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The Molecular Structure and Force Constants of Boron Trifluoride and Boron Trichloride

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The interatomic distances and the mean amplitudes of BF_3 and BCl_3 have been determined, by the sector-microphotometer method of gas electron diffraction, to be: $r_g(\mathrm{B-F})=1.3156\pm0.0044$ Å, $r_g(\mathrm{F\cdots F})=2.2733\pm0.0041$ Å, $l(\mathrm{B-F})=0.0398\pm0.0029$ Å, and $l(\mathrm{F\cdots F})=0.0541\pm0.0020$ Å for BF_3 and $r_g(\mathrm{B-Cl})=1.7421\pm0.0044$ Å, $r_g(\mathrm{Cl\cdots Cl})=3.0134\pm0.0060$ Å, $l(\mathrm{B-Cl})=0.0505\pm0.0023$ Å, and $l(\mathrm{Cl\cdots Cl})=0.0700\pm0.0023$ Å for BCl_3. The force constants have also been determined from the mean amplitudes. Their values are in good agreement with those obtained by the isotopic shifts and by the Urey-Bradley force field. The complex scattering factors for B, F, and Cl have been calculated from the Hartree-Fock potential, and it has been shown that the background intensity and the mean amplitudes of BF_3 and BCl_3 are much better accounted for by these scattering factors than by those calculated from the Thomas-Fermi potential.

The force constants of molecules are usually determined from their vibrational frequencies. In most cases, however, the number of observable frequencies is not sufficient for all the force constants in a general quadratic form of the potential function to be determined. In order to overcome this difficulty, it is a common procedure to assume a simple model such as the Urey-Bradley force field, or to use the isotopic shifts of the vibrational frequencies. A more desirable way for determining the force field directly from experiment is to make use of the phenomena closely connected with the force field of the molecule. The mean amplitudes obtained by electron diffraction have thus been used to measure the force constants of several molecules with the aid of vibrational frequencies.1-3)

The principal purpose of the present report is to determine the structure of boron trifluoride and boron trichloride as accurately as possible, and also to determine the force constants of these molecules from the experimental mean amplitudes. The resulting force constants will be compared with those obtained by other methods. The theoretical scattering factors will also be critically examined on the basis of the experimental mean amplitudes and backgrounds.

The atomic distances in boron trifluoride and trichloride were formerly determined by the visual method. The results obtained by Lévy and Brockway4) were: $r(\text{B–F})=1.30\pm0.02$ Å, $r(\text{F–F})=2.25\pm0.03$ Å, $r(\text{B–Cl})=1.73\pm0.02$ Å and $r(\text{Cl–Cl})=2.99\pm0.03$ Å, while the results obtained by Braune and Pinnow5) and those obtained by Sutton et al.6) were $r(\text{B–F})=1.31$ Å and $r(\text{B–Cl})=1.76\pm0.02$ Å respectively.

During the course of the analysis of the mean amplitudes, it has been made clear that some property of the *l-l* curve is closely related to an empirical law known in spectroscopy regarding the off-diagonal elements of the $\boldsymbol{L}$ matrix. The results will be discussed in the Appendix.

Experimental

The diffraction photographs were taken with an apparatus equipped with an r^3-sector7) at the camera length of 11.8 cm. The accelerating voltage (43—49 kV.) was automatically stabilized within 0.1%.

The sample of boron trifluoride was kindly provided by Dr. Ryohei Nakane of the Institute of Physical and Chemical Research, and that of boron trichloride, by the Central Research Institute of the Tokyo Shibaura Electric Co. The gas sample was led into the diffraction chamber through a drum-type nozzle at the temperature of 16°C for BF_3 and at 31°C for BCl_3. KEL-F stopcock grease was used to avoid the erosion of the lubricant. The vacuum of the chamber, initially 1—2 $\times10^{-5}$ mmHg, was kept under 1×10^{-4} mmHg even when the gas was introduced into the chamber. The beam current was about 0.006 μ amp., and the exposure time was about 3 minutes.

The patterns were recorded on Fuji Process Hard plates and were developed at 20°C for 5 min. with an FD-131 developer. The wavelengths of the primary electron beam were measured by using the transmission patterns of gold foil.

In order to make sure that the reference gold foil was placed exactly at the position of the diffraction center, gas patterns were also taken with the nozzle rotated around the nozzle axis by 180° by using the sample of boron trifluoride3) (Fig. 1).

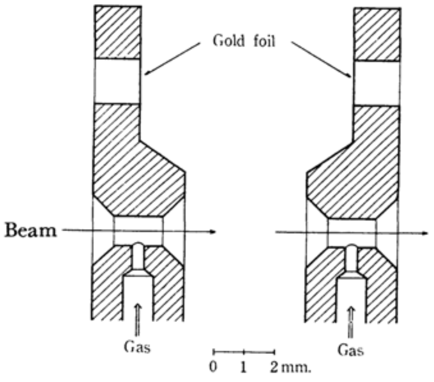

Fig. 1. Cross section of the nozzle used in the present study: normal orientation (left) and reversed orientation (right).

Photographic densities were measured using a Rigaku-Denki MP-3 microphotometer. In order to eliminate undesirable effects of the time lag of this recorder, the plates were scanned along the diameter; the charts thus obtained were measured and averaged on both sides of the center.8) Four plates at the normal position of the nozzle and three plates at the reversed position were used for the structure analysis of boron trifluoride. Six plates at the normal position were used for the analysis of boron trichloride.

The optical densities of these plates were all between 0.6 and 0.1, where the linear relation between the density and the electron intensity has been confirmed.9)

Analysis

The molecular intensity curve was obtained by drawing a smooth background line through the intensity curve, which had been corrected for the deviation of the sector shape from an ideal r^3 curve. In order to investigate the effects of atomic scattering factors on the molecular parameters, three

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

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

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

4) H. A. Lévy and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 2085 (1937).

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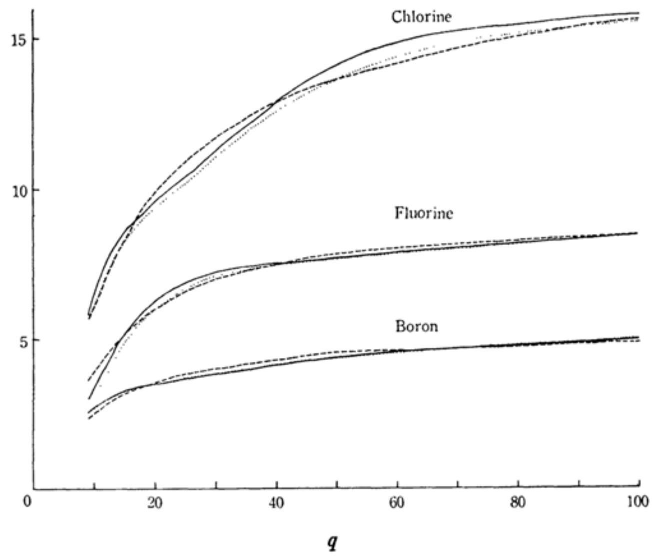

Fig. 2. The atomic scattering factors for electron diffraction.

—— $\frac{\boldsymbol{h}^2 s^2}{8\pi^2 \boldsymbol{m}\boldsymbol{e}^2} f^{\mathrm{B}} = Z - f_{\mathrm{X}}$, where f^{B} is the Born scattering factor and f_{X} is the atomic form factor for X-rays.

---- $\frac{\boldsymbol{h}^2 s^2}{8\pi^2 \boldsymbol{m}\boldsymbol{e}^2} |f|_{\mathrm{T.F.}}$, where $|f|_{\mathrm{T.F.}}$ is the absolute value of the complex scattering factor calculated from the Thomas-Fermi potential.

...... $\frac{\boldsymbol{h}^2 s^2}{8\pi^2 \boldsymbol{m}\boldsymbol{e}^2} |f|_{\mathrm{H.F.}}$, where $|f|_{\mathrm{H.F.}}$ is the absolute value of the complex scattering factor calculated from the Hartree-Fock potential.

kinds of atomic scattering factors were used for each atom (Fig. 2). The first, the Born scattering factor, f^{B}, was obtained by taking an appropriate average of the atomic form factors, f_{X}, calculated by several authors.10–13) In the first Born approximation, the scattering factor, f^{B}, is equal to $8\pi^2 \boldsymbol{m}\boldsymbol{e}^2 (Z\text{-}f_{\mathrm{X}})/\boldsymbol{h}^2 s^2$.14) The second was the complex atomic scattering factor, $|f|_{\mathrm{T.F.}} e^{i\eta_{\mathrm{T.F.}}}$, calculated by Ibers and Hoerni using the partial-waves method based on the Thomas-Fermi potential.15) The phase shift, $\eta_{\mathrm{T.F.}}$, was also used, together with the f^{B} of the first set as $f^{\mathrm{B}} e^{i\eta_{\mathrm{T.F.}}}$. The third was the scattering factor, $|f|_{\mathrm{H.F.}} e^{i\eta_{\mathrm{H.F.}}}$, calculated by the present authors by using the partial-waves method based on the Hartree-Fock potential16) (Table I). The inelastic scattering factors were taken from the table given by Bewilogua.17)

By using the intensity curve from each plate, the molecular structure was analyzed by the method of least squares.18) The theoretical expression of the molecular intensity is:

$$qM(q) = k\sum_i \sum_j{}' A_{ij}\mu_{ij} \cos \Delta\eta_{ij} \sin \frac{\pi}{10} q\left[r_{aij} - \left(\frac{\pi}{10} q\right)^2 \kappa_{ij}\right] \exp\left[-\frac{1}{2}\left(\frac{\pi}{10} q\right)^2 l_{ij}{}^2\right] \quad (1)$$

$$A_{ij} = \frac{10}{\pi} \frac{1}{r_{aij}} \frac{Z_i Z_j}{\sum_k Z_k (Z_k + 1)} \quad (2)$$

$$\mu_{ij} = \frac{|F_i||F_j|}{\sum_k |F_k|^2 + \sum_k S_k} \frac{\sum_k Z_k (Z_k + 1)}{Z_i Z_j},$$

$$|F| = \boldsymbol{h}^2 s^2 |f| / 8\pi^2 \boldsymbol{m}\boldsymbol{e}^2 \quad (3)$$

The parameters to be determined by the least-squares analysis were the atomic distances, r_a(B–X) and r_a(X–X), the mean amplitudes, l(B–X) and l(X–X), and the index of resolution, k.

The anharmonicity parameters, κ, were estimated by assuming potential functions of the Morse type for both the bonded B–X and the non-bonded X–X pairs; they were not varied as parameters. The following rough approximation was used:3,19)

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10) J. A. Ibers, *Acta Cryst.*, **10**, 86 (1957).
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14) P. Debye, *J. Chem. Phys.*, **9**, 55 (1941).
15) J. A. Ibers and J. A. Hoerni, *Acta Cryst.*, **7**, 405 (1954).
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17) L. Bewilogua, *Physik. Z.*, **32**, 740 (1931).
18) Y. Morino, K. Kuchitsu, T. Iijima and Y. Murata, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 803 (1962).
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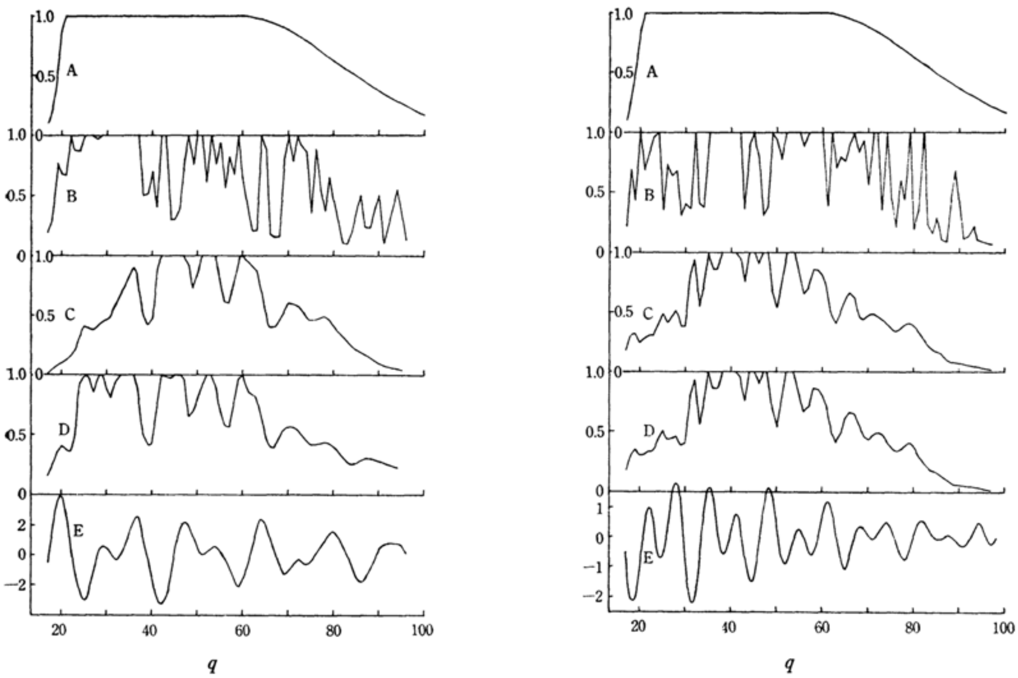

Fig. 3a. Fig. 3b.

Fig. 3. Weight functions for the least-squares analysis.
(a) Weight functions used for BF_3. (b) Weight functions used for BCl_3.
(A) A conventional weight function. (B) Weights assumed to be inversely proportional to the square of the standard deviation $\sigma(q)$ of the molecular intensities $qM(q)$. (C) Weights estimated from the residuals of the least-squares fitting by the procedure described in Ref. 21. (D) Modification of (C) by the use of σ_m estimated from the standard deviation $\sigma(q)$ of the observed intensity curves. (E) Molecular intensity curves, $qM(q)$.

$$\kappa(\text{B-X}) \simeq \frac{1}{9} l^2(\text{B-X})\langle \Delta z(\text{B-X})\rangle \simeq \frac{a}{6} l^4(\text{B-X})$$

$$\kappa(\text{X-X}) \simeq \frac{\sqrt{3}}{9} l^2(\text{X-X})\langle \Delta z(\text{B-X})\rangle$$

$$\simeq \frac{\sqrt{3}}{6} a l^2(\text{B-X}) l^2(\text{X-X}) \qquad (4)$$

The anharmonicity constant, a, was estimated to be about 2 Å^{-1}.[20]

The initial least-squares analysis was based on a conventional weight function, A, which is shown in Fig. 3. In order to examine the effect of the choice of weight functions on the parameter values, however, three additional weight functions were estimated (Fig. 3). The weight function B was assumed to be inversely proportional to the square of the standard deviation, $\sigma(q)$, of the molecular intensities, $qM(q)$.[9] The other functions, C and D, were calculated by estimating the standard deviation of the population of $qM(q)$, σ_m, which is related to the errors of the measurement of the abscissa and the ordinate of the photometer chart as follows:[21]

$$\sigma_m{}^2 = G_x{}^2 \cdot \sigma_x{}^2 + G_y{}^2 \cdot \sigma_y{}^2 \qquad (5)$$

The weight C was obtained in a way similar to that reported previously;[3] that is, $\sigma_m{}^2$ was first estimated from the residuals of the least-squares fitting and was then improved by eliminating the non-essential irregularities of σ_y.

The estimation of $\sigma_m{}^2$ by this procedure is not always reliable, since it tends to put too much weight on the points where the residuals are accidentally very small, while the weights for other points may be severely underestimated. Such effects may be partly compensated for, because the residuals are averaged over several plates and because the weight function is modified by the smoothing of σ_y. It seems to be preferable, however, to estimate $\sigma_m{}^2$ by the variance of the observed intensity curves, $\sigma^2(q)$, and not by the least-squares residuals alone. The weight function D was, accordingly, obtained from $\sigma^2(q)$, with modification by means of Eq. 5. The weight functions were normalized in such a way that about 15% of the observations had the full weight. Figure 4 shows a typical illustration of the observed and smoothed σ_y values which is similar to Fig. 2a of Ref. 21. The σ_y curve was

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[20] E. R. Lippincott and R. Schroeder, ibid., **23**, 1131 (1955).

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

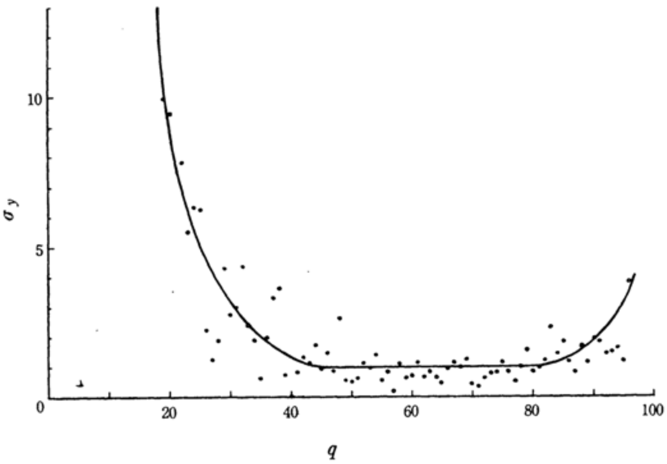

Fig. 4. A typical illustration of the standard error σ_y in the measurement of the ordinate of the photometer chart estimated from the standard error σ_m of $qM(q)$ based on the residuals of the least-squares fitting.

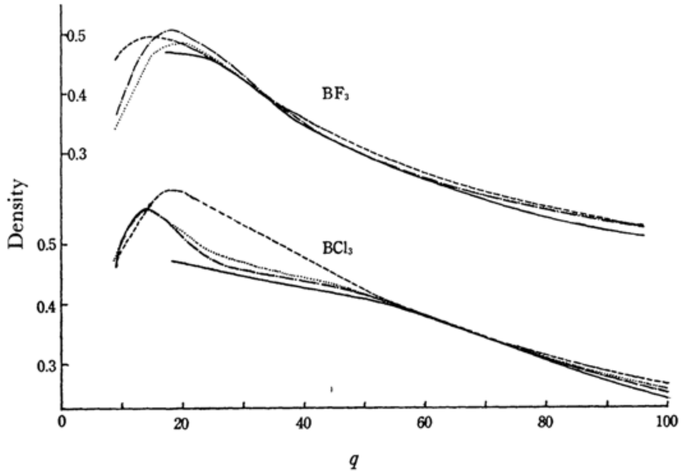

Fig. 5. Comparison of the observed with the theoretical background.

——— Observed.
—·—· f^B
------ $|f|_{T.F.}$
········ $|f|_{H.F.}$
Theoretical.

TABLE I. COMPLEX SCATTERING FACTORS AT 40 kV. CALCULATED FROM THE HARTREE-FOCK POTENTIALS ($|f|$ in Å units and η in radians)

$\theta°$	s(Å^{-1})	B		F		Cl	
		$\|f\|$	η	$\|f\|$	η	$\|f\|$	η
0	0	3.06	0.041	1.93	0.087	5.22	0.121
1	1.822	1.98	0.058	1.66	0.098	3.93	0.152
2	3.644	0.912	0.100	1.15	0.129	2.17	0.239
4	7.288	0.273	0.193	0.501	0.227	0.761	0.467
6	10.929	0.134	0.252	0.249	0.334	0.403	0.630
8	14.567	0.082	0.294	0.146	0.425	0.255	0.753
10	18.201	0.055	0.332	0.096	0.496	0.175	0.865
12	21.829	0.040	0.360	0.068	0.554	0.126	0.967
16	29.064	0.023	0.415	0.040	0.643	0.074	1.15
20	36.263	0.015	0.462	0.027	0.715	0.049	1.29
24	43.418	0.011	0.498	0.019	0.777	0.034	1.41
28	50.521	0.008	0.523	0.014	0.828	0.026	1.51

found to be a slowly-varying function of q, while the magnitude of the random experimental errors of the ordinate measurements was comparable with the uncertainty associated with the minimum scale division, as was discussed in Ref. 21.

The results of the least-squares analysis obtained by using the above four kinds of weight functions are listed in Table II. The symbol σ_1 in the table denotes the standard deviation derived by the least-squares fitting, divided by $\sqrt{n}$ so as to represent the

TABLE II. RESULTS OF THE LEAST-SQUARES ANALYSIS
(r and l in Å units)

(A) Conventional weights

		r_a(B–X)	r_a(X–X)	l(B–X)	l(X–X)	index
BF_3	Average	1.3154	2.2737	0.0410	0.0568	0.983
normal	σ_1	0.0004	0.0005	0.0007	0.0007	0.008
direction	σ_2	0.0016	0.0016	0.0009	0.0008	0.008
BF_3	Average	1.3138	2.2705	0.0412	0.0569	0.974
reversed	σ_1	0.0006	0.0007	0.0009	0.0009	0.010
direction	σ_2	0.0014	0.0016	0.0011	0.0006	0.006
BCl_3	Average	1.7421	3.0143	0.0506	0.0736	1.010
normal	σ_1	0.0006	0.0004	0.0008	0.0006	0.008
direction	σ_2	0.0015	0.0018	0.0008	0.0005	0.016

(B) Weights estimated from the variance in the molecular intensities.

		r_a(B–X)	r_a(X–X)	l(B–X)	l(X–X)	index
BF_3	Average	1.3149	2.2732	0.0395	0.0560	0.969
normal	σ_1	0.0005	0.0006	0.0008	0.0007	0.007
direction	σ_2	0.0013	0.0014	0.0009	0.0005	0.007
BF_3	Average	1.3131	2.2697	0.0389	0.0563	0.959
reversed	σ_1	0.0007	0.0008	0.0010	0.0010	0.010
direction	σ_2	0.0012	0.0013	0.0011	0.0009	0.006
BCl_3	Average	1.7419	3.0140	0.0505	0.0736	1.011
normal	σ_1	0.0005	0.0004	0.0007	0.0005	0.007
direction	σ_2	0.0014	0.0016	0.0006	0.0004	0.013

(C) Weights estimated from the residuals of the least-squares fitting

		r_a(B–X)	r_a(X–X)	l(B–X)	l(X–X)	index
BF_3	Average	1.3154	2.2739	0.0407	0.0567	0.978
normal	σ_1	0.0003	0.0004	0.0006	0.0006	0.007
direction	σ_2	0.0017	0.0016	0.0010	0.0007	0.009
BF_3	Average	1.3138	2.2707	0.0409	0.0566	0.964
reversed	σ_1	0.0004	0.0005	0.0008	0.0007	0.009
direction	σ_2	0.0014	0.0017	0.0010	0.0005	0.004
BCl_3	Average	1.7418	3.0135	0.0503	0.0739	1.009
normal	σ_1	0.0005	0.0004	0.0007	0.0005	0.007
direction	σ_2	0.0014	0.0017	0.0008	0.0006	0.015

(D) Modifications of (C) by the use of the σ_m estimated from the standard deviation $\sigma(q)$ of the observed intensity curves.

		r_a(B–X)	r_a(X–X)	l(B–X)	l(X–X)	index
BF_3	Average	1.3151	2.2736	0.0403	0.0561	0.970
normal	σ_1	0.0004	0.0005	0.0008	0.0007	0.008
direction	σ_2	0.0016	0.0015	0.0010	0.0008	0.009
BF_3	Average	1.3136	2.2704	0.0399	0.0563	0.957
reversed	σ_1	0.0006	0.0007	0.0010	0.0009	0.010
direction	σ_2	0.0014	0.0017	0.0011	0.0008	0.005
BCl_3	Average	1.7417	3.0136	0.0503	0.0738	1.007
normal	σ_1	0.0005	0.0004	0.0007	0.0005	0.007
direction	σ_2	0.0014	0.0017	0.0007	0.0006	0.015

standard deviation for the average value where n is the number of intensity curves. The symbol σ_2 is the standard deviation evaluated by the fluctuation among several sets of the observed values,[3,21] $\sigma_2=\sqrt{\sum(X_i-X)^2/n(n-1)}$. While there are no appreciable differences among the results based on different weights for boron trichloride, the values of the index and the amplitudes differ slightly among one another for boron trifluoride.

The differences between the bond lengths obtained from the plates taken with the normal and the reversed directions of the nozzle were 0.11% for r(B–F) and 0.14% for r(F–F). The average, 0.12%, may be regarded as the difference in the scale factors between the two nozzle directions; the interval between the position of the gold foil and the center of diffraction is, therefore, about 0.06% of the camera length, i. e., about 0.07 mm. This is shorter than the interval of about 0.12 mm. which was determined in a similar way for the asymmetric nozzle used in the study of silicon tetrachloride.[3] The scale factor for boron trichloride must, then, be corrected by 0.06%, since the photographs were taken only for the normal nozzle direction. The results corrected for the difference in the camera lengths due to the different nozzle directions are shown in Table III. The σ_1 and σ_2 values of BF_3 in this table were calculated by the following relation:

$$\sigma=\sqrt{\frac{7}{40}}\,[2\sigma^2{}_{\text{normal}}+\sigma^2{}_{\text{reversed}}]^{1/2} \qquad (6)$$

The apparent increases in the mean amplitudes

TABLE III. SUMMARY OF THE RESULTS OF THE LEAST-SQUARES ANALYSIS
(r and l in Å units)

Weights - (D)
Atomic scattering factors, $f^{B}e^{i\eta_{T.F.}}$.
Corrected for the nozzle asymmetry

		r_a(B–X)	r_a(X–X)	l(B–X)	l(X–X)	index
	Average	1.3144	2.2720	0.0401	0.0562	0.964
BF_3	σ_1	0.0003	0.0004	0.0006	0.0006	0.006
	σ_2	0.0011	0.0011	0.0007	0.0006	0.006
	Average	1.7407	3.0118	0.0503	0.0738	1.007
BCl_3	σ_1	0.0005	0.0004	0.0007	0.0005	0.007
	σ_2	0.0014	0.0017	0.0007	0.0006	0.015

TABLE IV. APPARENT INCREASES IN THE MEAN AMPLITUDES DUE TO THE DISTRIBUTION OF GAS MOLECULES

	f^B	$\lvert f\rvert_{T.F.}$	$\lvert f\rvert_{H.F.}$
l(B–F)	0.0007	0.0009	0.0007
l(F–F)	0.0017	0.0022	0.0017
l(B–Cl)	0.0014	0.0021	0.0017
l(Cl–Cl)	0.0028	0.0042	0.0034

TABLE V. LIMITS OF ERROR OF THE ATOMIC DISTANCES (in Å units)

Source of error	r(B–F)	r(F–F)	r(B–Cl)	r(Cl–Cl)
Random error (2.5 σ)	0.0028	0.0028	0.0035	0.0043
Drift of voltage	0.0007	0.0011	0.0009	0.0015
Calibration of wavelength	0.0009	0.0016	0.0012	0.0021
Inclination of plates	0.0010	0.0017	0.0013	0.0023
Difference in the camera lengths between the sample and the reference			0.0010	0.0017
Effects of κ	0.0030	0.0015	0.0015	0.0015
Total error	0.0044	0.0041	0.0044	0.0060

TABLE VI. LIMITS OF ERROR OF THE MEAN AMPLITUDES AND INDICES (l in Å units)

Source of error	l(B–F)	l(F–F)	index of BF_3	l(B–Cl)	l(Cl–Cl)	index of BCl_3
Random error (2.5σ)	0.0018	0.0015	0.015	0.0018	0.0015	0.038
Sample size (50% of the correction)	0.0004	0.0009		0.0007	0.0014	
Uncertainty in the phase shift	0.0010			0.0010		
Arbitrary choice of the weight function	0.0020	0.0010	0.019	0.0002	0.0002	0.003
Total error	0.0029	0.0020	0.024	0.0022	0.0021	0.038

were determined by measuring the distribution of gas molecules on the basis of the discrepancies in the observed and theoretical backgrounds[22] (Fig. 5) (Table IV). The estimates of these corrections depend on the kind of scattering factors used.

The Estimation of Experimental Errors

The reliability of the observed parameters may be represented by the 99% confidence interval. This interval is equal to 2.5 σ if we assume the normal distribution of errors with a standard deviation, σ.[21] The greater of the σ_1 and σ_2 values of each parameter may safely be taken as the standard deviation, σ, corresponding to random errors. The random errors, 2.5 σ, and various systematic errors (which are considered to correspond to the above confidence interval) are listed in Tables V and VI.

For atomic distances the systematic errors were estimated as follows.[22] The error of the wavelength of the primary electron beam is less than 0.05% because the accelerating voltage was stabilized within 0.1%. When the wavelengths are determined from the reference gold foil, the uncertainty in the lattice constant of the gold foil and the personal errors in the measurement committed by the observer constitute systematic errors which influence the bond distances. The errors associated with the corrections for the inclination of photographic plates were estimated previously.[9]

As the photographs for BCl_3 were taken with only the normal orientation of the nozzle, the errors associated with the correction due to the deviation of the center of diffraction from the position of the gold foil should be taken into consideration. One half of the correction is, therefore, assigned to this source of error in Table V. The errors of the anharmonicity constants, κ, were estimated from the difference in the outputs of the least-squares analyses where the κ constants were either taken as variable parameters or as constants based on the various estimation.

For mean amplitudes, the errors associated with the correction for the distribution of gas molecules around the nozzle were assumed to be 50% of the correction. Errors coming from the arbitrariness of the weights were taken into consideration for both molecules.

The confidence intervals were estimated from the square root of the squared sum of errors, by assuming that these errors occur independently.

Results and Discussion

Atomic Distances and Mean Amplitudes.—The final results of the molecular constants obtained by using the Born scattering factors, $f^{B}e^{i\eta_{T.F.}}$, are given in Table VII. The average interatomic

TABLE VII. MOLECULAR CONSTANTS OBTAINED BY USING THE BORN SCATTERING FACTOR f^B AND THE PHASE SHIFT $\eta_{T.F.}$ (r, l and δ_g in Å units)

BF_3

	B–F	F–F
r_g	1.3156 ± 0.0044	2.2733 ± 0.0041
r_α	1.3130 ± 0.0044	2.2723 ± 0.0041
l	0.0394 ± 0.0029	0.0545 ± 0.0020
index	$0.964\ \pm0.024$	
δ_g	0.0054 ± 0.0057 (calcd. 0.0037)	

BCl_3

	B–Cl	Cl–Cl
r_g	1.7421 ± 0.0044	3.0135 ± 0.0060
r_α	1.7387 ± 0.0044	3.0120 ± 0.0060
l	0.0489 ± 0.0022	0.0710 ± 0.0021
index	$1.007\ \pm0.038$	
δ_g	0.0039 ± 0.0041 (calcd. 0.0044)	

TABLE VIII. MOLECULAR CONSTANTS OBTAINED BY USING THE COMPLEX SCATTERING FACTORS FOR THE THOMAS-FERMI POTENTIAL (r, l and δ_g in Å units)

BF_3

	B–F	F–F
r_g	1.3156 ± 0.0044	2.2734 ± 0.0041
r_α	1.3130 ± 0.0044	2.2724 ± 0.0041
l	0.0382 ± 0.0029	0.0528 ± 0.0021
index	$0.946\ \pm0.024$	
δ_g	0.0053 ± 0.0058	

BCl_3

	B–Cl	Cl–Cl
r_g	1.7421 ± 0.0044	3.0134 ± 0.0060
r_α	1.7387 ± 0.0044	3.0119 ± 0.0060
l	0.0495 ± 0.0024	0.0687 ± 0.0026
index	$0.995\ \pm0.038$	
δ_g	0.0040 ± 0.0041	

TABLE IX. MOLECULAR CONSTANTS OBTAINED BY USING THE COMPLEX SCATTERING FACTORS FOR THE HARTREE-FOCK POTENTIALS[a)]
(r, l and δ_g in Å units)

BF_3

	B–F	F–F
r_g	1.3156 ± 0.0044	2.2733 ± 0.0041
r_α	1.3130 ± 0.0044	2.2723 ± 0.0041
l	0.0398 ± 0.0029	0.0541 ± 0.0020
index	$0.960\ \pm0.024$	
δ_g	0.0054 ± 0.0057	

BCl_3

	B–Cl	Cl–Cl
r_g	1.7421 ± 0.0044	3.0134 ± 0.0060
r_α	1.7387 ± 0.0044	3.0119 ± 0.0060
l	0.0505 ± 0.0023	0.0700 ± 0.0023
index	$1.006\ \pm0.038$	
δ_g	0.0040 ± 0.0041	

a) The parameters listed in this table should be regarded as the final results of this study.

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[22] K. Kuchitsu, This Bulletin, **32**, 748 (1959).

distances, r_g, were calculated from r_a by the relation: $r_g=r_a+l^2/r_a$, and the mean amplitudes were corrected for the finite sample size. The results obtained by the use of the complex scattering factors, $|f|_{\text{T.F.}}e^{i\eta_{\text{T.F.}}}$ and $|f|_{\text{H.F.}}e^{i\eta_{\text{H.F.}}}$, are also listed in Tables VIII and IX respectively. For the reason given in the next subsection, the values listed in Table IX should be regarded as the final results of this study.

If the BX_3 molecules were exactly in a rigid planar triangular form, the X–X distance should be equal to $\sqrt{3}$ times the B–X distance. However, when we calculate $\delta_g=\sqrt{3}\,r_g(\text{B–X})-r_g(\text{X–X})$, it is not equal to zero, because of the perpendicular amplitudes caused by thermal vibrations.[23] It was found in this experiment that $\delta_g=0.0054\pm0.0057$ Å for BF_3 and $\delta_g=0.0040\pm0.0041$ Å for BCl_3.

The shrinkage mentioned above was calculated by the following relation:

$$\delta_g(\text{calcd.}) = \sqrt{3}\left(\frac{\langle\Delta x^2\rangle+\langle\Delta y^2\rangle}{2r_e}\right)_{\text{B-X}} - \left(\frac{\langle\Delta x^2\rangle+\langle\Delta y^2\rangle}{2r_e}\right)_{\text{X-X}} \qquad (7)$$

where the perpendicular amplitudes, $\langle\Delta x^2\rangle$ and $\langle\Delta y^2\rangle$, can be calculated by using the $\boldsymbol{L}$ and $\boldsymbol{G}$ matrix elements. For the B–X pair,

$$\langle\Delta x^2\rangle = \frac{2}{9}\left(L_{43}{}^2\langle Q_3{}^2\rangle + L^2{}_{44}\langle Q_4{}^2\rangle\right)$$

$$\langle\Delta y^2\rangle = \frac{1}{9}L_{22}{}^2\langle L_2{}^2\rangle$$

and for the X–X pair.

$$\langle\Delta x^2\rangle = \frac{1}{6}\{(\sqrt{3}L_{33}-L_{43})^2\langle Q_3{}^2\rangle + (\sqrt{3}L_{34}-L_{44})^2\langle Q_4{}^2\rangle\}$$

$$\langle\Delta y^2\rangle = 0$$

The thermal-average distance, r_α, is defined as[24] the sum of the equilibrium distance, r_e, and an anharmonic term, $\langle\Delta z\rangle$; that is, $r_\alpha=r_g-(\langle\Delta x^2\rangle+\langle\Delta y^2\rangle)/2r_e-\delta r$. The centrifugal stretching terms, δr, were calculated to be 0.0003 Å, 0.0006 Å, 0.0005 Å and 0.0009 Å for the B–F, F–F, B–Cl and Cl–Cl pairs respectively.[25] The observed r_α distances are listed in Tables VII, VIII and IX. In this average structure, the nonlinear shrinkage effect should disappear if the molecule is exactly in a planar triangular form. The ratio of the B–X distance to the X–X distance in this structure, $r_\alpha(\text{F–F})/r_\alpha(\text{B–F})=1.7306\pm0.0045$, $r_\alpha(\text{Cl–Cl})/r_\alpha(\text{B–Cl})=1.7323\pm0.0023$, is equal to $\sqrt{3}$ within the range of experimental error. It is therefore proved, to within an order of 0.001 Å, that the BF_3 and BCl_3 molecules take a planar triangular form in the average structure, and also in the equilibrium structure.

Although the above results are consistent with those given in previous papers[4-6] within their ranges of experimental error, the present study has provided more direct and confirmative support for the planarity of these molecules.

The thermal average B–F distance, $r_g=1.3156\pm0.0044$ Å, is significantly larger than the effective distance, $r_0=1.295_1$ Å, obtained by Nielsen[26] from the rotational constant, B_0, in the analysis of the infrared ν_2 band of BF_3. While a part of this discrepancy stems from the difference in the definition of the internuclear distance, their assignment seems to be questionable. This problem will be studied in more detail in a forthcoming paper.

A Comparison of the Atomic Scattering Factors.—A similar electron diffraction analysis for boron tribromide[27] has revealed that the complex atomic scattering factors, $|f|_{\text{H.F.}}e^{i\eta_{\text{H.F.}}}$, calculated from the Hartree-Fock potentials provide a value of the mean amplitude, l(B–Br), more reasonable than the other scattering factors, $f^{\text{B}}e^{i\eta_{\text{T.F.}}}$ and $|f|_{\text{T.F.}}e^{i\eta_{\text{T.F.}}}$, and that the theoretical background line calculated from $|f|_{\text{H.F.}}$ is in better agreement with the observations than those calculated from the scattering factors, f^{B} and $|f|_{\text{T.F.}}$. Accordingly, it seemed desirable to compare the background lines calculated from these atomic scattering factors for the other halides.

The effects of the difference in the scattering factors appear on the mean amplitudes and on the backgrounds, but not appreciably on the atomic distances. The observed mean amplitudes obtained from the three scattering factors are shown in Fig. 6, where the closed areas show the limits of error of the mean amplitudes obtained by using the Hartree-Fock scattering factors, $|f|_{\text{H.F.}}e^{i\eta_{\text{H.F.}}}$.

As may be seen in Fig. 5, the theoretical backgrounds of boron trifluoride based on the three scatter-ing factors are in good agreement with the observed curve. Slight differences, each within the limits of error, are observed in the mean amplitudes listed in Tables VII—IX however. The results based on $f^{\text{B}}e^{i\eta_{\text{T.F.}}}$ and $|f|_{\text{H.F.}}e^{i\eta_{\text{H.F.}}}$ are compatible with the spectroscopic value within the limits of error, while that based on $|f|_{\text{T.F.}}e^{i\eta_{\text{T.F.}}}$ is in poorer agreement. For the mean amplitudes of boron trichloride, the result based on each scattering factor is in good agreement with the spectroscopic value, with the exception that the $|f|_{\text{T.F.}}$ factor gives a poor result for the background. It thus seems that the results based on the $|f|_{\text{T.F.}}$ factor are not quite satisfactory. This may be ascribed to the inadequacy of the Thomas-Fermi potential

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[23] Y. Morino, S. J. Cyvin, K. Kuchitsu and T. Iijima, *J. Chem. Phys.*, **36**, 1109 (1962).

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

[25] M. Iwasaki and K. Hedberg, ibid., **36**, 2961 (1962).

[26] A. H. Nielsen, ibid., **22**, 659 (1954).

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

TABLE XI. FORCE CONSTANTS DETERMINED FROM THE MEAN AMPLITUDES, ISOTOPIC SHIFTS AND THE ASSUMPTION OF THE UREY-BRADLEY FORCE FIELDS WITH $F' = -(1/10)F$ (in md/Å units)

BF_3

		Mean amplitudes	Isotopic shifts	U.B.F.F.
F_{11}	8.82 ± 0.10			
F_{22}	0.293 ± 0.005			
F_{33}		7.4 ± 2.3	7.6 ± 1.5	6.675 ± 0.027
F_{34}		-0.9 ± 0.9	-0.7 ± 0.6	-0.362 ± 0.009
F_{44}		0.58 ± 0.09	0.53 ± 0.03	0.513 ± 0.013

BCl_3

		Mean amplitudes	Isotopic shifts	U.B.F.F.
F_{11}	4.63 ± 0.10			
F_{22}	0.135 ± 0.003			
F_{33}		3.6 ± 1.3	3.4 ± 1.4	3.384 ± 0.043
F_{34}		-0.36 ± 0.44	-0.22 ± 0.43	-0.209 ± 0.010
F_{44}		0.26 ± 0.06	0.25 ± 0.10	0.230 ± 0.011

for such light elements as boron, fluorine and chlorine.

Force Constants.—The BX_3 molecules belong to the point group D_{3h} and have four fundamental frequencies. ν_1 is a totally symmetric stretching vibration (A_1' species), ν_2 is an out-of-plane vibration (A_2'' species), and ν_3 and ν_4 are doubly-degenerate vibrations (E' species). Although the force constants of A_1' and A_2'' species can easily be determined from the vibrational frequencies alone, those of E' species cannot be determined uniquely because the number of the force constants (three) exceeds that of the frequencies (two).

So far, several sets of force constants have been calculated by using the frequencies of the boron isotopes as additional observables. Since, however, the mass ratio of ^{10}B to ^{11}B is nearly unity, small experimental errors in the frequencies may lead to large errors in the force constants. The Urey-Bradley force constants of boron trihalides have also been reported.[28,29] The force constants can also be determined more precisely if the Coriolis coupling constants are observed. Thus far, one of the Coriolis constants of boron trifluoride has been determined from the band shape of the ν_4 frequency and used to calculate the force constants.[30] Nevertheless, this finding does not seem to be well-grounded experimentally, since the Coriolis constant was determined only indirectly. For this reason, it seems profitable to calculate the force constants from the mean amplitudes observed by electron diffraction.

The general quadratic potential function, in terms of the internal coordinates for BX_3 molecules, is:

$$2V = \sum f_r(\Delta r_i)^2 + 2\sum f_{rr}(\Delta r_i)(\Delta r_j) + f_\tau(r_0\Delta\tau)^2$$
$$+ \sum f_\alpha(r_0\Delta\alpha_i)^2 + 2\sum f_{\alpha\alpha}(r_0\Delta\alpha_i)(r_0\Delta\alpha_j)$$
$$\sum f_{r\alpha}(\Delta r_i)(r_0\Delta\alpha_i) + 2\sum f'_{r\alpha}(\Delta r_i)(r_0\Delta\alpha_j) \quad (8)$$

The internal coordinates are Δr_1, Δr_2, Δr_3, $r_0\Delta\alpha_1$, $r_0\Delta\alpha_2$, $r_0\Delta\alpha_3$ and $r_0\Delta\tau$, where Δr_i is the change in the length of the ith bond, $\Delta\alpha_i$ is the change in the bond angle opposite to r_i, and r_0 is the bond distance. $\Delta\tau$ is the change in the angle between any one of the bonds and the molecular plane.*

The following symmetry coordinates are used:

$$A_1' \text{ species,} \quad S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3)$$
$$A_2'' \text{ species,} \quad S_2 = r_0\Delta\tau$$
$$E' \text{ species,} \quad S_3 = \frac{1}{\sqrt{6}}(2\Delta r_3 - \Delta r_1 - \Delta r_2)$$
$$S_4 = \frac{1}{\sqrt{6}} r_0(2\Delta\alpha_3 - \Delta\alpha_1 - \Delta\alpha_2)$$
$$S_3' = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$
$$S_4' = \frac{1}{\sqrt{2}} r_0(\Delta\alpha_1 - \Delta\alpha_2) \quad (9)$$

The elements of the $\boldsymbol{F}$ matrix in the symmetry coordinates have the following relations to the constants in Eq. 8:

$$A_1' \text{ species,} \quad F_{11} = f_r + 2f_{rr}$$
$$A_2'' \text{ species,} \quad F_{22} = f_\tau$$
$$E' \text{ species,} \quad F_{33} = f_r - f_{rr}$$
$$F_{34} = f_{r\alpha} - f'_{r\alpha}$$
$$F_{44} = f_\alpha - f_{\alpha\alpha} \quad (10)$$

When the above transformation (9) is expressed in

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[28] G. J. Janz and Y. Mikawa, *J. Mol. Spectry.*, **5**, 92 (1960).
[29] E. Meisingseth, *Acta Chem. Scand.*, **16**, 1601 (1962).
[30] J. L. Duncan, *J. Mol. Spectry.*, **13**, 338 (1964).

* If the displacements of the Cartesian coordinates perpendicular to the molecular plane are denoted as y, they are related to $\Delta\tau$ as $r_0\Delta\tau = y_1 + y_2 + y_3 - 3y_0$, while the $\boldsymbol{G}$ matrix for A_2'' species is given by $G_{22} = 3/m_X + 9/m_B$.

a matrix form:

$$\boldsymbol{S}=\boldsymbol{UR}, \tag{11}$$

the mean amplitudes of vibration are given by[31]:

$$\langle \boldsymbol{R}\tilde{\boldsymbol{R}} \rangle = \tilde{\boldsymbol{U}}\boldsymbol{L}\,\langle \boldsymbol{Q}\tilde{\boldsymbol{Q}} \rangle\,\tilde{\boldsymbol{L}}\boldsymbol{U} \tag{12}$$

where $\langle \boldsymbol{Q}\tilde{\boldsymbol{Q}} \rangle$ is a diagonal matrix having the elements of:

$$\langle Q_i{}^2 \rangle = \frac{\boldsymbol{h}}{8\pi^2\nu_i}\coth\left(\frac{\boldsymbol{h}\nu_i}{2\boldsymbol{k}T}\right) \tag{13}$$

From Eq. 12 the mean square amplitudes for the BX_3 molecules are found to be:

$$l^2(\mathrm{B\text{–}X}) = \frac{1}{3}L_{11}{}^2\langle Q_1{}^2\rangle + \frac{2}{3}\{L_{33}{}^2\langle Q_3{}^2\rangle + L_{34}{}^2\langle Q_4{}^2\rangle\}$$

$$l^2(\mathrm{X\text{–}X}) = L_{11}{}^2\langle Q_1{}^2\rangle + \frac{1}{6}\{(\sqrt{3}L_{33} - L_{43})^2\langle Q_3{}^2\rangle + (\sqrt{3}L_{34}-L_{44})^2\langle Q_4{}^2\rangle\} \tag{14}$$

In a rigorous sense, the normal frequencies, ν_e, should be used in the calculation of the force field, but at present we do not have enough knowledge of vibrational anharmonicities to convert the fundamental frequencies, ν, to ν_e for boron trihalide.[32] Table X shows the fundamental frequencies used for the calculation[26,33,34] and the uncertainties of the frequencies which are estimated by analogy with other simple polyatomic molecules. When these observed ν values are used, the force constants have only one degree of freedom, and the two mean amplitudes, l(B–X) and l(X–X), cannot be independent. The curve of l(X–X) versus l(B–X) is illustrated in Fig. 6. The spread of the curves corresponds to the errors in the frequencies estimated above. Any one point on the curve corresponds to a set of the force constants. The ranges of the observed mean amplitudes based on the scattering factors, $|f|_{\mathrm{H.F.}}e^{i\eta_{\mathrm{H.F.}}}$, are within the ellipses drawn in solid lines in Fig. 6, while the overlapping regions of the curves indicate reasonable sets of the force constants. The observed value of l(B–F) is smaller than that to be expected from vibrational frequencies by about 0.003 Å, possibly because of some unknown systematic error. The uncertainties in the force constants of boron trifluoride were estimated from the overlapping region of the l-l curve and an ellipse displaced by 0.003 Å parallel to the l(B–F) axis. The displaced ellipse is shown by a dashed line in Fig. 6. The force constant, F_{34}, was determined from the corresponding region in the curve of F_{34} versus (B–X) in Fig. 7, while the other constants, F_{33} and F_{44}, were obtained from the value of F_{34}. The force constants obtained in this way are shown in Table XI.

TABLE X. FUNDAMENTAL FREQUENCIES USED FOR THE CALCULATION OF FORCE CONSTANTS (in cm⁻¹ units)

	$^{11}BF_3$	$^{10}BF_3$	Uncertainty[d]
ν_1[a]	888	888	±5
ν_2[b]	691.45	718.23	±1.5
ν_3[c]	1453.9	1504.8	±6
ν_4[a]	480.4	482.0	±5
	$^{11}BCl_3$	$^{10}BCl_3$	Uncertainty[d]
ν_1[a]	471	471	±5
ν_2[a]	454.9	474.3	±5
ν_3[a]	954.2	993.7	±5
ν_4[a]	243	243	±5

a) Ref. 33
b) Ref. 26
c) Ref. 34
d) Limits of uncertainty estimated in the present study.

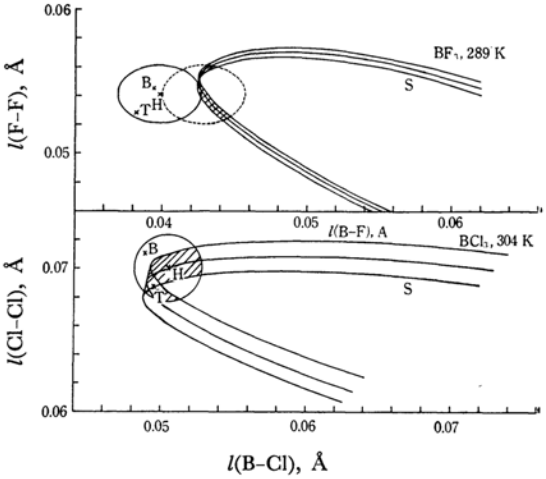

Fig. 6. Correlation curve of the mean amplitudes.
B, T, H: Observed values obtained by using the scattering factors, $f^{\mathrm{B}}e^{i\eta_{\mathrm{T.F.}}}$, $|f|_{\mathrm{T.F.}}e^{i\eta_{\mathrm{T.F.}}}$ and $|f|_{\mathrm{H.F.}}e^{i\eta_{\mathrm{H.F.}}}$, respectively.
S: Calculated values from spectroscopic data.
The small ellipses drawn in solid lines show the limits of error of the mean amplitudes obtained by using the Hartree-Fock complex scattering factors, $|f|_{\mathrm{H.F.}}e^{i\eta_{\mathrm{H.F.}}}$. The dashed curve was used to estimate the uncertainties in the force constants of boron trifluoride (see text). The shaded areas indicate the regions in which the diffraction and spectroscopic data are thought to be compatible.

It is found that the force constants determined from the mean amplitudes are in good agreement with those obtained by the isotopic shifts and the Urey-Bradley force fields (Table XI). The errors

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[31] Y. Morino, K. Kuchitsu and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952); Y. Morino and E. Hirota, ibid., **23**, 737 (1955).

[32] C. W. F. T. Pistorius, ibid., **29**, 1174 (1958). He has reported anharmonicity corrections for boron trihalides, but his corrections are questionable.

[33] L. P. Lindeman and M. K. Wilson, ibid., **24**, 242 (1956).

[34] J. Vanderryn, ibid., **30**, 331 (1959).

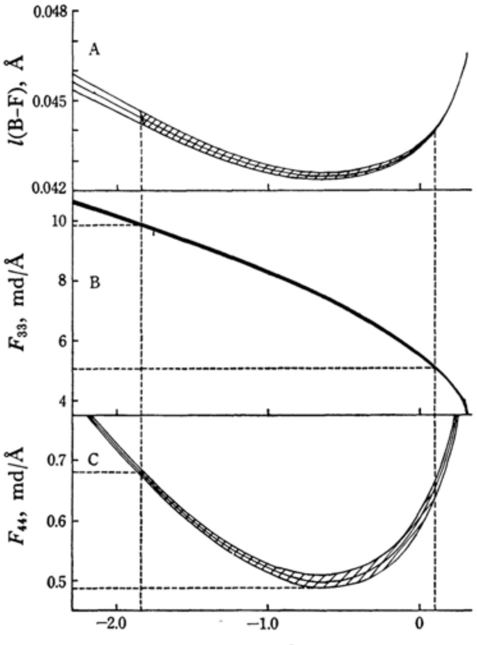

Fig. 7a.

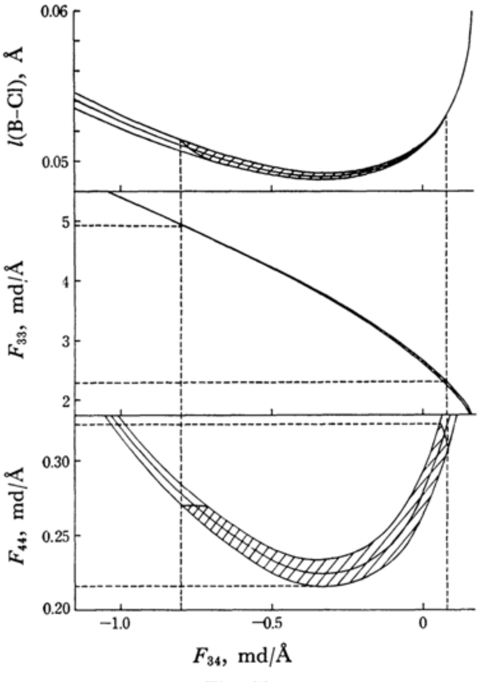

Fig. 7b.

Fig. 7. Determination of the force constants. (a) BF_3, (b) BCl_3.
(A) Correlation curves of l(B–X) and F_{34}.
(B) Correlation curves of F_{33} and F_{34}.
(C) Correlation curves of F_{44} and F_{34}.
The shaded area indicates reasonable sets of the force constants.

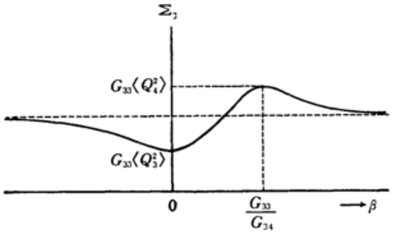

Fig. 8. Dependence of the mean amplitudes $\sum_3$ on the parameter β.

in the force constants derived from the mean amplitudes are similar in magnitude to those of the force constants obtained by the isotopic shifts. Nevertheless, the force constants are now considered to have been confirmed, since the two different experimental methods have given coincident results.

As is shown in Fig. 6, the positions of the observed mean amplitudes of BF_3 and BCl_3 are at the left-hand edge of the l-l curve. Similar phenomena have also been observed in the CCl_4, $GeCl_4$$^{1)}$, $SiCl_4$$^{3)}$, $TiCl_4$$^{8)}$ and $BBr_3$$^{27)}$ molecules which have previously been studied in our laboratory. It, therefore, seems unlikely that this is merely a coincidence. An analysis to be shown in the Appendix will prove that the physical meaning of this effect is related to a well-known empirical rule that the normal modes of stretching vibrations have essentially no dependence on the bending coordinates.35)

Summary

The atomic distances and the mean amplitudes of boron trifluoride and boron trichloride have been determined by the sector-microphotometer method of gas electron diffraction (Table IX). The force constants determined from the mean amplitudes and the vibrational frequencies are in good agreement with those obtained by the isotopic shifts and by the Urey-Bradley force field.

It has been found that the Born scattering factors and the complex scattering factors for boron trifluoride and boron trichloride calculated from the Hartree-Fock potential give more reasonable mean amplitudes and theoretical backgrounds than the complex scattering factors calculated from the Thomas-Fermi potential.

The authors wish to express their gratitude to Dr. Ryohei Nakane for providing the boron trifluoride, and to the Central Research Institute of the Tokyo Shibaura Electric Co. for supplying the boron trichloride. They are also grateful to of the Ministry Education for a research grant.

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35) T. Oka and Y. Morino, *J. Mol. Spectry.*, **11**, 349 (1963).

Appendix

A simple relation has been observed empirically between the observed mean amplitudes of the X-Y and Y-Y distances for the tetrahedral XY_4 molecules (CCl_4, $GeCl_4$[1], $SiCl_4$[3] and $TiCl_4$[8]) and for the planar trigonal XY_3 molecules (BF_3, BCl_3 and BBr_3[27]). Without exception, the observed values of l(X-Y) and l(Y-Y) fall close to the left-hand edge of the l-l ellipse, as is shown in Fig. 6.

We will here show that this phenomenon can be explained quite simply with relation to the characteristic modes of molecular vibrations, that is, by the empirical rule $L_{ij}(i<j)\fallingdotseq 0$, where the normal coordinates and the symmetry coordinates are numbered from the higher to the lower frequencies. According to the following argument, the mean amplitudes of a bonded pair, X-Y, takes a minimum value when $L_{34}=0$.

The l(X-Y) amplitude is related to the $\boldsymbol{L}$ matrix elements as follows:

$$l^2(\text{X-Y}) = \frac{1}{3}\Sigma_1 + \frac{2}{3}\Sigma_3 \qquad \text{for } XY_3 \qquad \text{(A1)}$$

$$= \frac{1}{4}\Sigma_1 + \frac{3}{4}\Sigma_3 \qquad \text{for } XY_4 \qquad \text{(A2)}$$

$$\Sigma_1 = L_{11}^2\langle Q_1^2\rangle \qquad \text{(A3)}$$

$$\Sigma_3 = L_{33}^2\langle Q_3^2\rangle + L_{34}^2\langle Q_4^2\rangle \qquad \text{(A4)}$$

where Σ is the mean amplitude matrix defined by Cyvin.[36] The first terms of Eqs. A1 and A2 have definite values, because $L_{11}^2=G_{11}=1/m_Y$, while the second terms depend on the choice of the force constants, because L_{33} and L_{34} change with the force constants. Therefore, it is sufficient to prove that Σ_3 takes a minimum value in order to prove that the l(X-Y) takes a minimum. Using the relation $\boldsymbol{G}=\boldsymbol{L}\tilde{\boldsymbol{L}}$, we obtain the following formulas:

$$G_{33} = L_{33}^2 + L_{34}^2$$

$$G_{34} = L_{33}L_{43} + L_{34}L_{44}$$

$$G_{44} = L_{43}^2 + L_{44}^2$$

$$\therefore\ (G_{33} - L_{34}^2)(G_{44} - L_{44}^2) = L_{33}^2L_{43}^2$$

$$= (G_{34} - L_{34}L_{44})^2 \qquad \text{(A5)}$$

From these equations, we can express L_{34} in terms of the $\boldsymbol{G}$ matrix elements and a parameter, β, where $\beta=L_{34}/L_{44}$:

$$L_{34}^2 = \frac{\beta^2G_{44}|\boldsymbol{G}|}{(\beta G_{44}-G_{34})^2+|\boldsymbol{G}|},\ |\boldsymbol{G}| = G_{33}G_{44} - G_{34}^2 \qquad \text{(A6)}$$

Then Σ_3 can also be expressed in terms of the parameter β:

$$\Sigma_3 = L_{33}^2\langle Q_3^2\rangle + L_{34}^2\langle Q_4^2\rangle$$

$$= G_{33}\langle Q_3^2\rangle + L_{34}^2(\langle Q_4^2\rangle - \langle Q_3^2\rangle)$$

$$= G_{33}\langle Q_3^2\rangle + \frac{\beta^2G_{44}|\boldsymbol{G}|}{(\beta G_{44}-G_{34})^2+|\boldsymbol{G}|}$$

$$\times(\langle Q_4^2\rangle-\langle Q_3^2\rangle) \qquad \text{(A7)}$$

Since $|\boldsymbol{G}|$ and $(\langle Q_4^2\rangle - \langle Q_3^2\rangle)$ are both positive, it is clear that Σ_3 takes a minimum when $\beta=0$, that is, when $L_{34}=0$, and takes a maximum when $\beta=G_{33}/G_{34}$, that is, when $L_{33}=0$. The curve of Σ_3 is shown in Fig. 8.

For molecules of the bent XY_2 type, l(X-Y) takes the minimum value when $L_{12}=0$, since the following relation is the same as those for the planar XY_3 and tetrahedral XY_4 molecules.

$$l^2(\text{X-Y}) = \frac{1}{2}(\Sigma_1 + \Sigma_3) \qquad \text{(A8)}$$

$$\Sigma_1 = L_{11}^2\langle Q_1^2\rangle + L_{12}^2\langle Q_2^2\rangle \qquad \text{(A9)}$$

$$\Sigma_3 = L_{33}^2\langle Q_3^2\rangle \qquad \text{(A10)}$$

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[36] S. J. Cyvin, *Spectrochim. Acta*, **15**, 828 (1959).