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Effect of Temperature on the Molecular Structure of Iodine Observed by Gas Electron Diffraction

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The bond distance and its mean square amplitude for the iodine molecule were measured at 80°C, 300°C, and 500°C by gas electron diffraction. The observed temperature dependences of the above parameters were in good agreement with those calculated on the basis of an anharmonic-oscillator model and experimental spectroscopic constants.

Recent development in the technique of gas electron diffraction has made it possible to measure small changes in internuclear distances and mean square amplitudes with temperature. As first demonstrated for phosphorus(III) chloride by Hedberg and Iwasaki,1) studies of this sort can be used effectively for investigating the effect of intramolecular vibrations on structure and for assessing the accuracy of the diffraction experiments made at high temperatures. The present study has been carried out as a primary step toward this goal.

Iodine is one of the most suitable molecules for the examination of the temperature effect because of its low vibrational frequency (214 cm^{-1}) and its chemical stability to several hundred degrees. Therefore, the bond distance and its mean square amplitude observed at different temperatures have been compared with those calculated from spectroscopic data. The results of the least-squares analysis have been tested by using theoretical molecular intensity function based on the probability distribution function of a one-dimensional anharmonic oscillator expanded to the fourth order.

Experimental and Analysis

Electron diffraction photographs were taken at 80°C, 300°C, and 500°C by the use of a diffraction unit with a high temperature nozzle, which has been reported elsewhere.2) The accelerating voltage was 41.04 kV. Five plates for each temperature were selected for analysis. The temperature was measured by a thermocouple attached to the nozzle assembly. In order to measure the temperature of the vapor at the nozzle tip, the thermocouple was calibrated by the following procedure. Fine pieces of crystals of known melting points, such as 2-aminodiphenylamine [80°C], anthraquinone [286°C], and zinc iodide [445°C], were placed on top of the nozzle capillary, through which the iodine vapor was emitted into the diffraction chamber while the temperature was raised gradually. Melting of a fine edge of the crystal was observed under a microscope. It was found that the temperature of the vapor measured by the above procedure agreed with that of the nozzle indicated by the thermocouple within a few degrees.

Photographic densities were measured by a self-recording microphotometer with spinning of the plate around the center of the halos at about 600 r. p. m. The microphotometer charts were analyzed by the method described in previous papers.3)

The bond distance r_a, the mean amplitude l_m, the phase parameter κ, and the index of resolution i were obtained from a least-squares analysis.3) The experimental reduced molecular intensity was fitted to the following theoretical equation:

$$M(s)=iAC\exp(-l_m{}^2s^2/2)\sin[s(r_a-\kappa s^2)]/sr_a \quad (1)$$

where A is a normalization constant, nearly equal to unity, which appears in the probability distribution function described below, and C is a known function of s related to the elastic and inelastic scattering factors of the iodine molecule. The mean internuclear distance r_g was calculated from the experimental r_a distance by

$$r_g = r_a + l_m{}^2/r_a \quad (2)$$

The probability distribution function for a one-dimensional anharmonic oscillator at the absolute zero temperature has been given by Kuchitsu and Bartell.4) This function has recently

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

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

3) Y. Morino, K. Kuchitsu, T. Iijima and Y. Murata, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 803 (1962); Y. Murata, T. Ito and K. Kuchitsu, *Bussei*, **5**, 91 (1964). Y. Morino, K. Kuchitsu and Y. Murata, *Acta Cryst.*, **18**, 549 (1965).

4) K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **35**, 1945 (1961).

been extended in order that the equation may be valid for any nonzero temperature⁵⁾ by using a harmonic mean amplitude l_h^2 in place of the corresponding zero-point amplitude l_α^2 defined in Ref. 4,

$$P(x)=$$

$$A(2\pi l_h^2)^{-1/2}(1+\sum_{n=1}^{\infty} c_n x^n)\exp(-x^2/2l_h^2) \quad (3)$$

where

$$x = r - r_e - \delta r \quad (4)$$

$$l_h^2 = l_\alpha^2(1+\chi)/(1-\chi) \quad (5)$$

$$l_\alpha^2 = \boldsymbol{h}/8\pi^2\mu\boldsymbol{c}\omega_e \quad (6)$$

and

$$\chi = \exp(-\boldsymbol{hc}\omega_e/\boldsymbol{k}T) \quad (7)$$

The coefficients c_n in Eq. 3 can be calculated by a second-order perturbation method on the basis of a fourth-order potential function.⁵,⁶⁾ Numerical values of c_n for iodine, listed in Table I, were obtained by using the experimental values of ω_e, α_e, and x_e determined by ultraviolet spectroscopy.⁷⁾ The correction for the centrifugal distortion, δr, is equal to $\boldsymbol{k}T/2\pi^2\mu\boldsymbol{c}^2\omega_e^2 r_e$.

TABLE I. VALUES OF c_n (in Å^{-n} units)

c_n	80°C	300°C	500°C
c_0	0.997	0.996	0.995
c_1	0.256	0.105	0.059
c_2	−0.324	−0.163	−0.097
c_3	2.227×10^2	1.531×10^2	1.171×10^2
c_4	-8.828×10^2	-1.042×10^2	-0.900×10^2
c_5	0	0	0
c_6	2.480×10^4	1.172×10^4	0.686×10^4

The reduced molecular intensity of scattered electrons,

$$M(s)=$$

$$C\int_{-\infty}^{\infty} P(x)\mathrm{d}x[\sin s(r_e+\delta r+x)]/s(r_e+\delta r+x) \quad (8)$$

can be written in terms of c_n as

$$M(s)=$$

$$AC(\sigma_1^2+\sigma_2^2)^{1/2}\exp(-l_h^2s^2/2)\sin[s(r_a+\phi(s))]/sr_e \quad (9)$$

where σ_1 and σ_2 are infinite polynomial functions of c_n given by

$$\sigma_1 = \sum_{n=0}^{\infty}(-1)^n\varepsilon_{2n+1}(l_h^2s)^{2n+1} \quad (10)$$

$$\sigma_2 = \sum_{n=0}^{\infty}(-1)^n\varepsilon_{2n}(l_h^2s)^{2n} \quad (11)$$

$$\varepsilon_n = \sum_{m=0}^{\infty}[(n+2m)!/2^m n!m!]d_{n+2m}l_h^{2m} \quad (12)$$

$$d_n = c_n - d_{n-1}/r_e \quad (13)$$

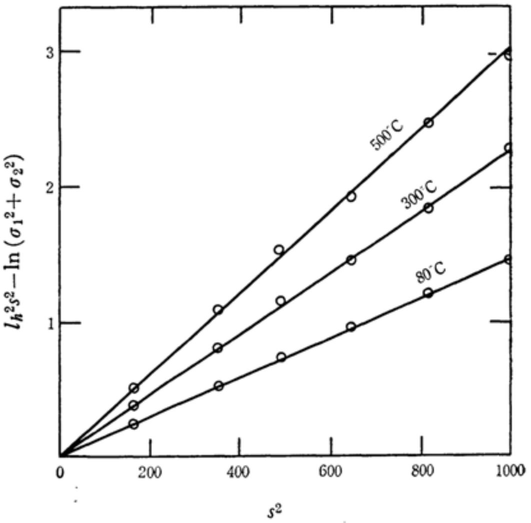

Fig. 1. Plots of $l_h^2s^2-\ln(\sigma_1^2+\sigma_2^2)$ vs s^2; calculated values are shown in open circles.

and $d_0=1$. The present calculation for iodine indicates the following features of Eq. 9. First, each polynomial function ε_n converges so rapidly that the summation of the first few terms of the series is sufficient for the calculation of $M(s)$. Second, the term $(\sigma_1^2+\sigma_2^2)^{1/2}\exp(-l_h^2s^2/2)$ can be substituted for nearly exactly by $\exp(-l_m^2s^2/2)$ with a parameter l_m taken as constant. The effective mean amplitude l_m can thus be given by

$$l_m \approx [l_h^2 - s^{-2}\ln(\sigma_1^2+\sigma_2^2)]^{1/2} \quad (14)$$

The plots of $l_h^2s^2-\ln(\sigma_1^2+\sigma_2^2)$ against s^2, shown in Fig. 1, can be approximated by straight lines for the temperature range studied. Third, the phase function $\phi(s)$ can be approximated by a quadratic function of s,

$$\phi(s) = (1/s)\arctan(\sigma_1/\sigma_2) - r_a = -\kappa s^2 + \cdots \quad (15)$$

The constant phase parameter κ can further be represented by⁵⁾

$$\kappa \approx (1/6)a_3l_h^4[1+8\chi/(1+\chi)^2] \quad (16)$$

in terms of a cubic anharmonic parameter a_3 of the potential function,⁸⁾

$$V(x) = (1/2)f(x^2-a_3x^3+\cdots) \quad (17)$$

and the Boltzmann factor χ for temperature T. The plots of $\phi(s)$ at 80°C, 300°C, and 500°C against s^2 are shown in Fig. 2; they are found to be linear, except for a slight deviation found in the 500°C curve beyond 25 in the s-value. The values of κ predicted by Eq. 16 are practically equal to those obtained from the slopes of the $\phi(s)$ vs. s^2 curves shown in Fig. 2. It has thus been shown that Eq. 1 is a good approximation

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5) K. Kuchitsu This Bulletin, to be published.

6) A. Reitan, *Det Kgl. Norske Videnskabers Selskabs Skrifter* (1958), NR 2.

7) R. D. Verma, *J. Chem. Phys.*, **32**, 738 (1960).

8) K. Kuchitsu and Y. Morino, This Bulletin, **38**, 805 (1965).

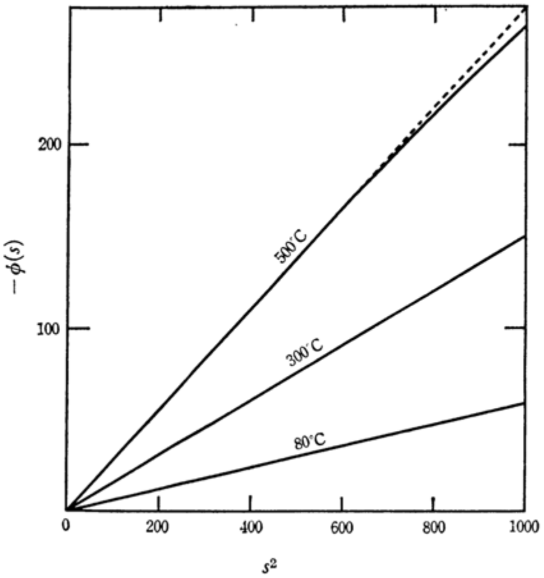

Fig. 2. Curves of $-\phi(s)$ (10^{-4} Å) of Eq. 9 plotted against s^2 for 80°C, 300°C and 500°C.

of Eq. 9 for iodine even at a temperature as high as 500°C.

Results and Discussion

The experimental r_g values derived from the least-squares analysis (exp) are compared in Table II with the corresponding values (calc) calculated by[5]

$$r_g = r_e + [(\varepsilon_0 + \varepsilon_1 r_e + 2\varepsilon_2 l_h^2)/(\varepsilon_0 r_e + \varepsilon_1 l_h^2)]l_h^2 \qquad (18)$$

The values of l_m (calc) in Table II are determined from the slopes of the curves shown in Fig. 1, while that of κ(calc) in the same table are calculated by Eq. 15.

TABLE II. COMPARISON OF THE OBSERVED STRUCTURAL PARAMETERS WITH THEORETICAL VALUES

	80°C	300°C	500°C
r_g(calc)	2.6756 Å	2.6808 Å	2.6855 Å
r_g(exp)[a]	2.672_3 $\pm 0.003_4$	2.679_0 $\pm 0.001_8$	2.687_2 $\pm 0.002_3$
l_m(calc)	0.0551 Å	0.0691 Å	0.0796 Å
l_m(exp)	0.061_5 $\pm 0.005_2$	0.070_5 $\pm 0.004_3$	0.077_1 $\pm 0.005_1$
κ(calc)	59 10^{-7}Å^3	152 10^{-7}Å^3	275 10^{-7}Å^3
κ(exp)	39±84	100±112	130±102
i(exp)	0.986 ±0.051	1.003 ±0.093	0.924 ±0.105

a) Experimental errors represent the estimated limit of systematic errors plus 2.5 times the standard error obtained from the least-squares analysis. See Ref. 3.

A comparison of the observed molecular intensity (80°C) with the corresponding calculated intensity based on the optimized set of the parameters is illustrated in Fig. 3.

The least-squares fit to the observed molecular intesity is based on Eq. 1 with the structural parameters r_a, l_m, κ, and i. Since this procedure depends on the approximations stated above, it was thought desirable to examine the validity of this procedure. Iodine is a suitable molecule for this test, because the molecule is simple and its molecular parameters necessary for the calculation of the molecular intensity are precisely known.

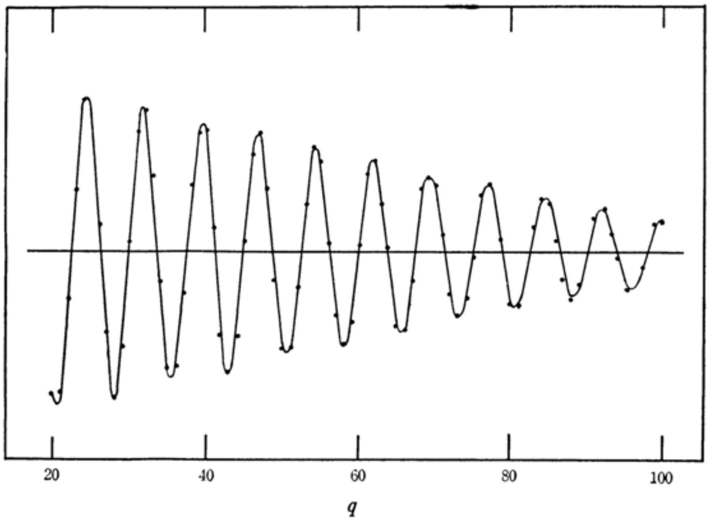

Fig. 3. Comparison of the observed and calculated molecular intensities plotted against $q=10s/\pi$. The solid line shows the experimental molecular intensity curve. The dots are the best-fit molecular intensities obtained from the least-squares analysis.

TABLE III. RESULTS OF THE LEAST-SQUARES ANALYSIS OF THE THEORETICAL $M(s)$ FUNCTION

	80°C	300°C	500°C
r_a(calc)	2.6745 Å	2.6789 Å	2.6830 Å
r_a(LS)	2.6745 ±0.0001	2.6789 ±0.0001	2.6828 ±0.0002
l_e(calc)	0.0562 Å	0.0713 Å	0.0835 Å
l_m(calc)	0.0551	0.0691	0.0796
l_m(LS)	0.0556 ±0.0001	0.0692 ±0.0001	0.0795 ±0.0002
k(calc)	59 10^{-7}Å^3	152 10^{-7}Å^3	275 10^{-7}Å^3
κ(approx)	60	153	260
κ(LS)	60±2	157±4	282±8

r_a(calc), l_e(calc): Average values based on the probability function given in Eq. 3.

l_m(calc): Effective amplitudes estimated from Eq. 14.

κ(approx): Calculated by Eq. 16.

(LS): Outputs of the least-sqares analyses of the theoretical $M(s)$ function given by Eq. 9.

Accordingly, the molecular intensity was calculated by Eq. 9 for integral q values ($q=10s/\pi$) in the region where the experimental data are present, and a least-squares fit was made to those calculated values as if they were experimental data. The output structural parameters thus obtained are compared in Table III with the corresponding rigorous values derived directly from the original equations 14, 15, and 18. The agreement indicates that in this case the present method of least-squares analysis should result in nearly exact estimates for the effective parameter values if it is applied to a perfect set of experimental data.

The experimental bond distance r_g agrees with the calculated values to within 0.1% for the three temperatures. The agreement of the experimental and calculated mean amplitudes is also satisfactory, except for a slight discrepancy in the value for 80°C. The observed values of the phase parameter κ for 80°C and 300°C are comparable with the theoretical counterparts within large experimental errors, while the discrepancy in the value at 500°C is even larger, probably because a systematic error is involved in the experimental molecular intensity for s beyond 25. No evidence was observed in the present study for the s-independent phase shift reported by Karle.9)

The above comparison shows that the temperature effects on r_g and l_m as observed by the present experiment are for the most part in agreement with those expected by theory. Further efforts are being made to reduce experimental standard errors and to make similar high-temperature measurements on the structural parameters of other molecules.

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