BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 64—71 (1966)

Molecular Structure Determination by Gas Electron Diffraction at High Temperatures. I. Arsenic

By Yonezo MORINO,† Takeshi UKAJI††,* and Tetsuzo ITO†,**

†*Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo*
††*Department of Chemistry, Ibaraki University, Mito*

(Received April 17, 1965)

A high-temperature nozzle assembly for gas-electron diffraction has been designed and constructed. The molecular structure of gaseous arsenic at 485°C has then been investigated by the use of this nozzle. The regular tetrahedral structure of the molecule has been confirmed from the observed index of resolution; the interatomic distance has been determined to be r_g(As-As)= 2.435±0.004Å, while the mean amplitude has been determined for the first time (l(As-As)= 0.085±0.006Å). The observed amplitude has led to the evaluation of the bond-stretching force constant, f_r(As-As)=1.5±0.3 mdyn./Å.

Recent technical and theoretical developments in the method of gas electron diffraction have made it possible to determine interatomic distances and the mean amplitudes of thermal vibrations in molecules with a precision of a few thousandths of an angstrom. These data are important for elucidating molecular structure. For instance,

* Present address: Ikutoku Kosen, Atsugi, Kanagawa.
** Present address: The Institute of Physical and Chemical Research, Komagome, Tokyo.

the observed interatomic distances reveal various effects of thermal vibrations, and the mean amplitudes afford information on intramolecular forces. However, almost all such high-precision data have been obtained at room temperature; experiments at higher temperatures are usually much more difficult.

About thirty years ago, Maxwell and his co-workers investigated the molecular structure of alkali halides[1] and other molecules[2] at temperatures up to about 1300°C by the visual method. Since then, several investigators have designed and used high temperature nozzles for determining the molecular structure of compounds with low vapor pressures. For example, Kimura and Aoki (1953)[3] investigated acetamide and *N*-methylacetamide at about 250°C by the visual method; Bauer and his co-workers (1960)[4] studied lithium chloride at about 820°C by the same method, and Akishin and his co-workers (1958–) studied alkali halides[5] and other molecules[6,7] in the temperature range up to about 1500°C by the sector-microphotometer method.[8] The uncertainties in the observed interatomic distances ranged from 0.02 to 0.04 Å, and the values of mean amplitudes were only tentative even when they were reported. More recently, Hedberg and Iwasaki (1962)[9] for the first time observed the temperature effects on the interatomic distances and mean amplitudes of phosphorus trichloride by taking diffraction photographs at 27 and 232°C and by applying a least-squares treatment to the molecular intensity curves.

For the present work, a high-temperature nozzle assembly for high-precision studies was designed, constructed, and used for the study of the molecular structure of arsenic in the vapor phase. When the structure of this molecule was studied by Maxwell and his co-workers (1935)[2] at about 500°C by the visual method of gas electron diffraction, they observed one interatomic distance, 2.44 ± 0.03 Å; with the aid of the vapor density data,[10] which indicate that the molecule is predominantly tetratomic below 800°C, they concluded that the molecule has a regular tetrahedral structure. No spectroscopic information has up until now been available on the force field of this molecule.

Experimental

The Construction of the High-Temperature Nozzle Assembly.—After a series of preliminary tests on possible difficulties which were expected to arise in electron-diffraction experiments at high temperatures (the chemical and thermal instability of materials, difficulty in the control of the rate of gas effusion, the fogging of photographic plates due to radiation from the heated assembly, etc.), a nozzle assembly useful for high-precision studies in the temperature range up to 600°C was designed and constructed.

A diagram of the nozzle assembly is shown in Fig. 1. The sample is heated to a required temperature in the oven, 1; the stopcock valve, 2, is then opened, and the vapor is ejected through the capillary nozzle, 3, into the diffraction camera, where it scatters electron beams at about 0.4 mm. above the nozzle outlet. About 2 cm. above the nozzle, there is a brass cold trap cooled with liquid nitrogen designed to condense the ejected vapor. The distinctive features of this nozzle assembly are the material of the nozzle and the construction of the stopcock valve. The oven and the nozzle are made of quartz, which is suitable because of its chemical and thermal stability (the linear expansion coefficient: 4.8×10^{-7}/deg.; the softening temperature: 1300°C). The thermal stability of the nozzle is essential for the accurate determination of the camera length. The nozzle is equipped with a stopcock valve lubricated with a small amount of fine graphite powder in order that the gas can be introduced into the camera chamber for a desired length of time; it also enables a fine control of the rate of sample effusion. Diffraction photographs can be obtained at any fixed temperatures up to 600°C by the use of this valve. The valve is also useful for the study of a reaction system in the vapor phase because it prevents any one of the reactants from evaporating out of the oven through the outlet before the system attains the thermal equilibrium at the desired temperature.

The oven, the capillary nozzle and the cover-framework, 4, are all made of quartz. The oven, about 15 ml. in volume, contains enough sample gas for three successive 4-mmHgl. exposures. The length of the capillary nozzle is about 20 mm., while the inner diameter at the outlet is about 0.2 mm. The edge of the top of the nozzle is cut off lest it should interrupt the scattered electrons. The upper part of the nozzle is covered with gold foil grounded through a fine wire in order to avoid the charging-up of the nozzle, which might cause a drift of the electron beam.

The oven and the nozzle are individually heated with a 10—40 V. a. c. current supplied through coils of nichrome wires, which are supported by a number of small projections of quartz attached to the walls of the oven and the nozzle and which are covered with quartz-wool. The magnetic field produced by the electric current is minimized by a dual winding of nichrome wires in opposite directions. The fluctuation of the electron beam due to the magnetic field is found to be negligible under these working conditions (the electric current up to about 1 amp.). The temperatures of the oven and the nozzle are measured with two alumel-

1) L. R. Maxwell, S. B. Hendricks and V. M. Moseley, *Phys. Rev.*, **52**, 968 (1937).
2) L. R. Maxwell, S. B. Hendricks and V. M. Moseley, *J. Chem. Phys.*, **3**, 699 (1935).
3) M. Kimura and M. Aoki, This Bulletin, **26**, 429 (1953).
4) S. H. Bauer, T. Ino and R. F. Porter, *J. Chem. Phys.*, **33**, 685 (1960).
5) P. A. Akishin and N. G. Rambidi, *Z. Phys. Chem.*, **213**, 111 (1960).
6) P. A. Akishin, V. A. Naumov and V. M. Tachevskiy, *Moscow University Report* (*U. S. S. R.*), **1**, 229 (1959).
7) V. P. Spiridonov, P. A. Akishin and V. I. Tsirelinikov, *J. Structural Chem.* (*U. S. S. R.*), **3**, 329 (1962).
8) P. A. Akishin, M. I. Vinogradov, K. D. Danilov, N. P. Levkin, E. N. Martinson, N. G. Rambidi and V. P. Spiridonov, *Instruments and Experimental Technique* (*U. S. S. R.*), **2**, 70 (1958).
9) K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, **36**, 589 (1962).
10) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, London (1929), p. 23.

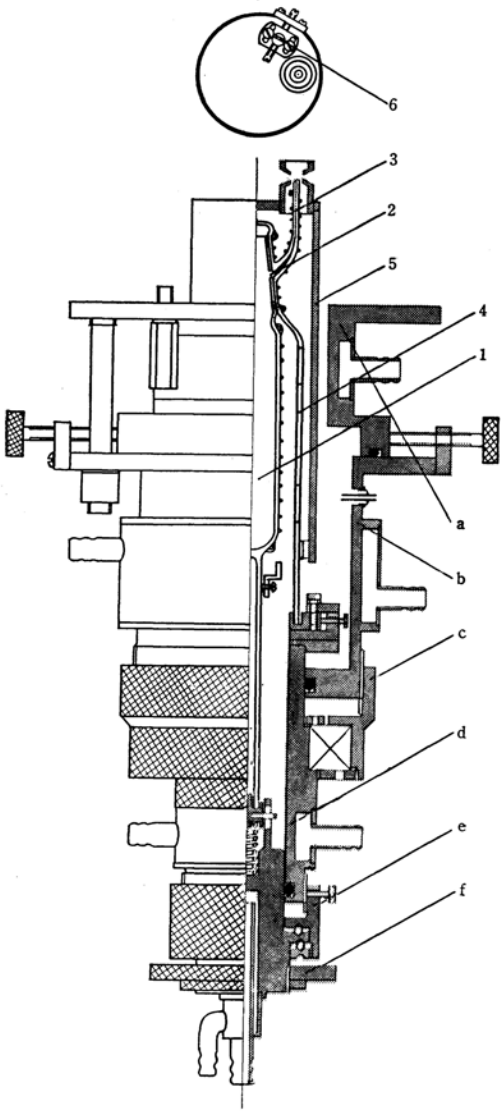

Fig. 1. High-temperature nozzle assembly.
1 Oven, 2 Stopcock, 3 Nozzle, 4 Framework, 5 Shield, 6 Gold-foil support, a—f Parts of the oven holder.

chromel thermocouples placed in contact with the walls. The difference between the temperature of the ejected gas and that of the nozzle, as measured by the thermocouple, is estimated to be less than 30°C.* The oven and the nozzle can be heated to 600°C in about 15 min. A little degassing from the nozzle assembly during heating does not affect the vacuum of the diffraction camera (ca. 2×10^{-5} mmHg). In the temperature range up to 600°C, the fogging of photographic plates due to radiation from the heated assembly is easily eliminated by means of a radiation shield, 5, which covers the oven and the nozzle. A support, 6, for mounting the gold foil necessary for the calibration of the electron wavelength and the camera distance is attached to the shield.

The oven and the cover-framework are supported by an oven-holder which consists of the following six parts, a to f. Part a is designed for fixing the whole assembly on to the diffraction camera; Part b, for adjusting the position of the nozzle in a plane parallel to the electron beam; Part c, for changing the height of the nozzle, and Part d, for rotating the assembly in such a way that the gold foil is placed in the beam, and also for supporting the cover-framework of the oven. (The framework is cemented to the support with the epoxy adhesive "Araldite.") The vacuum-tightness of the stopcock is assured by Part e, which pushes the oven against the cover-framework, while Part f supports the oven and transmits to the axis of the oven the rotation necessary for opening and shutting the stopcock. A steel spring is inserted between Part f and the axis in order to apply proper pressures on the stopcock and to make allowance for any possible mechanical eccentricity of the male part of the stopcock with respect to the female part. The sample can be easily loaded and unloaded by pulling down the oven, together with Part e and Part f. All parts are made of brass, and Parts a, b, d and f are water-cooled. Various parts of the assembly are made vacuum-tight with O-rings; they are operated independently by means of ball-bearing systems. The whole assembly was processed in the workshop of the Tokyo Shibaura Electric Co.

The Calibration of the Camera Length.—The nozzle assembly was attached to a diffraction camera equipped with an r^3-sector.[11] The cold trap which covered the nozzle was replaced by a glass-window, and the plate-to-gold foil distance, L_g, was adjusted so as to be equal to the camera length, L_c (the distance from the plate to the center of the nozzle outlet) using a comparator. Fine adjustments were made by means of a screw attached to the gold-foil support. The error in the agreement between L_g and L_c was kept to within 0.05 mm., a value which could introduce an error of only about 0.05% in the scale factor, since the camera length was 106 mm. Deviations in the camera length during the heating up to 600°C were also found to be within 0.05 mm.

During the diffraction experiments, however, the rotation of the nozzle assembly necessary for locating the center of the gold foil in the electron beam could not be adjusted using a comparator, since the cold trap obstructed the field of vision. The adjustment was thus made by observing, through a side-window, the images of the electron beam and of the gold-foil support on a fluorescent screen. Another sheet of gold foil was placed in front of the nozzle assembly in order to make the images during the adjustments. An uncertainty in the angle of rotation of the nozzle assembly could be another source of the error in the scale factor.

Figure 2 shows a schematic diagram of the top-view of the nozzle assembly, where R is the radius of the circumference on which the centers of the nozzle outlet

* The temperature measured by the thermocouple was calibrated at 270°C by the following procedure. A small crystal of anthraquinone was placed on top of the nozzle above the outlet while heated iodine gas was ejected through the capillary nozzle. The temperature, as measured by the thermocouple, was 270°C when the crystal began to melt. This temperature was in agreement with the observed melting point of the crystal within a range of experimental error of about ±5°C.

11) Y. Morino, K. Kuchitsu and E. Hirota, "Experimental Chemistry" (Jikken Kagaku Koza), Vol. 3, Maruzen Co., Tokyo (1957), p. 253.

and of the gold foil move, and O is the center of rotation. As is evident from the figure, an error in the angle of rotation, $\Delta\theta$, introduces an error in the camera distance:

$$\Delta Lc = R\Delta\theta\sin\theta$$

In order to assure a 0.1% accuracy in the scale factor, ΔLc must be less than 0.1 mm. If we take the radius of the gold foil, 1 mm., as approtimately the maximum of $R\Delta\theta$, it is necessary to adjust θ to be less than 6°. In the following experiments, care was taken to adjust the center of the rotation of the nozzle assembly to just below the electron beam, as well as to minimize errors in the angle or rotation.

By the use of this nozzle assembly, diffraction photographs of iodine vapor have recently been taken at 80°C, 300°C and 500°C by one of the present authors.[12] A preliminary analysis has shown that the observed interatomic distances r_g(I-I) at these temperatures are in agreement with the values calculated from the spectroscopic data[13,14] within 0.15%. This uncertainty can be regarded as a measure of the total error in the scale factor of this nozzle assembly.

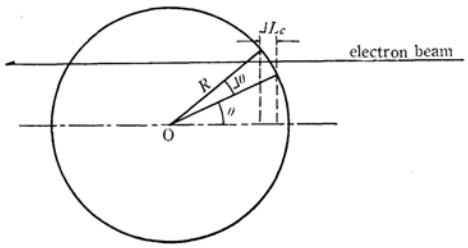

Fig. 2. Error in the camera distance ΔLc caused by the error in the angle of rotation $\Delta\theta$.

Diffraction Photographs of Arsenic. — Solid arsenic was kindly supplied by the Tokyo Shibaura Electric Co. The oxide which had covered the surface of the crystal was easily removed by heating it to about 300°C in a vacuum. The diffraction photographs were taken on Fuji Process-hard plates, with a camera distance of 106 mm., an accelerating voltage of the electron beam of about 43 kV., a beam current of about 0.005 μamp., and exposure times of from two to three minutes. The nozzle temperature was 485±30°C. The photographs were developed for five minutes in a FD-131 developer diluted twice at 20°C. The optical densities of the photographs ranged from 0.1 to 0.4, and the measured range of the scattering angle was from 20 to 100 in the q-scale.

Analytical Procedure

The interatomic distance and the root-mean-square amplitude of arsenic in the vapor phase were determined from the diffraction photographs by a procedure similar to that usually applied.[15] The final results were obtained by a least-squares analysis of the molecular intensity curves, $qM(q)$. All the calculations were carried out by using an electronic computer, PC-2.[16]

Molecular Intensity.—Four diffraction photographs were selected for the analysis; they were traced across the diameter of the diffraction pattern with a Rigaku-Denki MP-3 microphotometer while being rotated rapidly around the center of the pattern. In order to record fine details of the pattern, the transmittancy range corresponding to the undulations of the curve was magnified to about five times the original scale (full scale; 24 cm.) by the use of an electronic amplifier built into the photometer. The magnification ratio was later determined by a least-squares fit of the magnified curve to that of the original scale.

The photometer curves of the magnified and the original scales were measured at intervals of $\Delta q=1$; a value taken from one side of a curve was combined with the corresponding value from the other side, and an average was taken point by point. The distance, $x(q)$, on the abscissa of a photometer chart corresponding to the scattering angle, q, was calculated by using the value of $L_c\lambda$, which was obtained as $L_q\lambda$ from a transmission pattern of gold foil after L_q was corrected for the inclination of the photographic plate by the method of Iijima.[17],* A linear relation between the density and the intensity was assumed, since the densities of all the photographs used for the analysis were less than 0.4.[17]

After the intensity curve was corrected for the deficiency of the sector opening[18] (i. e., for the deviations from the defined opening of cr^3), it was divided by a levelling function, $f(q)$, in order to obtain a levelled intensity curve, $I_L(q)$, which facilitated the drawing of a background line, $I_B(q)$. The $f(q)$ function was derived by a least-squares fit of the intensity curve to a quadratic function. The most probable background line was obtained after two cycles of redrawing the line according to the non-negativity criterion with respect to the radial distribution curve, in which only one peak was observed. The artificial damping factor was so chosen as to reduce the molecular intensity to one-tenth of the original at $q=100$.

The experimental molecular intensity curve, $qM(q)$, was calculated as:

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

while the theoretical expression for a tetratomic molecule, As_4, is given by the equation;[15]

12) Y. Morino and T. Ukaji, to be published.
13) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Company, New York (1950), p. 541; L. S. Bartell, *J. Chem. Phys.*, **23**, 1219 (1955).
14) K. Kuchitsu and L. S. Bartell, ibid., **35**, 1945 (1961).
15) Y. Morino, Y. Nakamura and T. Iijima, *J. Chem. Phys.*, **32**, 643 (1960).
16) Y. Murata, T. Ito and K. Kuchitsu, "Bussei," **2**, 39 (1964).
17) Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).
* The inclinations of the photographic plates placed in the three positions, A, B and and C, were re-examined because the setting of the disk on which the three plates were mounted had been changed during recent leak tests. The following correction factors, which were not very different from those reported by Iijima, were obtained:
A −0.23±0.02%, B 0.06±0.03%, C 0.01±0.03%.
18) Y. Morino and Y. Murata, ibid., **38**, 104 (1965).

$$qM(q) = k(120/\pi r_a)\{|F_{As}(q)|^2/I'_B(q)\} \cdot\exp(-\pi^2q^2l^2/200) \cdot\sin(\pi q/10)(r_a-\pi^2q^2\kappa/100) \quad (2)$$

where k is the index of resolution; κ is the anharmonicity parameter, and $I_{B'}(q)$ is the sum of the coherent and incoherent atomic scattering.

Least-Squares Analysis.—The experimental intensity curve, Eq. 1, was fitted to the theoretical expression, Eq. 2 (for the tetratomic model), by the least-squares treatment, with the following four variable parameters: the apparent interatomic distance, r_a(As–As); the mean amplitude, l(As–As); the anharmonicity parameter, κ(As–As), and the index of resolution, k. According to the principle of the least-squares method, the weight function, $p(q)$, of the molecular intensity curve should be so chosen as to be inversely proportional to $\sigma^2(q)$, the square of the standard deviation at q. The standard deviation, $\sigma(q)$, was estimated[17] from the standard deviation of the four experimental molecular intensity curves used for the analysis. By this procedure, a discontinuous weight function, $p_d(q)$, was obtained. The elastic scattering factor, $|F_{As}(q)|$, was taken from the table of Ibers and Hoerni,[19] while the inelastic scattering factor, $S_{As}(q)$, was taken from the table of Bewilogua.[20]

The apparent interatomic distance, r_a, determined by the least-squares treatment was converted to r_g by the relation[15]:

$$r_g = r_a + l^2/r_a \quad (3)$$

The distance r_g is the interatomic distance averaged over the anharmonic vibrations of the two end-atoms; it is expressed as[21]:

$$r_g = r_e + \langle\Delta z\rangle + (1/2r_e)(\langle x^2\rangle + \langle\Delta y^2\rangle) + \delta_r \quad (4)$$

where the second and the third terms represent the effects of anharmonic and perpendicular vibrations respectively, and δ_r represents the centrifugal distortion. It should be noted that all the terms except for r_e depend on the temperature.

The Estimation of Errors.—Random and systematic errors in the molecular parameters as determined by gas-electron diffraction have been critically discussed by Kuchitsu,[22] and by Morino, Kuchitsu and Murata.[23] In the present work, the errors were estimated essentially according to their schemes.

Random Errors.—The most probable value, x_m, of a certain molecular parameter, x, was obtained as the arithmetic mean of the most probable values, x_i, derived from N molecular intensity curves (N is the number of plates used for the analysis; it was four in the present case):

$$x_m = \sum x_i/N \quad (5)$$

The random error associated with the most probable value, x_m, was estimated in two different ways[22]: $\sigma_1(x_m)$ and $\sigma_2(x_m)$. They were calculated as:

$$\sigma_1(x_m) = \bar{\sigma}(x)/\sqrt{N} \quad (6)$$

and:

$$\sigma_2(x_m) = \sum\{(x_i - x_m)^2/N(N-1)\}^{1/2} \quad (7)$$

where $\bar{\sigma}(x)$ is the arithmetic mean of N standard deviations of the least-squares treatment. The statistical treatment, Eq. 6, is valid only when the values, x_i, agree with each other within the range of $\bar{\sigma}(x)$. Therefore, σ_2 gives another useful measure of the random error; the larger, σ_1 or σ_2, was taken as the random error.

Systematic Errors.—The following possible sources of important systematic errors were taken into consideration:

i) For the Interatomic Distance:

a) The drift of the wave length of the electron beam, 0.05%.

b) Uncertainty in the lattice constant of the gold foil, 0.05%.

c) Uncertainty in the camera distance, 0.1%. The plate-to-gold foil distance was adjusted to be equal to the camera distance within the range of 0.1% uncertainty.

d) Uncertainty in the corrections for the inclinations of the plates, 0.04%. The camera distance was corrected for the inclination of the photographic plate. The uncertainty in the correction factors, 2.5 σ, was taken as the limit of error.

e) Uncertainty in the anharmonicity parameter. The difference between the most probable value of r_a when κ was taken as a variable parameter and that when κ was fixed at zero was taken as the limit of error.

ii) For the Mean Amplitude:

a) The effect of the finite sample size. The delocalization of the silicon tetrachloride gas near the nozzle outlet was studied by Murata[24] for a needle-type nozzle; it was shown there to be about a half of that for an ordinary drum-type nozzle; the corrections in the mean amplitudes were shown to be about −1.5%. The delocalization was expected to be even smaller for the high-temperature nozzle used in the present work because the inner diameter of the nozzle, 0.2 mm., was less than that of the nozzle used for the silicon tetrachloride, 0.55 mm., while the distance from the outlet to the electron beam was almost the same (about 0.4 mm.). Therefore, no correction was made for the effect of the finite sample size on the mean amplitude; the possible order of magnitude of the correction, which was estimated assuming the same distribution of the sample gas

19) J. A. Ibers and J. A. Hoerni, *Acta Cryst.*, **7**, 405 (1954).
20) L. Bewilogua, *Physik. Z.*, **32**, 740 (1931).
21) Y. Morino, K. Kuchitsu and T. Oka, *J. Chem. Phys.*, **36**, 1108 (1962).
22) K. Kuchitsu, This Bulletin, **32**, 748 (1959).
23) Y. Morino, K. Kuchitsu and Y. Murata, *Acta Cryst.*, to be published.
24) Y. Morino and Y. Murata, This Bulletin, **38**, 114 (1965).

TABLE I. RESULTS OF THE LEAST SQUARES ANALYSIS OF $qM(q)$ OF As_4 AT 485°C

Plate	I	II	III	IV	$\bar{\sigma}$*
r_a(As-As)	2.4313	2.4306	2.4328	2.4315	0.0014 Å
l(As-As)	0.0897	0.0828	0.0834	0.0825	0.0013 Å
κ(As-As)	1.46	0.11	0.25	1.78	0.54 10^{-5}Å^3
Index	1.04	0.91	0.98	0.93	0.02

* The arithmetic mean of four standard deviations.

as that of silicon tetrachloride, was regarded as the limit of error.

b) Uncertainty in the weight function. The mean amplitude was found to be influenced slightly by the choice of the weight function. The effect was estimated by using the following smooth-weight function in place of the discontinuous one, and the difference in the most probable value of l was taken as the limit of error;

$$p_s(q)=1 \quad \text{for} \quad q\leq 65$$
$$p_s(q)=\exp\{-0.001(q-65)^2\} \quad \text{for} \quad 65\leq q \qquad (8)$$

c) Uncertainty in the theoretical atomic-scattering factor. The error caused by this uncertainty was estimated by using the values of the atomic-scattering factor taken from different sources in the literature;[25] the largest discrepancy in the most probable value was regarded as the limit of error.

d) The effect of the extraneous scattering. This effect was estimated from a comparison of the results derived from $qM(q)$ with those derived from the molecular intensity curves of a slightly different form, $qN(q)$[26] which were expected to be less influenced by the extraneous scattering; the difference in the most probable value was taken as the limit of error.

Limit of Error.—The limit of error corresponding to the 99 per cent confidence interval was estimated as:

$$\text{Limit of error} = \{(2.5\sigma_r)^2 + \sigma_s^2\}^{1/2} \qquad (9)$$

where σ_r was the random error (the larger of σ_1 and σ_2), and σ_s^2 was the sum of the squares of all the systematic errors discussed above.

Results and Discussion

Molecular Structure.—One of the radial distribution curves is shown in Fig. 3. The results of the least-squares analysis of the molecular intensity curves, $qM(q)$, are listed in Table I, where $\bar{\sigma}$ in the last column denotes the arithmetic mean of the four standard deviations, all of which were found to be nearly equal; for instance, the $\sigma(r_a)$ values of Plates I to IV were 0.0015, 0.0015, 0.0014 and 0.0012 Å respectively. In Fig. 4 one of the experimental molecular intensity curves, $qM(q)$, is compared with the theoretical curve calculated with the parameters obtained above. The correction from the apparent distance, r_a, to the average

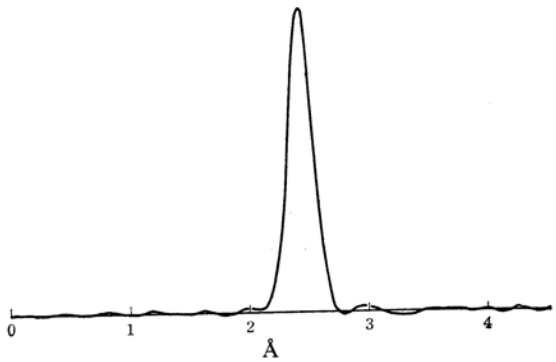

Fig. 3. Radial distribution curve of As_4 at 485°C.

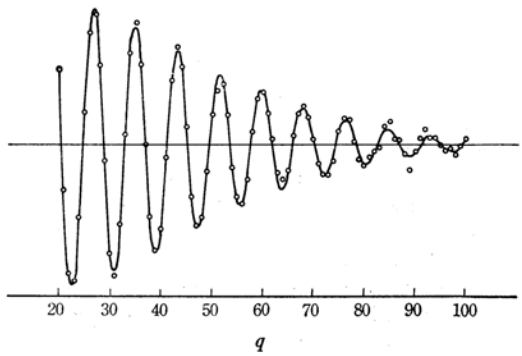

Fig. 4. Calculated and observed molecular intensity curves of As_4 at 485°C.
— Calcd.
○ Obs.

TABLE II. ERRORS IN THE INTERATOMIC DISTANCE

Source of error		r_g(As-As)
Random:		
$2.5\sigma_1$	0.0018 Å	
$2.5\sigma_2$	(0.0013)	
Systematic:		
scale factor total	0.13%	0.0032
a) drift of wavelength	0.05%	
b) lattice constant	0.05%	
c) camera distance	0.10%	
d) inclination of plate	0.04%	
e) effect of κ		0.0019
Limit of error:		0.0041

25) A. J. Freeman and R. E. Watson, "International Tables for X-Ray Crystallography," Vol. III, Kynoch press, Birmingham (1962), p. 206; M. Kimura, private communication.

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

Table III. Errors in the mean amplitude

Source of error	l(As-As)
Random:	
$2.5\,\sigma_1$	(0.0016) Å
$2.5\,\sigma_2$	0.0043
Systematic:	
a) sample size	0.0008
b) weight	0.0020
c) scattering factor	negligible
d) extraneous scattering	0.0037
Limit of error:	0.0061

Table IV. Final results of the molecular parameters of As_4 at 485°C

r_g(As-As)	l(As-As)	κ(As-As)
2.435±0.004 Å	0.085±0.006 Å	0.9±1.3×10^{-5}Å^3

distance, r_g, was +0.0030 Å. The estimates of the errors in the final values of r_g and l are summarized in Tables II and III respectively. The limit of error in the anharmonicity parameter, $\kappa\times10^5$ Å^3, was estimated to be 1.3; this comprised the random error, 2.5 σ_2, of 1.05 and the systematic error, 0.74, arising from the choice of the weight function. The final results of the molecular parameters are listed in Table IV.

The index of resolution was found to be 0.96± 0.07. The limit of error was estimated from the random error, $2.5\sigma_2$, of 0.07. Evidence for the tetratomic structure of at least the predominant part of the arsenic molecules at this temperature was given by the small deviation in the observed index from unity. This is evident from the following consideration. The molecular intensity, $qM(q)$, is proportional to the ratio of the number of the atom-pairs to the number of atoms in the molecule. Since the ratios for the diatomic, triatomic, and tetratomic structrues are 1/2, 3/3, and 6/4 respectively, analyses based on the tetratomic model must result in indices of about 0.33, 0.67, and 1, if the molecule has one of the above structures. The observed index of nearly unity clearly eliminates the possibilities of diatomic and triatomic structures.

Force Constants.—The mean amplitude and the anharmonicity parameter obtained above provide information on the intramolecular force field of the arsenic molecule, for which no spectroscopic studies of the vibrational frequencies have been made. The theory of correlating the mean amplitudes to the force constants has been developed by Morino and his co-workers[27] by using Wilson's ***GF*** matrix method, while an X_4 molecule (T_d symmetry) has been treated by Cyvin.[28]

The general quadratic potential function of the As_4 molecule (T_d symmetry) is given by:

$$2V = \sum f_r \Delta r_i^2 + 2\sum f_{rr} \Delta r_i \Delta r_j + 2\sum f_{rr'} \Delta r_i \Delta r_k \quad (10)$$

where Δr_i ($i=1,\cdots,6$) is the change in length of the ith bond, and the interaction constants, f_{rr} and $f_{rr'}$, correspond to the neighboring and the opposite bond pairs respectively. The mean-square amplitude of the As–As bond is given by[28]:

$$l^2 = (\mu/3)\,(2\Delta_1 + \Delta_2 + 3\Delta_3) \quad (11)$$

where μ is the reciprocal mass of the arsenic atom, and Δ_i is the mean square amplitude of the i th normal coordinate:

$$\Delta i = (\boldsymbol{h}/8\pi^2 c\,\nu_i)\coth(\boldsymbol{h}c\,\nu_i/2\boldsymbol{k}T) \quad (12)$$

It should be noted that the mean amplitude, l, is a function of the three force constants and of the temperature.

All of the three force constants can not be determined from a single observed value of the mean amplitude. The interaction constants, f_{rr} and $f_{rr'}$, therefore, tentatively assumed to be zero:

$$f_{rr} = f_{rr'} = 0 \quad (13)$$

The relation between the bond-stretching constant, f_r, and the amplitude, l, assuming Eq. 13 is shown in Fig. 5 for the three temperatures: 455°C (the lower limit), 485°C, and 515°C (the upper limit). As is shown in the figure, the observed value of l= 0.085 Å at 485°C corresponds to f_r=1.5 mdyn./Å, while the error caused by the uncertainties in the

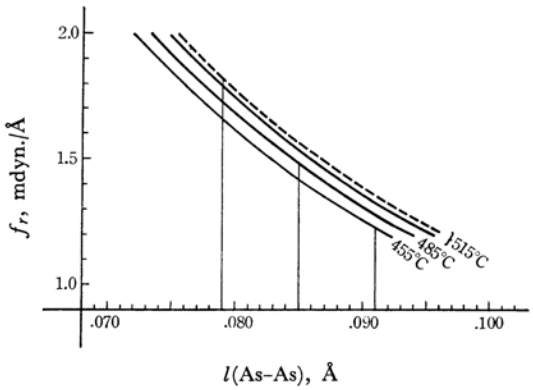

Fig. 5. Relation between the force constant f_r and the mean amplitude l(As-As) of As_4.
—— $f_{rr}=f_{rr'}=0$
---- $f_r : f_{rr} : f_{rr'}$ transferred from P_4

temperature and in the amplitude is ±0.28 mdyn./Å. The error in f_r introduced by the assumption of Eq. 13 was roughly estimated with reference to the P_4 molecule, which has the same T_d structure.[29] The force constants of P_4 have been determined by Pistorius[30] from the Raman spectra: f_r=2.065, f_{rr}=−0.122, and $f_{rr'}$=0.096 mdyn./Å.

27) Y. Morino, K. Kuchitsu and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952).
28) S. J. Cyvin, *Spectrochim. Acta*, **17**, 1219 (1961).
29) H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950).
30) C. W. F. T. Pistorius, ibid., **29**, 1421 (1958).

If the $f_r:f_{rr}:f_{rr'}$ ratios of the P_4 molecule are transferred to those of the As_4 molecule, the correlation curves in Fig. 5 are shifted by about 0.05 mdyn./Å, as is shown for the temperature of 515°C. Twice this shift, i. e., 0.1 mdyn./Å, was taken as a measure of the error due to the above assumption. Thus, the bond-stretching constant compatible with the observed mean amplitude was determined to be $f_r=1.5\pm0.3$ mdyn./Å, which is in agreement with the estimate, 1.5 mdyn./Å, from Badger's rule.[31] This shows the covalent nature of the As–As bond of this molecule. The corresponding estimates of the vibrational frequencies are $\nu_1(A_1)=350\pm30$, $\nu_2(E)=180\pm30$ and $\nu_3(F_2)=250\pm30$ cm^{-1}. However, no experimental observation has yet been made because of the difficulty of spectroscopic instrumentation.

The observed value of the anharmonicity parameter of $0.9\pm1.3\times10^{-5}$Å^3 may be compared with the values estimated from other sources. If a Morse-type potential function is assumed for the As–As bond, the anharmonicity parameter, κ, is approximately represented by[14]:

$$\kappa = (\alpha/6)l^4 \qquad (14)$$

where:

$$\alpha = (f_r/2D)^{1/2} \qquad (15)$$

is the asymmetry constant of the Morse function. When we insert the observed values of $l=0.085$Å and $f_r=1.5$ mdyn./Å, together with the binding energy, D, of 34 kcal./mol.,[32] into the above equations, κ is estimated to be 1.5×10^{-5}Å^3. Even though the observed and estimated values are both crude, the orders of magnitude are in essential agreement.

With the force constant obtained above, it is possible to estimate the apparent elongation of the As–As bond due to the perpendicular amplitudes and the elongation caused by the centrifugal force, represented by the third and the fourth terms of Eq. 4 respectively. The former is expressed as $\mu(\Delta_2+\Delta_3)/2r_e$ and is estimated to be 0.0022 Å at 485°C. The centrifugal elongation is estimated by the method of Iwasaki and Hedberg[33] as follows: $\delta_r(\text{As–As})=\boldsymbol{k}T/2F_1r_e=0.0014$Å at 485°C, where $F_1=f_r+f_{rr}+f_{rr'}$. The distance parameter, which is obtained by subtracting the above two terms from r_g, is denoted as r_α[20]; thus, r_α(As–As) is estimated to be 2.431Å at 485°C.

The authors wish to express their sincere gratitude to the Tokyo Shibaura Electric Co. for the constructioh of the nozzle assembly and for the kind gift of the sample. They are also indebted to Mr. Masakatsu Kochi for his assistance.

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

32) E. H. E. Pietsch ed., "Gmelins Handbuch der Anorganischen Chemie," Vol. 17, Verlag Chemie, Weinheim (1952), p. 115.

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