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The Molecular Structure and Force Constants of Antimony Tribromide as Determined by Gas-phase Electron Diffraction

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The molecular structure and mean amplitudes of SbBr_3 at 102°C have been determined by the sector-microphotometer method of gas-phase electron diffraction to be as follows: $r_g(\text{Sb-Br}) = 2.490 \pm 0.003 \text{ \AA}$, $r_g(\text{Br-Br}) = 3.76 \pm 0.01 \text{ \AA}$, $\theta_\alpha = 98.2^\circ \pm 0.6^\circ$, $l(\text{Sb-Br}) = 0.060 \pm 0.003 \text{ \AA}$ and $l(\text{Br-Br}) = 0.15 \pm 0.01 \text{ \AA}$. General quadratic force constants have been determined from the observed mean amplitudes and vibrational frequencies. The molecular structure supports the validity of the empirical rules between a bond length and the covalent radii and electronegativities of its constituent atoms. An empirical equation, $\theta(\text{YXY}) = 92 + 8x_{\text{X}} - 3x_{\text{Y}} (+x_{\text{Z}})$, has been proposed for the bond angles of Vb-group halides, $(\text{Z})\text{XY}_3$, and the electronegativities, x .

Precise measurements of the molecular structures of simple inorganic compounds are essential to our understanding of chemical bonds. Recently, many of the molecular structure of trihalides of Vb-group atoms have been reinvestigated, and the regularity of the structures has been discussed in connection with the covalent radii and electronegativities.¹⁻⁴⁾ However, we do have no up-to-date data on the molecular structures of several Vb-group trihalides.^{3,4)} The main purpose of the present study is to improve the structural data of antimony tribromide by the sector-microphotometer method of gas-phase electron diffraction. The structural parameters obtained by previous electron diffraction studies based on the visual method were: $r(\text{Sb-Br}) = 2.52 \pm 0.02 \text{ \AA}$, $\theta(\text{Br-Sb-Br}) = 96^\circ \pm 2^\circ$;⁵⁾ $r(\text{Sb-Br}) = 2.51 \pm 0.02 \text{ \AA}$, and $\theta(\text{Br-Sb-Br}) = 97^\circ \pm 2^\circ$.⁶⁾

The general quadratic force field of antimony tribromide has not yet been reported. For its determination, some supplementary information in addition to the vibrational frequencies is required. Spectroscopic data, such as the Coriolis coupling or centrifugal distortion constants, are not available, but the vibrational mean amplitudes, as measured by electron diffraction, can be used for the force-field determination.⁷⁻⁹⁾ It is another purpose of the present study to determine the general force field of Sb-Br_3 by a combined use of the vibrational frequencies and the mean amplitudes.

Experimental

The sample of antimony tribromide was an extra-pure reagent obtained from Nakarai Chemicals, Inc. The sample was vaporized by using a high-temperature nozzle.¹⁰⁾ Diffraction photographs were taken on Fuji process hard plates with a diffraction unit equipped with an r^3 -sector.¹¹⁾ The experimental conditions were as follows: camera length, 12.39 cm; accelerating voltage, about 42 kV; exposure time,

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

2) F. B. Clippard, Jr., and L. S. Bartell, *ibid.*, **9**, 805 (1970).

3) S. Konaka and M. Kimura, *This Bulletin*, **43**, 1693 (1970).

4) K. Kuchitsu, "Gas Electron Diffraction, Combined Use of Electron-Diffraction and Spectroscopic Methods for Determining Molecular Geometry and Motions," MTP International Review of Science, A Biennial Series, G. Allen, Ed., 1972.

5) A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Farad. Soc.*, **33**, 852 (1937).

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

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

8) M. Iwasaki and K. Hedberg, *ibid.*, **36**, 594 (1962).

9) S. Konaka, *This Bulletin*, **43**, 3107 (1970).

10) M. Ogasawara and M. Kimura, unpublished.

11) Y. Murata, K. Kuchitsu, and M. Kimura, *Japan. J. Appl. Phys.*, **9**, 591 (1970).

3–5 min; electron-beam current, about 0.28 μ A; nozzle temperature, about 102°C. The pressure in the diffraction chamber during exposures was about 7×10^{-5} Torr. The diffraction patterns of CS₂ molecules were taken at the same nozzle temperature just after those of the sample in order to determine the scale factor accurately. The developing and photometric process were described in previous papers.^{3,12)} Eight plates, five for SbBr₃ and three for CS₂, taken in the same sequence of exposure, were selected for structure analysis.

Data Analysis

The intensities converted from the densities according to the $E=D(1+0.03D)$ relation were corrected for the imperfection of the sector shape and then leveled by means of the theoretical backgrounds.¹³⁾ The elastic and inelastic scattering factors were taken from the literature.^{14–16)} The experimental background and molecular intensities were determined according to our routine procedure.^{3,12)} The interatomic distances, r_a , the mean amplitudes, l , and the index of resolution, k , were determined by the least-squares fittings of experimental molecular intensities to the corresponding theoretical expression. The asymmetry parameter, $\kappa_{\text{Sb-Br}}$, was fixed at $1.1 \times 10^{-5} \text{ \AA}^3$, which was estimated by diatomic approximation,¹⁷⁾ and the $\kappa_{\text{Br-Br}}$ was assumed to be zero.

The observed molecular intensity, $qM(q)$, and the theoretical one calculated by the use of best-fit parameters are shown in Fig. 1. The least-squares results are summarized in Table 1. An error matrix is given in Table 2. The thermal average distances, r_g , which were obtained as the sum of r_a and l^2/r_a , and the mean amplitudes are listed in Table 3, along with the estimated limits of error.

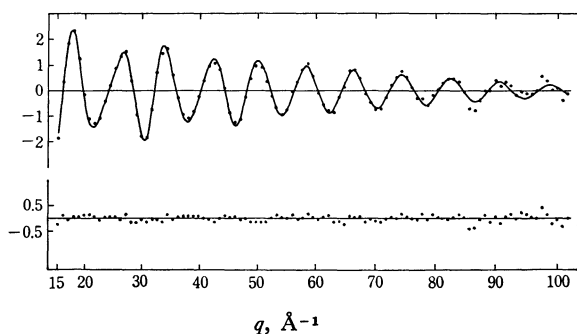


Fig. 1. Molecular intensity (dots for observed values and the solid curve for the best-fit theoretical intensity and the residuals).

12) S. Konaka and M. Kimura, This Bulletin, **46**, 404 (1973).

13) Numerical experimental data of the leveled total intensity has been deposited with the Chemical Society of Japan. A copy may be secured by citing the document number (Document No. 7306).

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16) R. F. Pohler and H. P. Hanson, *J. Chem. Phys.*, **42**, 2347 (1965).

17) K. Kuchitsu, This Bulletin, **40**, 505 (1967).

TABLE 1. RESULTS OF THE LEAST-SQUARES ANALYSIS
(r AND l IN \AA UNITS)

	Average ^{a)}	σ_1 ^{b)}	σ_2 ^{b)}
k	0.904	0.011	0.009
$r_a(\text{Sb-Br})$	2.4882	0.0006	0.0004
$l(\text{Sb-Br})$	0.0601	0.0008	0.0007
$r_a(\text{Br-Br})$	3.7549	0.0044	0.0012
$l(\text{Br-Br})$	0.1482	0.0033	0.0014

a) The averages of the results for five plates.

b) The definitions of σ_1 and σ_2 are given in Ref. 3.

TABLE 2. ERROR MATRIX^{a)}

	k	$r_a(\text{Sb-Br})$	$l(\text{Sb-Br})$	$r_a(\text{Br-Br})$	$l(\text{Br-Br})$
k	226	6	53	43	61
$r_a(\text{Sb-Br})$		12	-1	3	3
$l(\text{Sb-Br})$			17	10	14
$r_a(\text{Br-Br})$				86	-5
$l(\text{Br-Br})$					65

a) Units for r_a and l are 10^{-4} \AA and that for the index of resolution k dimensionless.

TABLE 3. MOLECULAR PARAMETERS OF ANTIMONY TRIBROMIDE AT 375 K AS DETERMINED BY ED
(r AND l IN \AA UNITS)

	Sb-Br	Br-Br
r_g	2.490 ± 0.003	3.761 ± 0.012
l	0.060 ± 0.003	0.148 ± 0.009
r_a	2.484 ± 0.003	3.755 ± 0.012
$\theta_a(\text{BrSbBr})$	$98.2 \pm 0.6^\circ$	

Results and Discussion

Force Constants. In order to determine the quadratic force constants of antimony tribromide, the observed mean amplitudes were used together with the four fundamental frequencies measured in the liquid state.¹⁸⁾ The general quadratic force field can be expressed in terms of the symmetry coordinates as follows:⁹⁾

$$2V = F_{11}S_1^2 + 2F_{12}S_1S_2 + F_{22}S_2^2 + F_{33}(S_{3a}^2 + S_{3b}^2) + 2F_{34}(S_{3a}S_{4a} + S_{3b}S_{4b}) + F_{44}(S_{4a}^2 + S_{4b}^2). \quad (1)$$

Here the symmetry coordinates are taken as:

$$S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3),$$

$$S_2 = \frac{1}{\sqrt{3}}r_e(\Delta\theta_{12} + \Delta\theta_{23} + \Delta\theta_{31}),$$

$$S_{3a} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2),$$

$$S_{4a} = \frac{1}{\sqrt{2}}r_e(\Delta\theta_{23} - \Delta\theta_{31})$$

$$S_{3b} = \frac{1}{\sqrt{6}}(\Delta r_1 + \Delta r_2 - 2\Delta r_3),$$

$$S_{4b} = \frac{1}{\sqrt{6}}r_e(\Delta\theta_{23} + \Delta\theta_{31} - 2\Delta\theta_{12}),$$

18) A. T. Kozulin and L. V. Biryulina, *Opt. Spectrosc.*, **28**, 135 (1970).

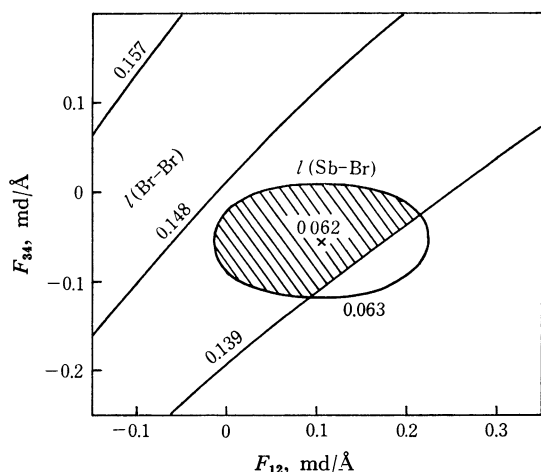


Fig. 2. Force constants of SbBr₃ allowed by the observed mean amplitudes at 375 K. An elliptical curve indicates the force constants giving the boundary of the observed value, 0.063 Å, for $l(\text{Sb-Br})$ and three parallel curves indicate those giving the observed value, 0.148 Å, and its boundary values, 0.157 Å and 0.139 Å, for $l(\text{Br-Br})$.

where Δr_i denotes the stretching of the i -th bond length; $\Delta \theta_{jk}$, the increase in the valence angle opposite to r_i , and r_e , the equilibrium bond length.

For given values of the off-diagonal force constants, F_{12} and F_{34} , the diagonal constants can be determined uniquely so as to reproduce the observed frequencies, under the condition that the stretching force constants, F_{11} and F_{33} , are larger than the bending ones, F_{22} and F_{44} respectively.⁹⁾ From the set of force constants, the corresponding mean amplitudes can be calculated. Figure 2 illustrates the force constants, F_{12} and F_{34} , allowed by the observed mean amplitudes. The shaded area denotes the force field compatible with all the experimental frequencies and mean amplitudes. The force constants thus determined are listed in Table 4.

TABLE 4. FORCE CONSTANTS OF SbBr₃ DETERMINED FROM THE OBSERVED MEAN AMPLITUDES AND VIBRATIONAL FREQUENCIES (IN md/Å UNITS)

A ₁ species		E species	
F_{11}	1.72 ± 0.17	F_{33}	1.33 ± 0.07
F_{12}	0.10 ± 0.11	F_{34}	-0.05 ± 0.07
F_{22}	0.14 ± 0.01	F_{44}	0.12 ± 0.01

Structure. By using the above force constants, the r_g distances were converted to the r_a distances. The stretchings due to the perpendicular thermal vibrations were computed to be 0.0047 and 0.0021 Å for Sb-Br and Br-Br respectively. The calculated values for the centrifugal stretching were 0.0011 and 0.0034 Å for the bonded and non-bonded pairs respectively. The r_a distances and the corresponding bond angle are given in Table 3. Both the bond length (r_g) and the bond angle agree with the previous electron-diffraction values, obtained by the visual method, within their estimated limits of error.

The bond length of the trihalides of group-Vb elements, XY₃, can be given approximately by a modified

Schomaker-Stevenson rule as:⁴⁾

$$r_{X-Y} = r_X + r_Y - c|x_X - x_Y|.$$

Here, r_X and x_X are the covalent radius and the electronegativity of the X atom respectively, and c is an empirical constant which takes different values for the fluorides and the other halides.^{4,19)} In a previous paper,³⁾ the present authors proposed a slightly different empirical equation for the trihalides of group-Vb elements:

$$r_{X-Y} = r_X + r_Y - 0.06(x_X - x_Y)^2. \quad (4)$$

The Sb-Br distance estimated by Kuchitsu using Eq. (3) with $c=0.04$ Å is 2.51 Å,⁴⁾ while Eq. (4) gives a value of 2.49 Å for the covalent radii²⁰⁾ and electronegativities²¹⁾ taken from the literature. Both are in agreement with the present observed value, 2.490 Å.

It has been found by recent experimental work⁴⁾ that the bond angles in the group-Vb-element trihalides generally decrease with an increase in the electronegativities of halogens relative to the central atoms, in accordance with the valence-shell electron-pair repulsion (VSEPR) theory proposed by Gillespie.²²⁾ The observed bond angle in SbBr₃ confirms this finding, for it has a value between the angles in SbCl₃ and SbI₃, and smaller than those in PBr₃ and AsBr₃ (Table 5). The relationship between the bond angles and the electronegativities has been stated only qualitatively in previous studies. By examining the experimental data of the bond angles accumulated so

19) Equation (3) was originally proposed by Schomaker and Stevenson with $c=0.09$ Å as applicable to more general cases: V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 37 (1941).

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

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

26) P. Kisliuk and C. H. Townes, *ibid.*, **18**, 1109 (1960).

27) K. Kuchitsu, T. Shibata, A. Yokozeki, and C. Matsumura, *Inorg. Chem.*, **10**, 2584 (1971).

28) D. M. Barnhart, cited by K. Hedberg, *Trans. Amer. Crystallogr. Assoc.*, **2**, 79 (1966).

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

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

31) C. Matsumura and H. Takeo, "Symposium on Molecular Structure," Fukuoka, October, 1969.

32) C. Matsumura, presented at the Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

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35) T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, **10**, 344 (1971).

36) J. H. Secrist and L. O. Brockway, *J. Amer. Chem. Soc.*, **66**, 1941 (1944).

37) R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, **46**, 357 (1967).

TABLE 5. BOND ANGLES $\theta(\text{YXY})$ OF GROUP-Vb HALIDES ZXY_3

	Obsd ^{a)}	Calcd ^{b)}		Obsd	Calcd
NF_3	102.37(3) ^{d)}	104. ₂	SbF_3	94.0(25) ^{o)}	94. ₆
NCl_3	107.1(5) ^{e)}	107. ₀		95.0(8) ^{p)}	
PF_3	97.8(2) ^{f)}	97. ₀	SbCl_3	97.2(9) ^{q)}	97. ₄
PCl_3	100.3(1) ^{g)}	99. ₈		96.8(5) ^{r)}	
	100.1(3) ^{h)}		SbBr_3	98.2(6) ^{s)}	98. ₀
PBr_3	101.0(4) ⁱ⁾	100. ₄	SbI_3	99.1 ^{t)}	98. ₈
$\text{PI}_3^{\text{c)}$	102(2) ^{j)}	101. ₂	SPF_3	100.3(3) ^{u)}	99. ₅
AsF_3	96.2(2) ^{k)}	96. ₂	SPCl_3	101.8(2) ^{v)}	102. ₃
	96.0(3) ^{l)}		$\text{SPBr}_3^{\text{c)}$	106(3) ^{w)}	102. ₉
AsCl_3	98.6(4) ^{l)}	99. ₀	OPF_3	101.3(2) ^{v)}	100. ₅
AsBr_3	99.7(3) ^{m)}	99. ₆	OPCl_3	103.3(2) ^{v)}	103. ₃
AsI_3	100.2(4) ⁿ⁾	100. ₄	$\text{OPBr}_3^{\text{c)}$	108(3) ^{w)}	103. ₉
			$\text{H}_3\text{B}\cdot\text{PF}_3$	99.8(1) ^{x)}	99. ₀

a) Values in parentheses are uncertainties to be attached to the last significant digit of the θ -values. b) Calculated by Eq. (5). c) Determined by the visual method of electron diffraction. d) Ref. 23. e) Ref. 24. f) Ref. 1. g) Ref. 25. h) Ref. 26. i) Ref. 27. j) Ref. 6. k) Ref. 2. l) Ref. 9. m) Ref. 28. n) Ref. 29. o) Ref. 30. p) Ref. 31. q) Ref. 12. r) Ref. 32. s) present results. t) Ref. 33. u) Ref. 34. v) Ref. 35. w) Ref. 36. x) Ref. 37.

far, it has been found that there exists the following simple empirical relation:

$$\theta(^{\circ}) = 92 + 8x_{\text{X}} - 3x_{\text{Y}}. \quad (5a)$$

The bond angles calculated by means of Eq. (5a) using the electronegativities²¹⁾ are all close to the experimental values, as is shown in Table 5.

According to the VSEPR theory,²²⁾ the YXY angle increases by the coordination of an atom to the lone-pair electrons of the central group-Vb atom. This has been confirmed by recent electron-diffraction work of phosphine compounds.^{34,35)} The YXY angles in ZXY_3 molecules may be approximated by the following equation, with an additional term, x_{Z} , to Eq. (5a):

$$\theta(^{\circ}) = 92 + 8x_{\text{X}} - 3x_{\text{Y}} + x_{\text{Z}}, \quad (5b)$$

where x_{Z} is the electronegativity of the coordinated Z atom. The calculated bond angles for the phosphine compounds are compared with the observed values in Table 5. Satisfactory agreements are seen except for the bromides. The elucidation of the origin of the discrepancy in SPBr_3 and OPBr_3 will be left for future investigations, as the data cited in Table 5 are those determined by the visual method.

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