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Molecular Structure Determination by Gas Electron Diffraction at High Temperatures. II. Arsenic Triiodide and Gallium Triiodide

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The precise molecular structures of arsenic triiodide and gallium triiodide in the vapor phase have been determined by the sector-microphotometer method of electron diffraction at the nozzle temperatures of 230°C and 255°C respectively. The results of gallium triiodide have confirmed the regular triangle structure of the molecule. The force constants of these molecules have been estimated from the observed mean amplitudes.

In the preceding paper (Part I),[1] a high-temperature nozzle assembly for electron diffraction was reported, together with the results of its application to the determination of the molecular structure of arsenic in the vapor phase. The purpose of the present work is to determine the precise molecular structures of arsenic triiodide and gallium triiodide in the vapor phase, and to obtain information on the force field of these molecules on the basis of the observed mean amplitudes.

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[1] Y. Morino, T. Ukaji and T. Ito, This Bulletin, **39**, 64 (1966).

The molecular structure of arsenic triiodide has been studied by the visual method of electron diffraction by several investigators; the findings of Finbak and Hassel (1941) (r(As–I)$=2.54$Å and θ(IAsI)$=98.5°$) and the preliminary findings of Swingle (1949) (r(As–I)$=2.55\pm0.03$Å and θ(IAsI) $=101\pm1.5°$) are cited by Sutton.[2] The mean amplitudes have never been observed. The Raman frequencies of the molecule in the $CHBr_3$ and carbon disulfide solutions have been observed by Stammreich and his co-workers.[3] Akishin and his co-workers (1959)[4] investigated the molecular structure of gallium triiodide by the sector-microphotometer method of electron diffraction, with r(Ga–I)$=2.44\pm0.03$Å; they concluded that the molecule has a planar, regular triangle structure. They also estimated the mean amplitudes from the radial distribution curve. No spectroscopic data are, however, now available concerning the force field of the molecule.

Experimental

A sample of arsenic triiodide was synthesized by the $AsCl_3+3KI\rightarrow AsI_3+3KCl$ reaction.[5] The melting point of the sample was found to be 140°C, which was lower than the value of 149°C cited in the literature. This was probably due to the potassium chloride remaining in the sample. However, the sample was not further purified, since the melting point of potassium chloride, 776°C, was so much higher than the nozzle temperature that this impurity did not interfere with the present experiment. A sample of gallium triiodide was synthesized by a direct reaction of the gallium and iodine elements.[6] Stoichiometric quantities of gallium and iodine were heated in a vacuum to about 300°C; the resulting gallium triiodide was then purified by sublimation in a vacuum.

The conditions of the diffraction experiments were almost the same as those used in Part I for the arsenic except that the nozzle temperatures were $230\pm30°$C and $255\pm30°$C for the arsenic triiodide and the gallium triiodide respectively. During the exposures for the arsenic triiodide sample, a slight change in the direction of the electron beam was observed at the early stages of the experiments; this was found to be caused by the electronic charge piled up on the sample condensed onto the cold trap. The drift was eliminated by widening the space between the cold trap and the electron beam from the ordinary space of about 2 cm. to about 5 cm. Since the gallium triiodide sample was strongly hygroscopic, it was degassed in the oven of the nozzle assembly in a vacuum for more than an hour at room temperature, and then for a few minutes at about 100°C, immediately before making exposures. The optical densities of the diffraction photographs ranged from 0.15 to 0.5.

Analytical Procedure

The diffraction photographs of the arsenic triiodide and the gallium triiodide were analyzed by almost the same procedure as that described in Part I. The final results were obtained by the least-squares analysis of the molecular intensity curves, $qM(q)$. A least-squares analysis of the molecular intensity curves of a slightly different form, $qN(q)$, was also carried out in order to examine the effects of the extraneous fogging of the photographic plates on the final values of the molecular parameters.

The experimental molecular intensity curve,

$$qM(q)=q(I_L-I_B)/I_B \qquad (1)$$

was fitted by the least-squares method to its theoretical expression:

$$qM(q)=k(10/\pi)\sum\sum(|F_i||F_j|/I_B')\cos\Delta\eta \cdot\exp(-\pi^2q^2l^2/200)(1/r_a')\sin(\pi q r_a'/10) \qquad (2)$$

where r_a' stands for $r_a-\pi^2q^2\kappa/100$, and the subscripts are omitted from $\Delta\eta$, l and r_a' for the sake of simplicity. The parameters to be determined were the interatomic distances, r_a', the root-mean-square amplitudes, l, and the index of resolution, k. The anharmonicity parameters, κ, were fixed to zero because the outputs of the successive cycles did not converge when they were taken as variable parameters. This was because of a strong correlation between r_a and κ, and because the molecular intensity curves could not afford information sufficient to determine r_a and κ separately. The interatomic distances as determined by the leaset-squares procedure are, therefore, not r_a but r_a', i. e., $r_a-\pi^2q^2\kappa/100$ averaged over the observed range of the scattering angle ($q=20$—100). The values of the elastic scattering factors, $|F_i|$, and of the complex phases, η_i were taken from the tables of Ibers and Hoerni.[7]

When the fogging of the photographic plate is not negligible, as indicated by an appreciable decrease in the index of resolution of gallium triiodide from the ideal value of unity ($k=0.8$), the experimental molecular intensity, Eq. 1, can not be directly compared with the theoretical expression, Eq. 2, since the experimental background, I_B, in Eq. 1 contains an extraneous scattering which might affect the final values of the molecular parameters, particularly those of the mean amplitudes. As it is difficult to estimate the extraneous scattering, and as the molecular term, I_L-I_B, in Eq. 1 was probably little influenced by the extraneous scattering, an analysis of the molecular intensity curves, $qN(q)$, described below was carried out, and the results compared with those obtained

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[2] L. E. Sutton et al. ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).

[3] H. Stammreich, R. Forneris and Y. Tavares, *J. Chem. Phys.*, **25**, 580 (1956).

[4] P. A. Akishin, V. A. Naumov and V. M. Tachevskiy, *Moscow University Report* (*U. S. S. R.*), **1**, 229 (1959).

[5] H. S. Booth ed., "Inorganic Syntheses," Vol. I, 103 (1939).

[6] G. Brauer ed., "Handbüch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), p. 637.

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

TABLE I. RESULTS OF THE LEAST SQUARES ANALYSIS OF $qM(q)$ OF AsI_3 AT 230°C

Plate	I	II	III	IV	$\bar{\sigma}$*
r_a'(As-I)	2.5503	2.5568	2.5531	2.5576	0.0017Å
r_a'(I-I)	3.9192	3.9080	3.9137	3.9201	0.0055Å
l(As-I)	0.0747	0.0788	0.0721	0.0711	0.0022Å
l(I-I)	0.1507	0.1495	0.1474	0.1424	0.0043Å
Index	1.02	1.07	0.89	0.79	0.03

* The arithmetic mean of four standard deviations.

from $qM(q)$. This type of molecular intensity curve has usually been used by the Norwegian group.[8] The experimental molecular intensity, $qN(q)$, was calculated as:

$$qN(q)=A(q)(I_L-I_B) \tag{3}$$

where $A(q)=f(q)q^2\{1-(\lambda q/40)^2\}^{-3/2}$. The multiplication of the $A(q)$* factor was necessary for a least-squares fit of the curve to the theoretical expression:

$$qN(q)=K\sum\sum|F_i||F_j|\cos\Delta\eta \cdot\exp(-\pi^2q^2l^2/200)(1/r_a')\sin(\pi qr_a'/10) \tag{4}$$

where K is an adjustable constant similar to the index of resolution, k, in Eq. 2 but with less physical importance, since it is difficult to know the absolute intensity of the scattered electrons either from experimental diffraction photographs or from theoretical calculations.

The apparent interatomic distances, r_a,' were converted to the average distances, r_g', by the $r_g'=r_a'+l^2/r_a'$ relation, while the bond angles, θ_g'(IMI) (where M denotes arsenic or gallium), were calculated from the average distances by the relation:

$$\sin(\theta_g'/2)=r_g'(\text{I-I})/2r_g'(\text{M-I}) \tag{5}$$

The errors in the observed interatomic distances and the mean amplitudes were estimated by the procedure described in Part I. Although the most probable values of the interatomic distances are, in general, not influenced by the weight functions taken in the course of the least-squares treatment, the effect of the weight function was not negligible in the case of gallium triiodide. The errors were estimated by using the smooth weight function, Eq. 8 of Part I, in place of the discontinuous one. The mean amplitude of a pair of atoms with different atomic numbers is influenced by possible errors in the theoretical phases, η_i, since $\cos\Delta\eta$ has a q-dependence almost the same as that of the exponential damping factor of thermal vibrations. The cosine factor of the As–I ($\Delta Z=20$) or the Ga–I ($\Delta Z=22$) pair, when reduced to the amplitude scale, is about one-tenth of the amplitude. The uncertainties in the values of η_i given by Ibers and Hoerni have been discussed by Karle and Bonham[9] for argon ($Z=18$) and for uranium ($Z=92$); they showed them to be less than 10%. Although uncertainties in the differences, $\Delta\eta$, are expected to be even smaller, 10% was regarded as the limit of error.

The random error in the bond angles was estimated in two ways: as 2.5 σ_2—from the fluctuation among the values derived from the individual plates according to Eq. 7 of Part I, and as 2.5 σ_1—from the errors, σ_1, in the interatomic distances obtained by applying the law of the propagation of errors to Eq. 5:

$$\sigma(\theta)=(360/\pi)\tan(\theta/2)[\{\sigma(r_1)/r_1\}^2+\{\sigma(r_2)/r_2\}^2]^{1/2}$$

where r_1 and r_2 stand for r_g'(M–I) and r_g'(I–I) respectively. The systematic errors in the interatomic distances, other than that introduced by the uncertainty in the weight function, do not influence the bond angles.

Results and Discussion

Arsenic Triiodide.—*Molecular Structure.*—Four diffraction photographs were used for the analysis. One of the radial distribution curves is shown in Fig. 1. The results of the least-squares analysis of the molecular intensity curves, $qM(q)$, are listed in Table I. It should be noted that the mean amplitudes derived from the four plates are in fairly good agreement with one another in spite of the large deviations in the indices of resolution. A typical experimental molecular intensity curve is compared with the best-fit theoretical one in Fig. 2. The corrections from r_a' to r_g' were +0.0022Å and +0.0056Å for the As–I and I–I distances respectively. A deviation of +0.0066Å was observed in the most probable value of l(I–I) when the real atomic scattering factors[10] were used in place of the complex ones. Since there was no suitable way to compare the reliabilities of the scattering factors, the mean of the two values was taken as the final value. The estimates of the errors in the

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[8] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

* $A(q)$ is proportional to $f(q)\{R(q)\}^2q^5/\alpha(q)\cos\theta$, where θ is the scattering angle; $f(q)$ is the levelling function; $R(q)$ is the distance from the nozzle to the point on the plate corresponding to the angle, θ, and $\alpha(q)$ is the sector function and is proportional to $\tan^3\theta$ for the r^3-sector. The cosine term in the denominator comes from the fact that the plate is perpendicular to the incident electron beam.

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

[10] A. J. Freeman and R. E. Watson, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), pp. 204—206; H. L. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957); M. Kimura, private communication.

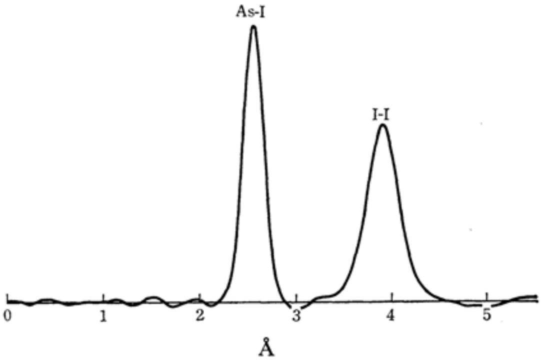

Fig. 1. Radial distribution curve of AsI_3 at 230°C.

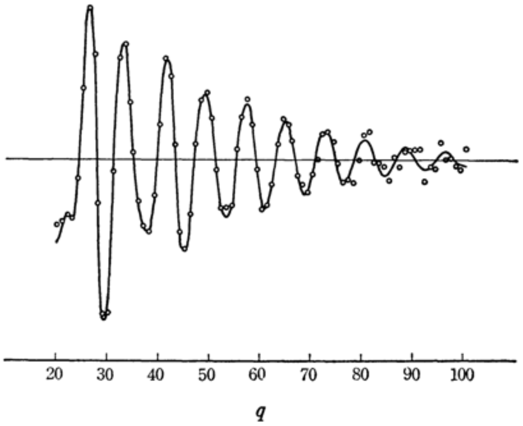

Fig. 2. Calculated and observed molecular intensity curves of AsI_3 at 230°C.
— Calcd. ○ Obs.

interatomic distances and the mean amplitudes are summarized in Tables II and III respectively. The index of resolution was found to be 0.94± 0.17. The limit of error, ±0.17, was estimated from the random error of 0.16 (2.5 σ_2), plus the systematic error, 0.07, due to the uncertainties in the scattering factors. The final results of the molecular parameters are listed in Table IV. The results of the least-squares analysis of the molecular intensity curves, $qN(q)$, are listed in Table V. They were in good agreement with the results obtained from $qM(q)$.

TABLE II. ERRORS IN THE INTERATOMIC DISTANCES OF AsI_3

Source of error	r_g'(As–I)	r_g'(I–I)
Random:		
2.5 σ_1	(0.0021)Å	(0.0069)Å
2.5 σ_2	0.0043	0.0069
Systematic:		
scale factor 0.13%	0.0033	0.0051
weight	negligible	negligible
Limit of error:	0.0054	0.0085

TABLE III. ERRORS IN THE MEAN AMPLITUDES OF AsI_3

Source of error	l(As–I)	l(I–I)
Random:		
2.5 σ_1	(0.0028)Å	(0.0053)Å
2.5 σ_2	0.0043	0.0054
Systematic:		
a) sample size	0.0010	0.0012
b) weight	0.0029	0.0027
c) scattering factor	negligible	0.0066
d) extraneous scattering	0.0022	0.0017
e) $\Delta\eta$	0.0007	none
Limit of error:	0.0057	0.0092

TABLE IV. FINAL RESULTS OF THE MOLECULAR PARAMETERS OF AsI_3 AT 230°C

	r_g'	l	θ_g'(IAsI)
As–I	2.557±0.005Å	0.074±0.006Å	100.2°±0.4°
I–I	3.921±0.009	0.151±0.009	

TABLE V. RESULTS OF THE LEAST SQUARES ANALYSIS OF $qN(q)$ OF AsI_3 AT 230°C

	r_g'	l	θ_g'(IAsI)
As–I	2.557±0.005Å	0.076±0.006Å	100.2°±0.4°
I–I	3.920±0.011	0.149±0.007	

Force Constants. — The relations between the mean amplitudes and the force constants of an XY_3 molecule (C_{3v} symmetry) have been discussed by Iwasaki and Hedberg[11] for phosphorus trichloride. The general quadratic potential function of arsenic triiodide is expressed by a set of six force constants, for example, by F_{11}, F_{12}, F_{22}, (A_1 species), F_{33}, F_{34}, and F_{44} (E species), in terms of the ordinary symmetry coordinates as defined in the reference. They are related to the force constants in terms of the internal coordinates:

$$\left.\begin{array}{ll} F_{11}=f_r+2f_{rr}, & F_{12}=2f_{r\theta}+f_{r\theta'}, \\ F_{22}=f_\theta+2f_{\theta\theta}, & F_{33}=f_r-f_{rr}, \\ F_{34}=f_{r\theta}-f_{r\theta'}, & F_{44}=f_\theta-f_{\theta\theta} \end{array}\right\} \qquad (6)$$

where f_r and f_θ are the stretching and bending force constants respectively, and where f_{rr}, $f_{\theta\theta}$, $f_{r\theta}$ and $f_{r\theta'}$ are the interaction constants corresponding to the neighboring bonds, neighboring angles, neighboring bond and angle, and opposite bond and angle respectively.

The four Raman frequencies, combined with the two observed mean amplitudes, are sufficient for the determination of all the force constants. It should be noted that the values of the force constants are restricted by a set of relations imposed by the four frequencies. This is due to the requirement that force constants be real quantities; it will be shown below for the A_1 species. If the observed

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[11] M. Iwasaki and K. Hedberg, *J. Chem. Phys.*, **36**, 594 (1962).

frequencies, ν_1 and ν_2, are substituted into the secular equation, $|\boldsymbol{GF}-\lambda_i\boldsymbol{E}|=0$, the following two equations are obtained for the three force constants:

$$\left.\begin{aligned}\lambda_1+\lambda_2&=G_{11}F_{11}+2G_{12}F_{12}+G_{22}F_{22}\\ \lambda_1\lambda_2&=(G_{11}G_{22}-G_{12}^2)(F_{11}F_{22}-F_{12}^2)\end{aligned}\right\} \qquad (7)$$

where $\lambda_i=(2\pi c\nu_i)^2$. By eliminating one of the force constants, say, F_{22}, from the above two equations, a quadratic equation for F_{11} and F_{12} is obtained. Then, from the requirement that F_{11} be real, F_{12} is limited to the $-0.03<F_{12}<1.17$ mdyn./Å range. Similarly, F_{34} is limited to the $-0.18<F_{34}<1.03$ mdyn./Å range.

Since the number of unknown force constants is six, a correlation curve (a biquadratic curve) is obtained on the (F_{12}, F_{34}) plane from the four frequencies and one mean amplitude. From the other set of the four frequencies and the remaining mean amplitude, the other curve is obtained. Thus, the force constants can be determined as the crossing point or points of the two curves. The two correlation curves, as calculated from the Raman frequencies in Table VI and the mean amplitudes in Table IV at the temperature of 230°C, are shown in Fig. 3. The curves corresponding to the limits of error of the mean amplitudes are also shown in the figure. The curve corresponding to the lower limit of l(As–I) of 0.068Å does not exist on the real plane. Contrary to the above expectation, the crossing did not appear for the most probable values. The two curves crossed only for the upper limits of the amplitudes. Thus, the most probable values of the mean amplitudes were found to be hardly compatible with the Raman frequencies. This inconsistency may be ascribed to errors in the Raman frequencies and in the measurement of the temperature in the present experiments. The Raman frequencies were obseved in the solution and not in the gas phase. For the time being, however, the frequencies were assumed to be correct, and the effects of the uncertainty of the temperature were examined. The correlation curves at 200°C and 260°C, corresponding to the lower and the upper limits of the temperature respectively, are shown in Fig. 4. At 200°C, the two curves corresponding to the most probable values of the mean amplitudes came closer, and the overlapped area increased, while at 260°C no crossing of the curves occurred at all.

TABLE VI. FUNDAMENTAL FREQUENCIES OF AsI_3[3)]

$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(E)$	$\nu_4(E)$	
216	94	221	70	cm^{-1}

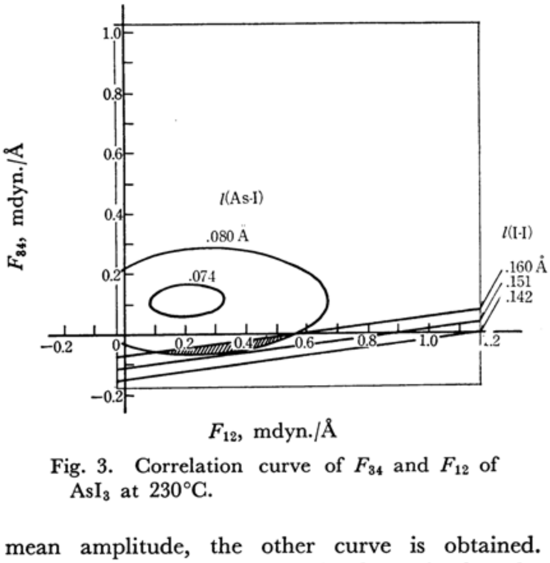

Fig. 3. Correlation curve of F_{34} and F_{12} of AsI_3 at 230°C.

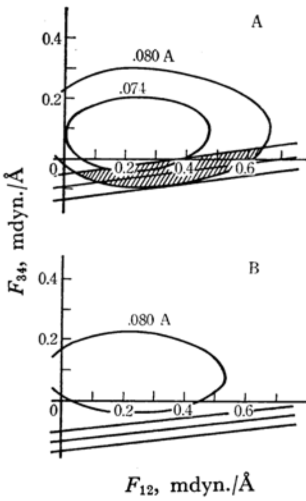

Fig. 4. Correlation curve of F_{34} and F_{12} of AsI_3 (cf. Fig. 3).
A: at 200°C, B: at 260°C

The force-constants, F_{12} and F_{34}, compatible with the observed Raman frequencies and the mean amplitudes were determined from the overlapped areas in Figs. 3 and 4 as follows: $F_{12}=0.3_5\pm0.3_0$ and $F_{34}=-0.0_3\pm0.0_7$ mdyn./Å The six force constants were determined accordingly; they are listed in Table VII, together with the force constants in terms of the internal coordinates. It must be mentioned that these force constants are subject to possible errors in the Raman frequencies used. The observed stretching constant of $1.4_7+0.2_2$ mdyn./Å is in agreement with the estimate, 1.3 mdyn./Å, derived from Badger's rule[12)] of $f=1.24/(r_e-d_{ij})^3$, if we define the parameter, d_{ij}, so as to reproduce the force constant of the diatomic molecule, GaI,[13)] i. e., if $d_{45}=1.57$Å. This parameter is also consistent with the observed stretching constant, f_r(Ga–I), of gallium triiodide. It should be noted that the interaction constant,

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12) R. M. Badger, ibid., **3**, 710 (1935).

13) S. S. Mitra, ibid., **22**, 2097 (1954); A. H. Barret and M. Mandrel, *Phys. Rev.*, **109**, 1572 (1958).

$f_{r\theta}'$, is of the same order of magnitude as f_θ and $f_{r\theta}$, although the associated errors are large; in fact, the assumption of the Urey-Bradley force field, $f_{\theta\theta}=f_{rr'}=0$, is not compatible with the frequencies of Table VI.

TABLE VII. FORCE CONSTANTS OF AsI_3

For symmetry coordinates		For internal coordinates	
F_{11}	$2.2_4\pm0.6_0$ mdyn./Å	f_r	$1.4_7\pm0.2_2$ mdyn./Å
F_{12}	$0.3_5\pm0.3_0$	f_{rr}	$0.3_8\pm0.2_1$
F_{22}	$0.1_6\pm0.0_5$	$f_{r\theta}$	$0.1_1\pm0.1_0$
F_{33}	$1.0_9\pm0.1_5$	$f_{r\theta'}$	$0.1_4\pm0.1_1$
F_{34}	$-0.0_3\pm0.0_7$	f_θ	$0.1_3\pm0.0_2$
F_{44}	$0.1_1\pm0.0_2$	$f_{\theta\theta}$	$0.0_2\pm0.0_2$

Gallium Triiodide. — *Molecular Structure.*— Three diffraction photographs were selected for analysis. The radial distribution curve is shown in Fig. 5. The results of the least-squares analysis are listed in Table VIII. One of the experimental molecular intensity curves is compared in Fig. 6 with the theoretical curve calculated from the parameters as determined by the least-squares treatment. The most probable value of the interatomic distance, r_g'(I–I), was shifted by −0.014 Å (−0.33%) when the smooth weight function, Eq. 8 of Part I, was used in place of the discontinuous one obtained from the fluctuation of the three molecular intensity curves. The discontinuous weight function can not be considered to be more reliable than the smooth one, since it was estimated from only three observations. Therefore, the average of the two values was taken as the final value, and the discrepancy was included in the estimate of the error The estimates of the errors in the interatomic distances and in the mean amplitudes are summarized in Tables IX and X respectively. The corrections from r_a' to r_g' were +0.0018 Å and +0.0060 Å for the Ga–I and for the I–I distances respectively. As was the case for arsenic triiodide, the mean amplitude, l(I–I), was influenced by the choice of the atomic scattering factors and was corrected by +0.0033 Å. The final results of the molecular parameters are listed in Table XI.

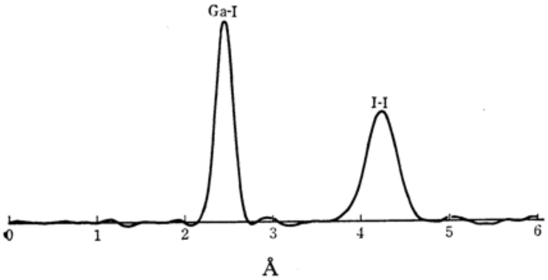

Fig. 5. Radial distribution curve of GaI_3 at 255°C.

TABLE VIII. RESULTS OF THE LEAST SQUARES ANALYSIS OF $qM(q)$ OF GaI_3 AT 255°C

Plate	I	II	III	$\bar{\sigma}$*
r_a'(Ga–I)	2.4559	2.4579	2.4535	0.0013Å
r_a'(I–I)	4.2536	4.2603	4.2563	0.0072Å
l(Ga–I)	0.0670	0.0662	0.0680	0.0018Å
l(I–I)	0.1600	0.1552	0.1641	0.0048Å
Index	0.82	0.78	0.79	0.02

* The arithmetic mean of three standard deviations.

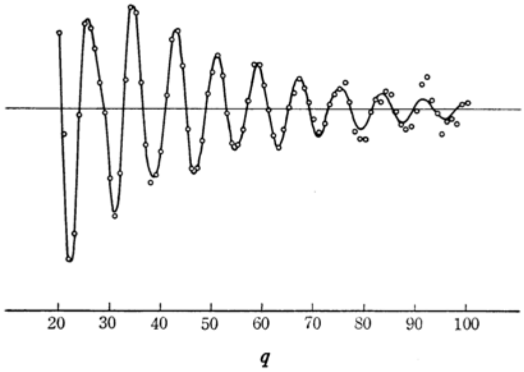

Fig. 6. Calculated and observed molecular intensity curves of GaI_3 at 255°C.
— Calcd. ○ Obs.

TABLE IX. ERRORS IN THE INTERATOMIC DISTANCES OF CaI_3

Source of error	r_g'(Ga–I)	r_g'(I–I)
Random:		
2.5 σ_1	(0.0022)Å	0.0103Å
2.5 σ_2	0.0031	(0.0082)
Systematic:		
scale factor 0.13%	0.0032	0.0055
weight	0.0013	0.0140
Limit of error:	0.0046	0.0182

TABLE X. ERRORS IN THE MEAN AMPLITUDES OF GaI_3

Source of error	l(Ga–I)	l(I–I)
Random:		
2.5 σ_1	0.0028Å	0.0071Å
2.5 σ_2	(0.0013)	(0.0064)
Systematic:		
a) sample size	0.0010	0.0013
b) weight	0.0012	0.0021
c) scattering factor	0.0017	0.0065
d) extraneous scattering	0.0014	0.0014
e) $\Delta\eta$	0.0009	none
Limit of error:	0.0040	0.0100

TABLE XI. FINAL RESULTS OF THE MOLECULAR PARAMETERS OF GaI_3 AT 255°C

	r_g'	l	θ_g'(IGaI)
Ga–I	2.458±0.005Å	0.067±0.004Å	120.0°±0.7°
I–I	4.256±0.018	0.163±0.010	

The observed bond angle of 120.0°±0.7° has confirmed the planar regular triangle structure of the molecule. It is also consistent with the results of the vapor-pressure measurement[14] and the mass-spectroscopic analysis[15], which indicate that the molecule is predominantly (about 97%[14]) monomeric at 255°C. The r_g'-structure determined above is different from the equilibrium structure (see Eq. 4 of Part I). Aside from the anharmonic contribution, the average distance, r_g', contains additional contributions due to the centrifugal distortion and the perpendicular amplitudes. The centrifugal distortion of the gallium triiodide molecule was estimated, using the force constant obtained from the observed mean amplitudes, to be $\delta_r=\boldsymbol{k}T/(f_r+2f_{rr})r_e(\text{Ga–I})=0.0017$ Å for the Ga–I bond. The distortion does not change the bond angle of the molecule, since it is totally symmetric. The effects of the perpendicular amplitudes were estimated as follows: $(L^2{}_{22}\varDelta_2+2L^2{}_{43}\varDelta_3+2L^2{}_{44}\varDelta_4)/18r_e(\text{Ga–I})=0.0074$ Å for the Ga–I bond, and $\{(\sqrt{3}L_{33}-L_{43})^2\varDelta_3+(\sqrt{3}L_{34}-L_{44})^2\varDelta_4\}/12r_e(\text{I–I})=0.0026$ Å for the I–I bond. (As for the notations, see the definitions following Eq. 9.) In the above estimate, ν_2 was assumed to be equal to ν_1. If the average distances, r_g', are corrected for the perpendicular amplitudes, the bond angle is 120.4°; this is different from the planar angle of 120°, but the discrepancy is within the range of experimental error.

The index of resolution was found to be 0.80±0.06. The limit of error was estimated from the random error of 0.03 (2.5 σ_2) plus the systematic error, 0.05, due to the uncertainty in the scattering factors. Since the rather large deviation of the observed index from unity was considered to be due to extraneous scattering, $qN(q)$ was analyzed in order to examine the effect of the extraneous scattering on the molecular parameters. The results of the least-squares analysis of $qN(q)$ are listed in Table XII. In spite of the small index of resolution, the results were in fairly good agreement with those obtained from $qM(q)$. The discrepancies in the mean amplitudes were less than those due to the uncertainties in the theoretical scattering factors. In Fig. 7 the experimental background line, which was obtained as the average of the three lines, is compared with the two theoretical lines; the theoretical background lines, denoted as C and R, were calculated from the complex and from the real[10] atomic scattering factors respectively. The lines are normalized to unity at $q=48$. The experimental background line lies between the theoretical lines, C and R. Therefore, it can be concluded that the extraneous scattering raised the background uniformly, and hence decreased the index of resolution; fortunately, however, it did not seriously affect the values of the mean amplitudes.

TABLE XII. RESULTS OF THE LEAST SQUARES ANALYSIS OF $qN(q)$ OF GaI_3 AT 255°C

	r_g'	l	θ_g'(IGaI)
Ga–I	2.456±0.005Å	0.066±0.004Å	120.2°±0.8°
I–I	4.258±0.020	0.162±0.011	

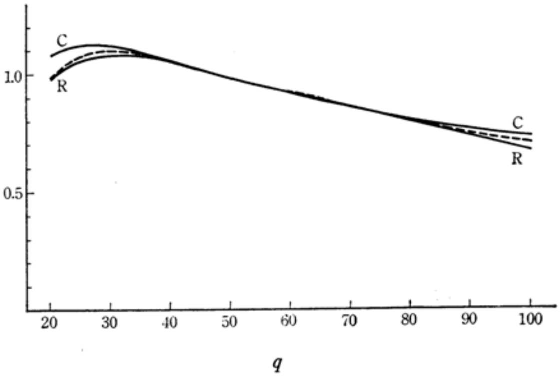

Fig. 7. Calculated and observed background lines of GaI_3.
Calc. C: Complex scattering factors (by partial-waves),
R: Real scattering factors (by the first Born approximation).
— Calcd. -- Obs.

Force Constants.—Since spectroscopic data regarding the force field of gallium triiodide are not available, we must resort to the approximation of the valence forces in order to estimate the stretching and bending force constants, f_r and f_θ, from the two observed mean amplitudes. The general quadratic potential function of a GaI_3 molecule (D_{3h} symmetry) in terms of the internal coordinates is given by:

$$\begin{aligned}2V=&\sum f_r\varDelta r_i^2+2\sum f_{rr}\varDelta r_i\varDelta r_j+2\sum f_{r\theta}\varDelta r_i(R\varDelta\theta_j)\\&+2\sum f_{r\theta}'\varDelta r_i(R\varDelta\theta_i)+\sum f_\theta(R\varDelta\theta_i)^2\\&+2\sum f_{\theta\theta}(R\varDelta\theta_i)(R\varDelta\theta_j)+f_\gamma(R\varDelta\gamma)^2\end{aligned}\tag{8}$$

where $\varDelta r_i$ and $\varDelta\theta_i$ are the changes in the ith bond and in the bond angle respectively; R is the Ga–I distance, and the $R\varDelta\gamma$ coordinate is the distance of the central gallium atom from the plane of the three iodine atoms. The number of independent force constants is reduced from seven to five when the potential function is expressed in terms of symmetry coordinates. By an ordinary procedure,[16] the mean-square amplitudes, l^2(Ga–I) and l^2(I–I), are expressed as:

$$\begin{aligned}l^2(\text{Ga–I})&=(1/3)L^2{}_{11}\varDelta_1+(2/3)(L^2{}_{33}\varDelta_3+L^2{}_{34}\varDelta_4)\\l^2(\text{I–I})&=L^2{}_{11}\varDelta_1+(1/6)(\sqrt{3}L_{33}-L_{43})^2\varDelta_3\\&\quad+(1/6)(\sqrt{3}L_{34}-L_{44})^2\varDelta_4\end{aligned}\tag{9}$$

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[14] W. Fischer and O. Jübermann, *Z. anorg. u. allgem. Chem.*, **227**, 227 (1936).

[15] T. Tsuchiya, private communication.

[16] Y. Morino, K. Kuchitsu and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952).

where L_{ij} is the element of the $\boldsymbol{L}$ matrix connecting the symmetry coordinates to the normal coordinates, and Δ_i is the mean-square amplitudes of the ith normal coordinate. The subscripts 1, 3 and 4 specify the symmetric stretching (A_1') and the degenerate stretching and bending (E_1') vibrations respectively. It should be noted that the out-of-plane vibration (A_2') has no influence on either of the amplitudes in this order of approximation.

When the approximation of the valence force field is introduced, i. e., when all the cross terms are assumed to be zero, the number of the force constants is reduced to two besides f_r, and a correlation diagram similar to those used for arsenic triiodide is obtained on the (f_r, f_θ) plane by using the values of the mean amplitudes as parameters. Figure 8 shows a diagram for the gallium triiodide at the temperature of 255°C. The correlation curves for the observed mean amplitudes and those corresponding to the limits of error are also shown in the figure. From the shaded area of the figure, the force constants were estimated as follows: $f_r=1.7\pm0.2$ mdyn./Å, $f_\theta=0.06\pm0.02$ mdyn./Å. The corresponding estimates of the vibrational frequencies are $\nu_1(A'_1)=150\pm10$, $\nu_2(E')=300\pm20$ and $\nu_4(E')=65\pm10$ cm^{-1}. The uncertainty in the temperature (±30°C) was taken into consideration in the estimates of the errors, while the uncertainty due to the approximation of the valence force field was not included.

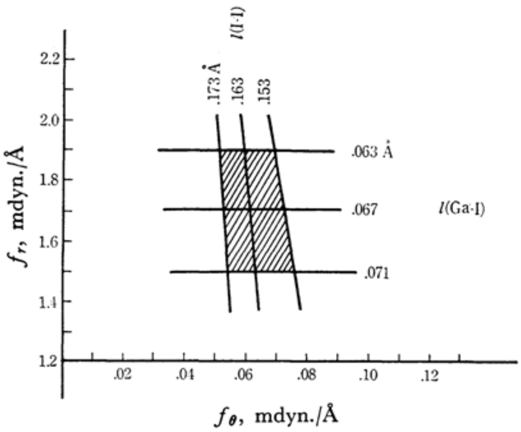

Fig. 8. Correlation curve of f_r and f_θ of GaI_3 at 255°C.

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