BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1146—1154 (1966)

The Mean Amplitudes and Atomic Scattering Factors of Boron Tribromide

By Shigehiro KONAKA*, Tetsuzo ITO* and Yonezo MORINO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

(Received August 4, 1965)

The mean amplitudes and the interatomic distances of BBr_3 have been determined by the sector-microphotometer method of gas electron diffraction. The B–Br and Br–Br distances (r_g) have been found to be 1.8932 ± 0.0054 Å and 3.2830 ± 0.0053 Å respectively. The values of the mean amplitudes are dependent on the atomic scattering factors used in the analysis. The complex scattering factors for B and Br, as calculated on the basis of the Hartree-Fock potential, have given mean amplitudes which are consistent with the vibrational frequencies observed by spectroscopy, while the mean amplitudes derived from the use of other scattering factors are less reasonable. It has been shown that the Hartree-Fock function for the Br atom is a better representation of the atomic potential function than the Thomas-Fermi function. The utility of the method of gas electron diffraction for the study of atomic scattering factors and atomic potential functions in some favorable cases has been pointed out.

Although the difference between the absolute values $|f|$ of the complex atomic scattering factor and the Born scattering factor, f^B, is large for atoms of large atomic numbers, it does not necessarily cause serious trouble in the analysis of usual molecules by gas electron diffraction, since in the calculation of the molecular intensity the difference which appears in the numerator (the total intensity) compensates for that in the denominator (the background).

For boron tribromide, however, the difference in the scattering factors has a serious effect on the observed value of the mean amplitude, l(B–Br). This suggests that information about the atomic scattering factors may be obtained from gas electron diffraction; it is possible to make a critical examination of the theoretical scattering factors by comparing the value of l(B–Br) estimated from the observed vibrational frequencies with the observed values of l(B–Br), which depend on the scattering factors used in the analysis. The experimental backgrounds should provide additional information about the theoretical scattering factors.

It also seems important to determine the molecular structure of boron tribromide as accurately as possible by taking into consideration the effect of the scattering factors. One electron diffraction study of boron tribromide has been carried out, by the visual method, by Lévy and Brockway.[1] Their results were: r(B–Br)$=1.87\pm0.02$ Å and r(Br–Br)$=3.25\pm0.03$ Å.

Experimental

The diffraction apparatus used in this study was the same as that reported on in a previous paper.[2] The diffraction patterns were taken on Fuji Process Hard plates by using an r^3 sector. The camera distances were either 11.8 cm. (short camera distance), which covered the region from $q=17$ to $q=98$, or 27.9 cm. (long camera distance), which covered the region from $q=6$ to $q=36$. The accelerating voltage (43 kV.) was automatically stabilized within 0.1% during the experiment. The sample of a commercial grade was purified by distillation. KEL-F stopcock grease was used to avoid the erosion of the lubricant by the sample. The gas sample was led into the diffraction chamber through a drum-type nozzle (the same as that reported on in a preceding paper)[3] at the temperature of 17°C. The beam current was about 0.005 and 0.002 μamp., and the exposure times were about 3 and 5 min. for the short and long camera distances respectively. The wavelengths of the primary electron beam were measured by making use of the transimission patterns of gold foil.

The densities of the photographs developed at 20°C for 5 minutes with an FD-131 developer were measured using a Rigaku-Denki MP-3 microphotometer. The undesirable effects of the time lag of the recorder were eliminated by the method described in a preceding paper.[3] Seven plates for each camera distance were used for analysis. The optical densities (0.1—0.6) of these plates were all within the range where the linearity between density and intensity has been established by experiment.[4]

Analysis

A molecular intensity curve was obtained by drawing a smooth background line through the undulation of the intensity curve corrected for imperfections in the sector shape. The background line was corrected according to the criterion of minimum ghosts in the radial distribution curve.[5]

Two sets of atomic scattering factors were used to calculate the radial distribution curves: the Born scattering factors, f^B, as calculated by several authors[6-8], and the absolute value, $|f|$, of the complex scattering factors as calculated by Ibers and Hoerni[9] (Fig. 1). The phase shifts, $\Delta\eta_{BBr}=\eta_{Br}-\eta_B$, taken from their table were used for both sets. The inelastic scattering factors were taken from the table of Bewilogua.[10]

The expression of molecular intensity is given by[11]:

$$qM(q)=k\sum A_{ij}\mu_{ij}\cos\Delta\eta_{ij} \times \sin\left(\frac{\pi}{10}qr_{ij}\right)\exp(-\alpha_{ij}q^2) \tag{1}$$

where:

$$\alpha_{ij}=\frac{1}{2}\left(\frac{\pi}{10}\right)^2 l_{ij}^2 \tag{2}$$

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

$$|F|=\boldsymbol{h}^2s^2|f|/8\pi^2\boldsymbol{me}^2 \tag{3}$$

The curves of the μ-factors $\mu_{BBr}\cos\Delta\eta_{BBr}$ and μ_{BrBr} are shown in Fig. 2. Since the values of $1-\mu_{BBr}\cos\Delta\eta_{BBr}$ are not small for a small q region ($q<17$) or for a large q region ($q>50$), the usual corrections[12] for non-nuclear scattering, $1-\mu_{ij}\cos\Delta\eta_{ij}$, are not suitable. The molecular intensity for the short camera distance was, therefore, modified into the following $qM(q)_c$ by adding the correction term of $\Delta qM(q)$ to Eq. 1, taking into account the apparent splitting of the B–Br distance because of the failure of the Born approximation:[11]

---

* Present address: Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo (S. K.), and the Institute for Physical and Chemical Research, Tokyo (T. I.).

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

[2] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958).

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

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

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

[6] J. A. Ibers, *Acta Cryst.*, **10**, 86 (1957).

[7] H. Viervoll and O. Ögrim, ibid., **2**, 277 (1947).

[8] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

[9] J. A. Ibers and J. A. Hoerni, *Acta Cryst.*, **7**, 405 (1954).

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

[11] R. Glauber and V. Schomaker, *Phys. Rev.*, **89**, 667 (1953).

[12] L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

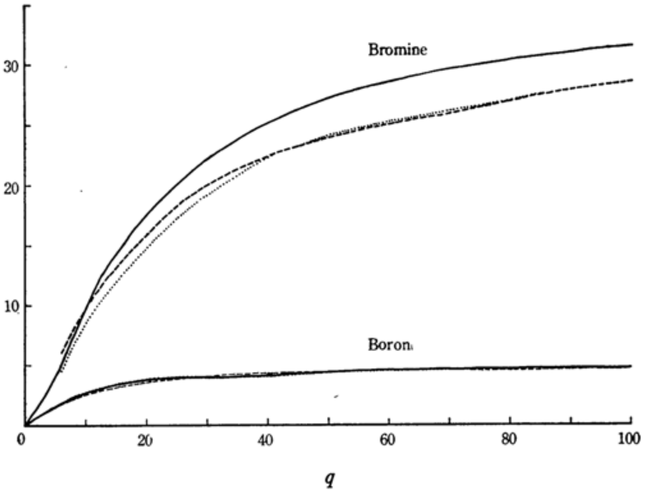

Fig. 1. Atomic scattering factors for the boron and bromine atoms.

—— $\frac{\boldsymbol{h}^2 s^2}{8\pi^2 \boldsymbol{m} \boldsymbol{e}^2} f^{\mathrm{B}} = Z - f_{\mathrm{x}}$, 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.

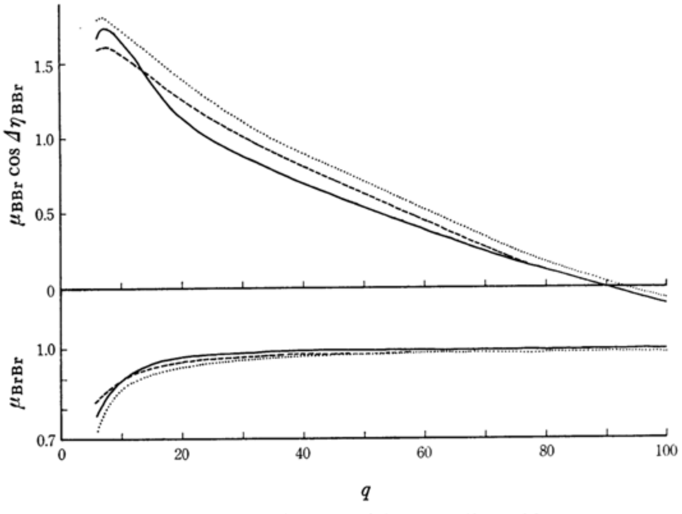

Fig. 2. μ-factors of boron tribromide.

—— $f^{\mathrm{B}} e^{i\eta_{\mathrm{T.F.}}}$, ---- $|f|_{\mathrm{T.F.}}{}^{i\eta_{\mathrm{T.F.}}}$, …… $|f|_{\mathrm{H.F.}} e^{i\eta_{\mathrm{H.F.}}}$.

$$qM(q)_{\mathrm{c}} = k\frac{A_{\mathrm{BBr}}}{2}\left\{\sin\left(\frac{\pi}{10}q(r_{\mathrm{BBr}}+\Delta r)\right) + \sin\left(\frac{\pi}{10}q(r_{\mathrm{BBr}}-\Delta r)\right)\right\} e^{-\alpha_{\mathrm{BBr}}q^2} + kA_{\mathrm{BrBr}}\sin\left(\frac{\pi}{10}qr_{\mathrm{BrBr}}\right)e^{-\alpha_{\mathrm{BrBr}}q^2} \tag{4}$$

$$\Delta qM(q) = kA_{\mathrm{BBr}}\left\{\cos\left(\frac{\pi}{10}q\Delta r\right) - \mu_{\mathrm{BBr}}\cos\Delta\eta_{\mathrm{BBr}}\right\} \times \sin\left(\frac{\pi}{10}qr_{\mathrm{BBr}}\right)e^{-\alpha_{\mathrm{BBr}}q^2} + kA_{\mathrm{BrBr}}(1-\mu_{\mathrm{BrBr}})\sin\left(\frac{\pi}{10}qr_{\mathrm{BrBr}}\right)e^{-\alpha_{\mathrm{BrBr}}q^2} \tag{5}$$

The molecular intensity for the long camera distance, on the other hand, was obtained by adding to Eq. 1 the correction term of $\Delta qM(q)$,

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

(A) The Born scattering factor f^B and the phase shift $\eta_{T.F.}$

	r_a(B–Br)	r_a(Br–Br)	l(B–Br)	l(Br–Br)	index
Average	1.8930	3.2832	0.0145*	0.0779	1.029
σ_1	0.0018	0.0005	0.0086	0.0006	0.007
σ_2	0.0016	0.0009	0.0029	0.0004	0.011

(B) The complex scattering factor, $|f|_{T.F.}e^{i\eta_{T.F.}}$, calculated from the Thomas-Fermi potential

	r_a(B–Br)	r_a(Br–Br)	l(B–Br)	l(Br–Br)	index
Average	1.8926	3.2833	0.0356*	0.0776	1.035
σ_1	0.0017	0.0005	0.0039	0.0006	0.007
σ_2	0.0017	0.0009	0.0022	0.0004	0.011

(C) The complex scattering factor, $|f|_{H.F.}e^{i\eta_{H.F.}}$, calculated from the Hartree-Fock potential

	r_a(B–Br)	r_a(Br–Br)	l(B–Br)	l(Br–Br)	index
Average	1.8929	3.2832	0.0526*	0.0778	1.042
σ_1	0.0015	0.0004	0.0024	0.0005	0.006
σ_2	0.0017	0.0009	0.0017	0.0004	0.011

* The minimum l(B–Br) value allowed by spectroscopic data is 0.0502 Å

which takes into account the apparent increase in the B–Br mean amplitude because of the slight deviation from the Born formula:[13]

$$qM(q)_c = k\gamma A_{BBr}\sin\left(\frac{\pi}{10}qr_{BBr}\right)e^{-\alpha'_{BBr}q^2} + kA_{BrBr}\sin\left(\frac{\pi}{10}qr_{BrBr}\right)e^{-\alpha_{BrBr}q^2} \tag{6}$$

$$\begin{aligned}\Delta qM(q) = {} & k\gamma A_{BBr}\left\{1-\frac{\mu_{BBr}\cos\Delta\eta_{BBr}}{\gamma\exp(-\beta q^2)}\right\} \\ & \times\sin\left(\frac{\pi}{10}qr_{BBr}\right)e^{-\alpha'_{BBr}q^2} \\ & + kA_{BrBr}(1-\mu_{BrBr}) \\ & \times\sin\left(\frac{\pi}{10}qr_{BrBr}\right)e^{-\alpha_{BrBr}q^2}\end{aligned} \tag{7}$$

where:

$$\alpha'_{BBr} = \alpha_{BBr} + \beta \tag{8}$$

and where γ is a constant.

As a result of the above modifications, the $\Delta qM(q)$ values, shown in Fig. 3, were made much smaller than the conventional correction terms, $1-\mu_{ij}\cos\Delta\eta_{ij}$.

When the backgrounds were revised by the non-negativity criterion of the radial distribution curve,[5] the molecular intensity for the long camera distance (q=6—36) agreed with that for the short distance (q=17—98), especially over the region q=18—25 (Fig. 4).

Seven molecular intensity curves were obtained by combining each one of the molecular intensity curves for the short camera distance with any one of those for the long distance in the above q region (18—25). The molecular parameters were determined by the least-squares fitting of the observed molecular intensity to the following theoretical expression,[14] including the anharmonicity parameters κ, which were neglected in the above treatment of the radial distribution curves:

$$\begin{aligned}qM(q) = {} & k\sum A_{ij}\mu_{ij}\cos\Delta\eta_{ij} \\ & \times\sin\frac{\pi}{10}q\left[r_{aij}-\left(\frac{\pi}{10}q\right)^2\kappa_{ij}\right] \\ & \times\exp\left[-\frac{1}{2}\left(\frac{\pi}{10}q\right)^2 l_{ij}{}^2\right]\end{aligned} \tag{9}$$

The anharmonicity parameters, κ, were estimated in the way reported on in a preceding paper[3]; they were not varied as parameters. The results of the least-squares analysis are listed in Table I.

Results and Discussion

Mean Amplitudes and Atomic Scattering Factors.—According to the scattering theory of partial waves, the atomic scattering factors, $f(\theta)$, which are required in the analysis of gas electron diffraction are given by:

$$f(\theta) \equiv |f(\theta)|e^{i\eta(\theta)} = (2ik)^{-1}\sum_{l=0}^{\infty}(2l+1)(\exp[2i\delta_l]-1)P_l(\cos\theta) \tag{10}$$

for the elastic scattering of electrons by a central potential, $V(r)$. Here k is the wave number of the electron, and δ_l is the phase shift of the lth partial wave. The complex scattering factors, $|f|e^{i\eta}$, were calculated by Ibers and Hoerni by this formula.[9]

The atomic scattering factors given by the first Born approximation is:

$$f(\theta) \simeq f^B(\theta) = -\frac{8\pi^2 \boldsymbol{m}}{\boldsymbol{h}^2}\int_0^\infty V(r)\frac{\sin sr}{sr}r^2 dr \tag{11}$$

---

[13] L. S. Bartell, and L. O. Brockway, *Nature*, **171**, 978 (1953).

[14] Y. Morino, K. Kuchitsu, T. Iijima and Y. Murata, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **83**, 803 (1962).

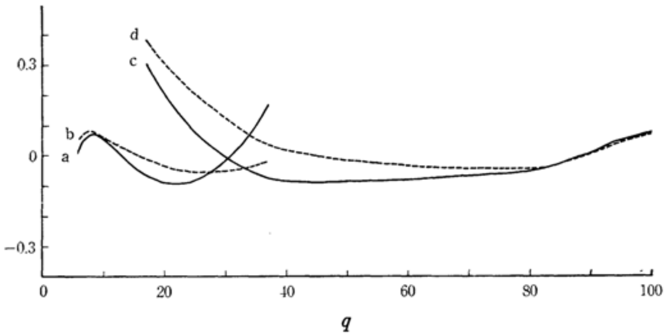

Fig. 3. Corrections for non-nuclear scattering.
—— $f^{\mathrm{B}}\mathrm{e}^{i\eta_{\mathrm{T.F.}}}$, $|f|_{\mathrm{T.F.}}\mathrm{e}^{i\eta_{\mathrm{T.F.}}}$.
a: $\dfrac{\mu_{\mathrm{BBr}}\cos\varDelta\eta_{\mathrm{BBr}}}{\gamma\exp(-\beta q^2)}-1$, $(\gamma=1.68,\ \beta=7.04\times10^{-4})$.
b: $\dfrac{\mu_{\mathrm{BBr}}\cos\varDelta\eta_{\mathrm{BBr}}}{\gamma\exp(-\beta q^2)}-1$, $(\gamma=1.53,\ \beta=4.00\times10^{-4})$.
c, d: $\mu_{\mathrm{BBr}}\cos\varDelta\eta_{\mathrm{BBr}}-\cos((\pi/10)q\varDelta r)$, $(\varDelta r=0.056\text{Å})$.

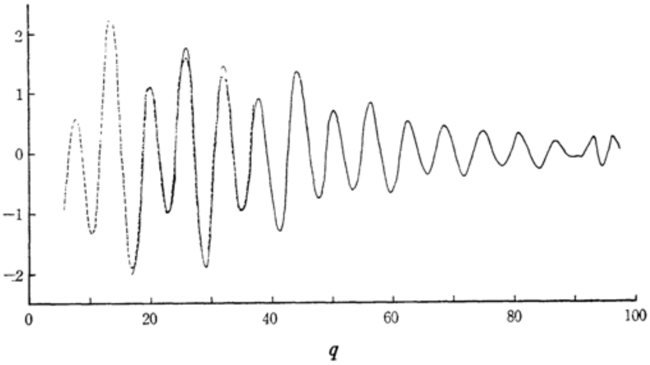

Fig. 4. The molecular scattering intensity observed at the short camera distance (solid line) and at the long camera distance (dashed line).

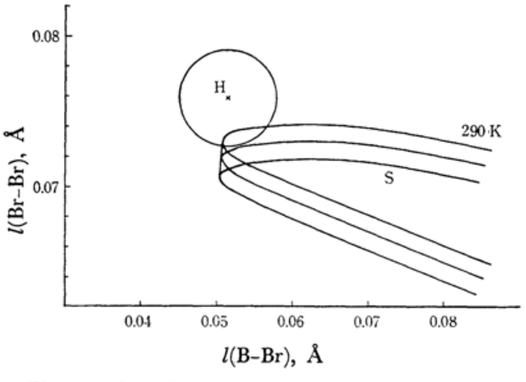

Fig. 5. Correlation curve of two mean amplitudes.
H: The observed values obtained by using the complex scattering factors calculated from the Hartree-Fock potential.
S: Calculated values from spectroscopic data.

which is related to the X-ray form factor, $f_{\mathrm{x}}(\theta)$, by:

$$f^{\mathrm{B}}(\theta)=\frac{8\pi^2\boldsymbol{m}\boldsymbol{e}^2}{\boldsymbol{h}^2s^2}(Z-f_{\mathrm{x}}(\theta)) \tag{12}$$

where $\boldsymbol{m}$ is the relativistic mass of the incident electron.

While the phase shift, η, calculated by the method of partial waves has been used in most of the recent analysis, the Born scattering factor, f^{B}, has sometimes been used in place of the absolute value, $|f|$. This is possibly due to the fact that f^{B} has been regarded as more reliable than the $|f|$ value as calculated by Ibers and Hoerni, since their partial-waves calculations for most atoms were based on the Thomas-Fermi potential.

The difference between $|f|$ and f^{B} is large for heavy atoms, but its effect is negligible for most molecules in the calculation of the molecular scattering intensity, $qM(q)$, since the scattering factors appear in the numerator and in the denominator of the μ-factor, so the effect is essentially cancelled. Consequently, the difference between the scattering factors, $|f|$ and f^{B}, is large for the bromine atom (Fig. 1), but it has only a negligible effect on the μ-factor of the Br–Br pair (Fig. 2). For the B–Br pair, however, the difference in the scattering factors has a great influence on the μ-factor, as is shown in Fig. 2. This can be easily understood from the following approximate expression of μ_{BBr}, which is obtained by neglecting the $|F|$ of the boron atom and the inelastic scattering factors, S_k, relative to the $|F|$ of the bromine atom in the denominator of f_{BBr}:

$$\mu_{BBr} \propto |F|_B/|F|_{Br} \qquad (13)$$

If the scattering factor $|f|$ is replaced by f^B in this fraction, the denominator changes considerably, while the numerator remains almost unchanged. The value of $\mu_{BBr} \cos \Delta\eta_{BBr}$ then changes the least-squares result of the mean amplitude, l(B–Br), seriously.

In a preceding paper,3) it was shown that the value of l(B–Br) takes a minimum value when one of the off-diagonal elements of the $\boldsymbol{L}$ matrix, L_{34}, equals zero. The minum value of l(B–Br) allowed by the observed vibrational frequencies is 0.0502 Å at 17°C. Since it is expected, on the basis of the well-known empirical rule stated in the preceding paper,3) that the value of L_{34} is very nearly zero, the true value of l(B–Br) is expected to be very close to the minimum value, 0.0502 Å. The $l-l$ curve of BBr_3 is shown in Fig. 5, while the vibrational frequencies used in the calculation are listed in Table II.15)

TABLE II. FUNDAMENTAL FREQUENCIES USED IN THE CALCULATION a)
(in cm^{-1} units)

	$^{11}BBr_3$	$^{10}BBr_3$	error b)
ν_1	278	278	±2
ν_2	370	395	±2
ν_3	819.8	856.1	±2
ν_4	148	148	±3

a) Ref. 15.
b) Limits of error assumed in the present study.

The least-squares result of l(B–Br) obtained by using f^B is much smaller than the above minimum value and the values of the mean amplitudes observed for ordinary molecules. The l(B–Br) value obtained by using the $|f|$ value calculated by Ibers and Hoerni is about twice the value given by f^B, but it is still inconsistent with the spectroscopic value. This is possibly to be ascribed to the errors associated with the use of the Thomas-Fermi potential function for the bromine atom in the partial-waves calculation of Ibers and Hoerni.9)

The complex scattering factors of the bromine atom have recently been calculated by using the Hartree-Fock potential by Bonham and Peacher,16) but those of the boron atom had never been calculated from the Hartree-Fock potential. The boron-scattering factors were, therefore, calculated in the present study by the method of partial waves by using the Hartree-Fock potential. The results of the calculations are shown in the Appendix.

The values of $|f(\theta)|$ are found to be nearly equal to those obtained from the Thomas-Fermi potential (Fig. 1), whereas the phase shifts $\Delta\eta(\theta)$ are appreciably smaller (Fig. 6); this makes the factor $\mu_{BBr} \cos \Delta\eta_{BBr}$ increase (Fig. 2). The least-squares results obtained by using the new μ-factors are shown in Table I (C). It is noticeable that the standard error of the least-squares analysis for l(B–Br) was made smaller by the use of the revised μ-factors.

The apparent increase in the mean amplitudes due to the sample delocalization was estimated by comparing the observed background line with the theoretical one obtained from the absolute values of the complex atomic scattering factors. The corrections were −0.0012 Å and −0.0019 Å for l(B–Br) and l(Br–Br) respectively.

The estimation of the experimental errors in the mean amplitudes is shown in Table III, while the final results obtained by using the scattering factors calculated from the Hartree-Fock potential

TABLE III. LIMITS OF ERROR OF THE MEAN AMPLITUDES AND INDEX (l in Å units)

Source of error	l(B–Br)	l(Br–Br)	index
Random error (2.5σ)	0.0060	0.0013	0.028
Sample size (50% of the correction)	0.0006	0.0010	
Uncertainty in the phase shift	0.0010		
Arbitrary choice of the weight function	0.0010	0.0010	0.021
D-E calibration	0.0015	0.0024	
Total error	0.0063	0.0031	0.035

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

Source of error	r(B–Br)	r(Br–Br)
Random error (2.5σ)	0.0043	0.0023
Drift of voltage	0.0009	0.0016
Calibration of wavelength	0.0013	0.0023
Inclination of plates	0.0014	0.0025
Difference in the camera lengths between the sample and the reference gold foil	0.0006	0.0010
Arbitrary choice of the weight function	0.0015	0.0003
Effects of κ	0.0020	0.0028
Total error	0.0054	0.0053

TABLE V. FINAL RESULTS OF THE MOLECULAR CONSTANTS OBTAINED BY USING THE SCATTERING FACTOR CALCULATED FROM THE HARTREE-FOCK POTENTIAL BY THE METHOD OF PARTIAL WAVES (r_g, l and δ_g in Å units)

	B–Br	Br–Br
r_g	1.8932±0.0054	3.2830±0.0053
l	0.0514±0.0063	0.0759±0.0031
index	1.042±0.035	
δ_g	−0.0039±0.0085 (calc. 0.0056)	

---

[15] T. Wentink, Jr. and V. H. Tiensuu, *J. Chem. Phys.*, **28**, 826 (1958).

[16] R. A. Bonham and J. L. Peacher, Private communication (1965).

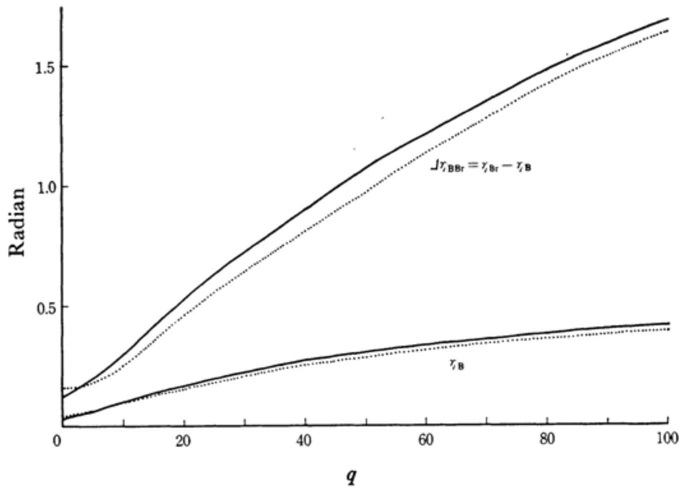

Fig. 6. Phase shift η_B and $\Delta\eta_{BBr}$.
—— Calculated from the Thomas-Fermi potential (Ref. 9).
…… Calculated from the Hartree-Fock potential.

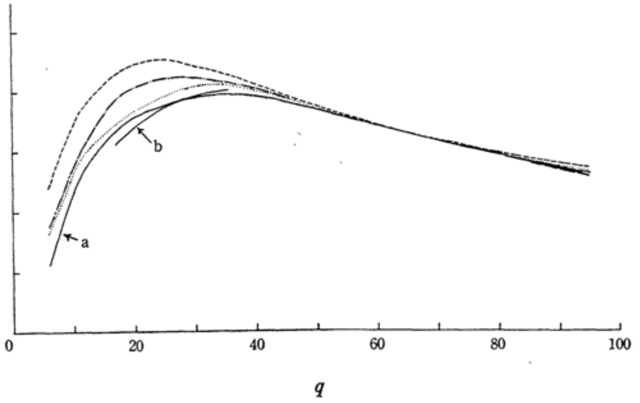

Fig. 7. Comparison of the observed and theoretical background intensities in an arbitrary scale.
—— Observed: (a) long camera distance (b) short camera distance.
—·—·— f^B
-------- $|f|_{T.F.}$ Theoretical.
……….. $|f|_{H.F.}$

by the method of partial waves are listed in Table V.

As is shown in Fig. 5, both the l(B–Br) and l(Br–Br) values are now compatible with those calculated from the observed vibrational frequencies. From the present gas electron diffraction study of boron tribromide, the Hartree-Fock function is, hence, found to be a better representation of the atomic potential function than the Thomas-Fermi function for the bromine atom, which has an intermediate atomic number.

Atomic Distances.—The corrections for the nozzle asymmetry stated in the preceding paper³⁾ are -0.0011Å and -0.0020 Å for r(B–Br) and r(Br–Br) respectively.

The limits of error of the atomic distances are estimated to be as shown in Table IV. Table V shows the final results obtained by using the scattering factor calculated from the Hartree-Fock potential by the method of partial waves. The results of the atomic distances are consistent with those given in a previous paper.¹⁾

A Comparison of the Theoretical and Observed Backgrounds.—In Fig. 7, the theoretical backgrounds calculated from the three atomic scattering factors are compared with the observed backgrounds. It is found that the $|f|_{T.F.}$ scattering factors gave a poorer background than the Born scattering factors. This tendency was also encountered in the analysis of boron trichloride.

For boron trifluoride and boron trichloride, the Born scattering factors gave results similar to those obtained from the Hartree-Fock complex scattering factors in the calculations of the mean amplitudes and the backgrounds.³⁾ For boron tribromide, however, the Born scattering factors were found to give less reasonable backgrounds than the $|f|_{\text{H.F.}}$ factors. This gives additional support for the conclusion of the previous subsection that the $|f|_{\text{H.F.}}$ scattering factor is superior to f^{B} for bromine.

Summary

Boron tribromide has been studied by the sector-microphotometer method of electron diffraction in order to make a critical examination of the atomic scattering factors. The complex atomic scattering factors, $|f|_{\text{H.F.}}e^{i\eta_{\text{H.F.}}}$, calculated from the Hartree-Fock potentials have provided a more reasonable value of the mean amplitude, l(B–Br), than the Born and Thomas-Fermi scattering factors, $f^{\text{B}}e^{i\eta_{\text{T.F.}}}$ and $|f|_{\text{T.F.}}e^{i\eta_{\text{T.F.}}}$. The theoretical background curve calculated from $|f|_{\text{H.F.}}$ is also in better agreement with the observed one than are those calculated from the other scattering factors. This indicates that the Hartree-Fock potential function is a better representation of the atomic potential function than the Thomas-Fermi function for the bromine atom. The present study suggests the usefulness of the method of gas electron diffraction for the study of atomic scattering factors and atomic potential functions in some favorable cases.

The authors wish to express their thanks to Professor R. A. Bonham for his advice in the calculation of the complex atomic scattering factors.

Appendix

Partial-waves Calculations of the Scattering Factors of the Boron and Bromine Atoms by the Use of the Hartree-Fock Potential.—The Hartree-Fock potential has been expressed by Bonham[17] in the following analytical expression:

$$V(r)=-\frac{Ze^2}{r}\left(\sum_{i=1}^{2}\gamma_i e^{-\lambda_i r}+r\sum_{j}\gamma_j e^{-\lambda_j r}\right) \tag{A1}$$

TABLE VI. PHASES OF PARTIAL WAVES δ_l OF BORON CALCULATED FROM THE HARTREE-FOCK POTENTIAL AT 40 kV.

l	Born phases calculated by Eq. A2	Asymptotic WKBJ phases calculated by Eq. A3
0	0.4020	0.4133
5	0.1831	0.1832
10	0.1276	0.1277
20	0.0794	0.0794
30	0.0556	0.0556
50	0.0299	0.0299
70	0.0164	0.0164
100	0.0068	0.0068

where j takes the values of 1 and 2 for boron, and 1, 2, and 3 for bromine. The phases of the partial waves[18] have been calculated by the Born phase formula:

$$\delta_l=-\frac{8\pi^2 mk}{h^2}\int_0^\infty V(r)[j_l(kr)]^2r^2\mathrm{d}r$$
$$=\alpha\left\{\sum_i\gamma_i Q_l\left[1+\frac{\lambda_i^2}{2k^2}\right]-\sum_j\frac{\gamma_j\lambda_j}{k^2}Q_l'\left[1+\frac{\lambda_j^2}{2k^2}\right]\right\} \tag{A2}$$

where α is $4\pi^2 me^2Z/h^2k$, Q_l is the Legendre polynomial

TABLE VII. VALUES OF COMPLEX SCATTERING FACTORS OF BORON AT 40 kV. CALCULATED FROM THE THOMAS-FERMI AND THE HARTREE-FOCK POTENTIALS

($|f(\theta)|$ in Å units and $\eta(\theta)$ in radians)

		Thomas-Fermi[a]		Hartree-Fock[b]	
θ°	s(Å^{-1})	$\|f(\theta)\|$	$\eta(\theta)$	$\|f(\theta)\|$	$\eta(\theta)$
0	0.	7.2	0.03	3.06	0.041
1	1.822	2.08	0.07	1.98	0.058
2	3.644	0.850	0.13	0.912	0.100
4	7.288	0.300	0.20	0.273	0.193
6	10.929	0.145	0.27	0.134	0.252
8	14.567	0.088	0.33	0.082	0.294
10	18.201	0.058	0.36	0.055	0.332
12	21.829	0.040	0.40	0.040	0.360
16	29.064	0.024	0.44	0.023	0.415
20	36.263	0.015	0.48	0.015	0.462
24	43.418	0.011	0.52	0.011	0.498
28	50.521	0.008	0.55	0.008	0.523

a) Interpolated values according to the table of Ibers and Hoerni (Ref. 9).

b) Present calculation.

TABLE VIII. COMPLEX SCATTERING FACTORS OF BROMINE AT 40 kV. CALCULATED FROM THE THOMAS-FERMI AND THE HARTREE-FOCK POTENTIALS

($|f(\theta)|$ in Å units and $\eta(\theta)$ in radians)

	Thomas-Fermi[a]		Hartree-Fock[b]	
	$\|f(\theta)\|$	$\eta(\theta)$	$\|f(\theta)\|$	$\eta(\theta)$
0	13.6	0.16	7.65	0.187
1	7.14	0.27	5.53	0.246
2	3.41	0.48	3.02	0.401
4	1.37	0.82	1·26	0.723
6	0.732	1.11	0.715	0.977
8	0.452	1.37	0.452	1.22
10	0.310	1.60	0.309	1.45
12	0.225	1.79	0.224	1.65
16	0.138	2.11	0.135	1.99
20	0.091	2.39	0.091	2.24
24	0.065	2.61	0.065	2.46
28	0.050	2.80	0.050	2.65

a) Interpolated values according to the table of Ibers and Hoerni (Ref. 9).

b) Ref. 16. Present calculations have given almost identical results.

---

[17] T. G. Strand and R. A. Bonham, *J. Chem. Phys.*, **40**, 1686 (1964).

[18] J. Karle and R. A. Bonham, ibid. **40**, 1396 (1964).

of the second kind, and Q_l' is the first derivative of Q_l. When l is large, this formula can be approximated by:

$$\delta_l = \alpha\left\{\sum_i \gamma_i K_0\left[\left(l+\frac{1}{2}\right)\lambda_i/k\right] + \frac{l+(1/2)}{k}\sum_j \gamma_j K_1\left[\left(l+\frac{1}{2}\right)\lambda_j/k\right]\right\} \tag{A3}$$

where K_0 and K_1 are the modified Bessel functions of the second kind. The phases can also be evaluated by the asymptotic WKBJ formula:

$$\delta_l = \frac{k\alpha}{Ze^2}\int_{(l+\frac{1}{2})/k}^{\infty} V(r)\left[k^2-\left(l+\frac{1}{2}\right)^2\Big/r^2\right]^{-1/2}\mathrm{d}r \tag{A4}$$

which is reduced to Eq. A3 by using Eq. A1 for the potential $V(r)$.[19,20] Selected values of the δ_l of the boron atom are listed in Table VI.

The sum in Eq. 10 in the text has been taken in the range of $0 \leq l \leq 250$ by using the phases of the partial waves given by Eq. A3, which may be good approximations for both the Born phases and the WKBJ phases. The results of the partial-waves calculations are shown in Tables VII and VIII.

---

[19] T. Tietz, ibid., **42**, 2251 (1965).

[20] J. A. Hoerni and J. A. Ibers, *Phys. Rev.*, **91**, 1182 (1953).