The force constants reported by Mirri correspond to the M_1 region.

Although there exists no set of force constants compatible with the above five observed quantities, the force constants represented by the M_2 region satisfy all the observed values comparably well. The final values of the force constants of AsF_3 were determined by the least-squares method.[36] The off-diagonal force constants, F_{12} and F_{34}, are chosen as parameters, while the observed values to be fitted are the l(As–F), l(F–F), D_J, D_{JK}, and ζ_4 values given in Table 4. The weights were taken to be inversely proportional to the squares of errors, ε_j, estimated in Table 4. That is, the most probable set of parameters was determined by the following condition:

$$V^*PV = \sum_{j=1}^{5} \left(\frac{m_j^{\rm obs} - m_j^{\rm calc}}{\varepsilon_j} \right)^2 = \text{minimum}. \qquad (13)$$

The standard errors of parameters were evaluated as:

$$\sigma_i = \sqrt{B_{ii}^{-1} \frac{V^*PV}{3}} \,. \qquad (14)$$

Here the notations correspond to those used in Ref. 36. The most probable set of force constants is given in Table 5, along with the limit of errors.

TABLE 5. THE MOST PROBABLE SET OF THE FORCE CONSTANTS OF AsF_3 WITH THE ESTIMATED LIMITS OF ERRORS (in md/Å unit)

Symmetry coordinate		Internal coordinate	
F_{11}	5.39±0.03	f_r	4.75±0.03
F_{12}	0.95±0.26	f_{rr}	0.32±0.02
F_{22}	0.64±0.09	f_θ	0.45±0.05
F_{33}	4.42±0.02	$f_{\theta\theta}$	0.10±0.04
F_{34}	−0.39±0.13	$f_{r\theta}$	0.45±0.13
F_{44}	0.35±0.02	$f_{r\theta'}$	0.06±0.17

TABLE 6. COMPARISON OF THE OBSERVED VALUES OF THE MEAN AMPLITUDES AND SPECTROSCOPIC CONSTANTS WITH THE CALCULATED VALUES OBTAINED BY USING THE FORCE CONSTANTS GIVEN IN TABLES 2 AND 5

(l and D are in Å and kc units, respectively)

	Obsd	Calcd
(a) $AsCl_3$		
l (As–Cl)	0.0470±0.00024[a]	0.0487±0.0002
l (Cl–Cl)	0.0945±0.0063[a]	0.0989±0.0018
D_J		0.71 ±0.05
D_{JK}		−1.06 ±0.09
ζ_3		0.34 ±0.14
ζ_4		−0.55 ±0.14
(b) AsF_3		
l (As–F)	0.0433±0.0022[a]	0.0422±0.0013
l (F–F)	0.0689±0.0044[a]	0.0761±0.0026
D_J	4.63 ±0.03[b]	4.59 ±0.46
D_{JK}	−6.17 ±0.05[b]	−6.22 ±1.1
ζ_3		0.03_5 ±0.08
ζ_4	−0.35 ±0.02	-0.32_6 ±0.08

a) Ref. 22. b) Ref. 27.

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31) J. H. Meal and S. R. Polo, *J. Chem. Phys.*, **24**, 1126 (1956).

32) W. F. Edgell and R. E. Moynihan, *ibid.*, **45**, 1205 (1966).

33) L. C. Hoskins and R. C. Lord, *ibid.*, **43**, 155 (1965).

34) Z. I. Slawsky and D. M. Dennison, *ibid.*, **7**, 509 (1939).

35) D. Kivelson and E. B. Wilson, Jr., *ibid*, **21**, 1229 (1953).

Three times σ_i was taken to be the limit of errors.

The mean amplitudes, the centrifugal distortion constants, and the Coriolis constants of $AsCl_3$ and AsF_3 were calculated from the force constants tabulated in Tables 2 and 5; they are compared with the observed values in Table 6. Agreements are good except for the case of l(F–F). The poor agreement for l(F–F) is perhaps due to some systematic errors in the observed l(F–F) overlooked in the preceding paper.[22)]

The correlation of the mean amplitudes with the index of resolution in the analysis of the electron-diffraction data may be considered to be a possible source of systematic errors. However, it is impossible for the observed value of l(F–F) to increase while that of l(As–F) does not as long as a single index of resolution is used in the analysis. An attempt was made to take the two indices of resolution, k(As–F) and k(F–F), as independent variable parameters in the least-squares fitting of molecular scattering intensities instead of assuming that they were equal.[36)] The results are compared with those obtained in the previous analysis in Table 7. Both results were consistent within the estimated limit of errors, although appreciable changes were found in l(F–F) and k(F–F). The l(F–F) value of Column A is consistent with the calculated value given in Table 6. It is, however, very doubtful that we should prefer the values of Column A to those of Column B, which were obtained in the previous analysis, since there is no sound physical basis for assuming an independent index of resolution for each of the atom-pairs in this molecule.[*2]

TABLE 7. MOLECULAR PARAMETERS OBTAINED BY TAKING TWO INDICES OF RESOLUTION AS INDEPENENT VARIABLE PARAMETERS (COLUMN A) AND THOSE OBTAINED BY ASSUMING THAT THEY ARE EQUAL (COLUMN B)
(r_g and l in Å unit)

	A	*B*
r_g (As–F)	1.7089±0.0016	1.7089±0.0016
r_g (F–F)	2.5370±0.0055	2.5374±0.0055
l (As–F)	0.0429±0.0022	0.0433±0.0022
l (F–F)	0.0748±0.0066	0.0689±0.0044
k (As–F)	0.92 ±0.05	0.93 ±0.05
k (F-F)	1.06 ±0.13	

The P–R splitting of the ν_3 band of AsF_3 was estimated to be 22 cm^{-1} from the calculated value of the Coriolis constant, ζ_3. It is about 7 cm^{-1} larger than Hoskins' value.[29)] However, it does not seem quite inconsistent with the ν_3 band observed by Hoskins and Lord.[33)]

Zero-point Average Structure

Conversion of r_g to r_z. The r_z distance can be derived from the r_g distance observed by ED. The r_g distance has the following relation to the equilibrium distance, r_e:[10)]

$$r_g = r_e + \langle \Delta z \rangle + \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2r_e} + \delta r_{\mathrm{rot}}, \qquad (15)$$

where the z-axis of the local Cartesian displacement coordinates is taken along the equilibrium positions of the atoms. Here $< \;\; >$ denotes the thermal average, $<\Delta z>$ and δr_{rot} are the stretchings due to anharmonic vibration and centrifugal force respectively, and $<\Delta x^2>$ and $<\Delta y^2>$ are perpendicular amplitudes. Since r_z is equal to $r_e + <\Delta z>_{0^\circ \mathrm{K}}$, it is necessary to calculate the following three terms in order to convert r_g to r_z:

1. Centrifugal stretching, δr_{rot}
2. Stretching due to perpendicular thermal motion, $(<\Delta x^2>+<\Delta y^2>)/2r_e$, and
3. Thermal extension of $<\Delta z>$, $\delta<\Delta z> \equiv <\Delta z>_{\mathrm{T}} - <\Delta z>_0$.

The centrifugal terms for $AsCl_3$ and AsF_3 were estimated by using the formulas derived by Iwasaki and Hedberg[37)] by balancing the centrifugal force with Hooke's restoring force. The sum of the perpendicular mean amplitudes was calculated by the use of the formula expressed by Cyvin's $\sum$ matrix,[38)] which was derived as shown in the Appendix.

The cubic potential constants must be known if we are to calculate the thermal change in $<\Delta z>$, but they have not been available for almost all pyramidal XY_3 molecules. For X–Y bonds, however, the Morse potential for diatomic molecules can be used to estimate $\delta<\Delta r>$ as:

$$\delta \langle \Delta r \rangle = \frac{3}{2} a_3 \delta \langle \Delta r^2 \rangle, \qquad (16)$$

where a_3 is the anharmonicity parameter of the Morse potential.[39)] By using the following relation:

$$\langle \Delta r \rangle = \langle \Delta z \rangle + (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2r_e, \qquad (17)$$

the thermal extension of $<\Delta z>$ for the X–Y bonds of $AsCl_3$ and AsF_3 was estimated as follows:

$$\delta \langle \Delta z \rangle = \frac{3}{2} a_3 \delta \langle \Delta r^2 \rangle - \delta((\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2r_e). \qquad (18)$$

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

[*2] Added in Proof: According to a recent electron-diffraction investigation by Clippard and Bartell (*Inorg. Chem.*, **9**, 805 (1970)), the mean amplitudes of AsF_3 are 0.048±0.003 Å and 0.078±0.003 Å for l(As–F) and l(F–F) respectively. The l(F–F) value is in good agreement with the calculated value given in Table 6, while the l(As–F) value is not.

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

38) S. J. Cyvin, *Spectrochim. Acta*, **15**, 828 (1959).

39) K. Kuchitsu and Y. Morino, This Bulletin, **38**, 805, 814 (1965).

The a_3 parameter was set as approximately equal to 2 Å^{-1}.[40] The above diatomic approximation is, however, not appropriate for non-bonded pairs. The thermal extension of $\langle\Delta z\rangle_{Y-Y}$ for $AsCl_3$ and AsF_3 was estimated by assuming that the thermal change of the average angle was negligible.[14] That is, the following approximation was used:

$$\delta\langle\Delta z\rangle_{Y-Y} = 2\delta\langle\Delta z\rangle_{X-Y}\sin\frac{\theta}{2}\,. \qquad (19)$$

The values of various correction terms were calculated for $AsCl_3$ and AsF_3 by using the potential constants listed in Tables 2 and 5. The results are tabulated in Table 8.

Table 8. Numerical values of the correction terms for reducing r_g to r_z (in 10^{-4} Å unit)

	$AsCl_3$		AsF_3	
	As–Cl	Cl–Cl	As–F	F–F
$(\delta r_{\mathrm{rot}})_T$	6	15	5	6
$\langle\Delta r\rangle_T$	72		53	
$\left(\dfrac{\langle\Delta x^2\rangle+\langle\Delta y^2\rangle}{2r_e}\right)_T$	25	12	20	12
$\langle\Delta z\rangle_T$	47	71	33	49
$(\delta r_{\mathrm{rot}})_0$	0	0	0	0
$\langle\Delta r\rangle_0$	54		48	
$\left(\dfrac{\langle\Delta x^2\rangle+\langle\Delta y^2\rangle}{2r_e}\right)_0$	10	5	12	7
$\langle\Delta z\rangle_0$	44	66	36	54
$\langle\Delta z\rangle_T-\langle\Delta z\rangle_0$	3	5	−3	−5
r_g-r_z	34 (±3)	32 (±9)	22 (±3)	13 (±9)

Note: T is equal to 291°K and 292°K for $AsCl_3$ and AsF_3, respectively. The values in parentheses are the uncertainties estimated.

Conversion of B_0 to B_z. The average rotational constant, B_z, corresponding to the r_z-structure can be derived by adding some correction terms to the effective constant, B_0.

$$B_z = B_0 + \delta B_{\mathrm{vib}} + \delta B_{\mathrm{cent}} + \delta B_{\mathrm{elect}}. \qquad (20)$$

Here δB_{vib}, δB_{cent} and $\delta B_{\mathrm{elect}}$ are the vibrational, centrifugal, and electronic corrections respectively. For the pyramidal XY_3 molecule, Shaffer[41] and Nielsen[1] derived the relation of the rotational constant, B_0, to the equilibrium rotational constant, B_e, by neglecting the motion of electrons. The first two correction terms, δB_{vib} and δB_{cent} in Eq. (20) can be calculated by using their results.[13]

The last term in Eq. (20) can be estimated if the g tensor of the rotational magnetic moment is known.[7] Since the values of the g tensor were not available for AsF_3 and $AsCl_3$, $\delta B_{\mathrm{elect}}$ was assumed to be zero in the present study. The error caused by this assumption is, however, perhaps negligibly small since $\delta B_{\mathrm{elect}}$ is inferred to be, at most, ten percent of δB_{vib}, judging from the results on formaldehyde.[7] The values of (B_0-B_z) calculated for $As^{35}Cl_3$, $As^{37}Cl_3$ and AsF_3 are tabulated in Table 9, along with their uncertainties due to those of the force constants.

Table 9. Estimated values of (B_0-B_z) (in Mc unit)

	$As^{35}Cl_3$	$As^{37}Cl_3$	AsF_3
B_0-B_z	2.70±0.04	2.52±0.04	10.93±0.41

Average Structures. The r_z-structures of $AsCl_3$ and AsF_3 were derived from the observed r_g distances[22] by using the correction values listed in Table 8. The moment of inertia, $I_b{}^z$, and the rotational constant, B_z, were calculated from the r_z distances. The results are summarized in Table 10.

The B_z constants were also obtained from the microwave B_0 values and the estimated values of (B_0-B_z). They are compared with the diffraction values in Table 10. There is no inconsistency between the experimental results of the microwave study and those of the electron-diffraction study.

Table 10. Zero-point average structures and average rotational constants derived from ED and MW data (r_z, $I_b{}^z$, and B_z are in Å, amu. Å^2, and Mc units, respectively)

	ED	MW
r_z(As–^{35}Cl)	2.1587±0.0034	2.1619±0.0024
r_z(^{35}Cl–^{35}Cl)	3.2741±0.0095	3.280±0.022
θ_z(^{35}Cl As^{35}Cl)	98°38′±36′	98°43′±1°3′
$I_b{}^z$($As^{35}Cl_3$)	234.93±0.82	235.66±0.03
B_z($As^{35}Cl_3$)	2151.2±7.5	2144.5±0.3
$I_b{}^z$($As^{37}Cl_3$)	246.72±0.88	247.47±0.04
B_z($As^{37}Cl_3$)	2048.3±7.3	2042.2±0.3
r_z(As–F)	1.7067±0.0017	
r_z(F–F)	2.5361±0.0056	
θ_z(FAsF)	95°59′±22′	
$I_b{}^z$(AsF_3)	85.99±0.22	86.1232±0.0061
B_z(AsF_3)	5877±15	5868.04±0.41

Table 11. Isotope effects in the r_z distances of $AsCl_3$ (in 10^{-4} Å unit)

	$As^{35}Cl_3$		$As^{37}Cl_3$	
	As–Cl	Cl–Cl	As–Cl	Cl–Cl
$\langle\Delta r\rangle_{0^\circ\mathrm{K}}$	54		53	
$\left(\dfrac{\langle\Delta x^2\rangle+\langle\Delta y^2\rangle}{2r_e}\right)_{0^\circ\mathrm{K}}$	10		10	
$\langle\Delta z\rangle_{0^\circ\mathrm{K}}$	44	66	43	64

r_z(As–^{35}Cl) − r_z(As–^{37}Cl) = 1(±1)

r_z(^{35}Cl–^{35}Cl) − r_z(^{37}Cl–^{37}Cl) = 2(±3)

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[40] E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1131 (1955).

[41] W. H. Shaffer, *ibid.*, **9**, 607 (1941).

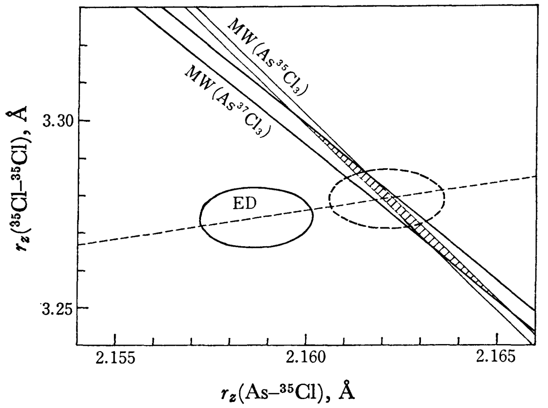

Fig. 4. r_z-Structures of As^{35}Cl$_3$ determined by microwave spectroscopy and electron diffraction. The values allowed by the MW rotational constants are shown by shadows. The ellipse described in solid line shows the ED values, which do not include the error estimated for the scale factor, while the dashed ellipse shows the ED values corrected for the scale factor. The most probable r_z values are obtained from the overlapping regions of the dashed ellipse and the MW region.

In the case of AsCl$_3$, the r_z-structures could be determined from only the microwave data by a tentative estimation of the isotope effects on the r_z distances, as is shown in Table 11. The relations of the r_z distances of As^{35}Cl$_3$ given by the two rotational constants are shown in Fig. 4. The two parallel lines correspond to the limits of errors of a rotational constant. The uncertainties in isotope effects are included as the spread of the curve, MW(As^{37}Cl$_3$). The structures corresponding to the shaded area are compared with those determined by ED in Table 10. It may be noted that the error of the bond angle is about twice as large as that in the results for ED.

The errors due to the uncertainty of the scale factors are the largest possible systematic errors in the results of ED, so that a more precise structure can be expected if the scale-factor errors are eliminated by using the microwave rotational constants.

In Figs. 4 and 5, the solid ellipses show the errors associated with the diffraction values, without including the errors for the scale factors. It is mainly because of the scale-factor errors that the centers of the ellipses do not lie on the microwave lines. New ellipses were obtained by shifting the centers of the ellipses along the dashed lines, on which the ratio of r_z(As–Y) to r_z(Y–Y) was kept constant. The most probable average distances were obtained from the overlapping regions of the new ellipses and the microwave lines. They are listed in Table 12, along with the corresponding r_g distances. Because of the steep slopes of the microwave lines, the errors in the As–Y distances became very small.

Table 12. r_z and r_g structures of As^{35}Cl$_3$, As^{37}Cl$_3$ and AsF$_3$ obtained by the combined use of ED and MW data (r in Å unit)

	As^{35}Cl$_3$	As^{37}Cl$_3$	AsF$_3$
r_z(As–Y)	2.1621 ±0.0009	2.1620 ±0.0009	1.7080 ±0.0004
r_z(Y–Y)	3.2789 ±0.0075	3.2787 ±0.0075	2.5380 ±0.0048
θ_z	98°38′±22′	98°38′±22′	95°58′±17′
r_g(As–Y)	2.1655 ±0.0010	2.1654 ±0.0010	1.7102 ±0.0005
r_g(Y–Y)	3.2821 ±0.0076	3.2819 ±0.0076	2.5393 ±0.0050
θ_g	98°33′±22′	98°33′±22′	95°52′±17′

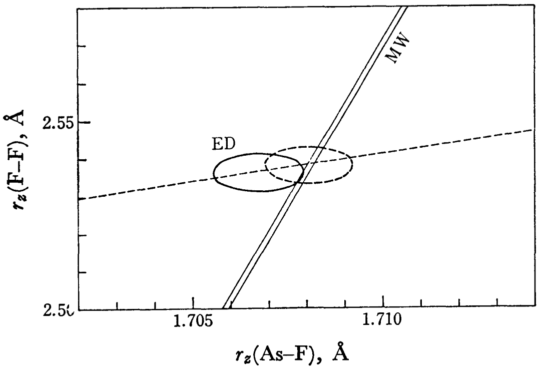

Fig. 5. r_z-Structures of AsF$_3$ determined by electron diffraction and microwave spectroscopy.
See the caption of Fig. 4.

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Appendix

Calculation of the Perpendicular Mean Amplitudes. For pyramidal XY$_3$ molecules, the formulas expressed in terms of the $\sum$ matrix[39] for calculating the parallel amplitudes $\langle\Delta z^2\rangle$ $(=l^2)$ have already been derived,[26] but those for the perpendicular amplitudes have not yet been presented. The formulas for calculating the sum of the perpendicular amplitudes, $\langle\Delta x^2\rangle$ and $\langle\Delta y^2\rangle$, can be derived by using the following realtion:

$$(\langle\Delta x^2\rangle+\langle\Delta y^2\rangle)_{ij}=\langle(\rho_i-\rho_j)^2\rangle-\langle\Delta z^2\rangle_{ij}. \qquad \text{(A1)}$$

Here ρ_i and ρ_j are the displacement vectors of the i and j atoms respectively.

The internal coordinates can be expressed in terms of the displacement vectors, ρ_i, and the unit vectors, e_{ij}, which start from the i atom and which points to the j atom. The relation was derived in a matrix form as:

$$\boldsymbol{R}=\boldsymbol{T\rho}, \qquad \text{(A2)}$$

where:

$$\boldsymbol{\rho}=\begin{bmatrix}\rho_1\\ \rho_2\\ \rho_3\\ \rho_4\end{bmatrix}, \qquad \text{(A3)}$$

and:

$$
\boldsymbol{T} = \begin{pmatrix}
-e_{14} & 0 & 0 & e_{14} \\
0 & -e_{24} & 0 & e_{24} \\
0 & 0 & -e_{34} & e_{34} \\
0 & \frac{1}{s}e_{34}-\frac{c}{s}e_{24} & \frac{1}{s}e_{24}-\frac{c}{s}e_{34} & \frac{c-1}{s}(e_{24}+e_{34}) \\
\frac{1}{s}e_{34}-\frac{c}{s}e_{14} & 0 & \frac{1}{s}e_{14}-\frac{c}{s}e_{34} & \frac{c-1}{s}(e_{34}+e_{14}) \\
\frac{1}{s}e_{24}-\frac{c}{s}e_{14} & \frac{1}{s}e_{14}-\frac{c}{s}e_{24} & 0 & \frac{c-1}{s}(e_{14}+e_{24})
\end{pmatrix}. \tag{A4}
$$

Here s and c are abbreviations of the sine and the cosine of the bond angle, θ, respectively. With this notation, the $\boldsymbol{G}$ matrix in the symmetry coordinates was expressed as:

$$\boldsymbol{G} = \boldsymbol{UTM}^{-1}\boldsymbol{T}'\boldsymbol{U}', \tag{A5}$$

where $'$ denotes transposed matrices, where $\boldsymbol{U}$ is a matrix defined by Eq. (2b), and where:

$$\boldsymbol{M}^{-1} = \begin{pmatrix} \mu_Y & & & \\ & \mu_Y & & \\ & & \mu_Y & \\ & & & \mu_X \end{pmatrix}. \tag{A6}$$

The elements of the $\boldsymbol{G}$ matrix are given in Eqs. (4) and (5).

The ρ_i vectors could be expressed in terms of the symmetry coordinates by using Eqs. (2b), (A2), and (A5):

$$\boldsymbol{\rho} = \boldsymbol{M}^{-1}\boldsymbol{T}'\boldsymbol{U}'\boldsymbol{G}^{-1}\boldsymbol{S}. \tag{A7}$$

This is essentially equal to the relation derived by Morino and Hirota.[42] By using Eq. (A7), the $\langle(\rho_i-\rho_j)^2\rangle$ term in Eq. (A1) was expressed in terms of the $\sum$ matrix elements after a rather lengthy manipulation. From the results, the contribution of the parallel amplitudes given in Eqs. (6) and (7) were subtracted, and the following results were obtained:

$$(\langle\Delta x^2\rangle+\langle\Delta y^2\rangle)_{X-Y} = \frac{1}{6}\frac{1+c}{1+2c}\Sigma_{22} + \frac{2}{3}\frac{1+c}{2+c}\Sigma_{44} + \frac{2(1-c)(1+2c)}{2+c}\mu_X{}^2\cdot P \tag{A8}$$

$$(\langle\Delta x^2\rangle+\langle\Delta y^2\rangle)_{Y-Y} = \frac{2}{3}\left\{\sin^2\frac{\theta}{2}\Sigma_{33} - 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\Sigma_{34} + \cos^2\frac{\theta}{2}\Sigma_{44}\right\} + \frac{2}{3}(1+2c)\mu_Y{}^2\cdot P, \tag{A9}$$

where:

$$P = \{(2+c)^2\Sigma_{33} + 2(2+c)s\Sigma_{34} + s^2\Sigma_{44}\}/\{3(1-c)\mu_X + (2+c)\mu_Y\}^2. \tag{A10}$$

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[42] Y. Morino and E. Hirota, *J. Chem. Phys.*, **23**, 737 (1955).