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Change in Density of Potassium Chloride Crystals upon Irradiation with X-Rays*

I. ESTERMANN, W. J. LEIVO,** AND O. STERN***
Department of Physics, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

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Alkali halide crystals become colored when irradiated with x-rays. Theoretical considerations indicate that the coloration is due to absorption centers which consist of electrons trapped at negative ion vacancies. Precision measurements of the density of uncolored crystals, however, indicate that it is very unlikely that there is a sufficient number of vacancies present in well annealed crystals to account for the number of color centers, which may be determined optically, unless vacancies are formed as a result of the irradiation.

Potassium chloride crystals were irradiated with x-rays. Their change in density was measured by the "crystal suspension method." It was found that the crystals changed in density, and that the number of vacancies calculated from the decrease in density was in reasonable agreement with the number of color centers determined by optical measurement.

I. INTRODUCTION

CRYSTALS of alkali halides may be colored by irradiation with x-rays or cathode rays, as well as by several other methods.[1] Among the different theories proposed for this phenomenon, the theory that it is due to the trapping of electrons in negative ion vacancies (color centers or F-centers), seemed to be the most free from objections. An experimental test of it is the subject of this paper.

Experiments with single crystals of KCl have shown that darkening by cathode rays leads to concentrations of several times 10^{18}(F-centers/cm^3) as determined by optical measurements. However, an analysis of the precision density measurements of several different crystals indicates that the number of vacancies which may be present in well annealed crystals is not sufficient to permit F-center concentrations of several times 10^{18}/cm^3 to be formed by simple trapping of electrons in negative ion vacancies unless vacancies are formed during the process of irradiation.

As a result, it was concluded that an accurate measurement of the difference in density, if any, of a crystal due to the formation of F-centers would be a crucial experiment to determine whether vacancies were produced during irradiation, and that the measurement of the difference in density could probably be made with sufficient accuracy by the method of crystal suspension which had been used to make precision measurements of densities of crystals. If no change in density should occur, the entire vacancy theory of F-centers would have a serious objection. If a change did occur, the vacancy theory would be greatly strengthened.

In the determination of difference in density by the method of "crystal suspension in a liquid," use is made of the fact that the temperature coefficient of expansion of a solid crystal is generally much smaller than that of a liquid which has the same density at some particular temperature. The difference in density between two crystals can be obtained by placing the crystals in the liquid and then observing at what particular temperature each crystal will remain suspended in the liquid. From the difference in the suspension temperatures the difference in density can be computed. In making density measurements with crystals colored by cathode rays, a difficulty arose because the surface of the crystal became pitted to such an extent that density measurements were not reliable. Crystals colored by x-rays would have been satisfactory except that the highest concentrations of F-centers produced by x-rays in a single crystal were reported to be of the order of 10^{16}/cm^3. This concentration would not produce a

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* This work was begun in September, 1943, by O. Stern and W. J. Leivo and was continued since June, 1945, by I. Estermann and W. J. Leivo.

** Abstract of Thesis submitted by W. J. Leivo in partial fulfillment of the requirements for the degree of Doctor of Science at Carnegie Institute of Technology.

*** Now at Berkeley, California.

[1] See, for example, R. W. Pohl, Physik. Zeits. **39**, 36 (1938); also Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940); F. Seitz, Rev. Mod. Phys. **18**, 384 (1946).

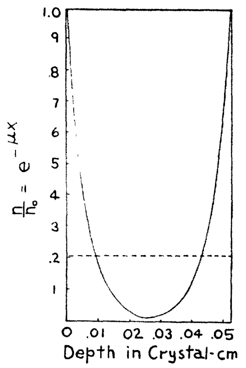

FIG. 1. Variation of the concentration of *F*-centers in a KCl crystal with the distance from the surface of the crystal.

sufficient change in density to be detectable. Higher concentrations than this had been produced on evaporated screens, but the screens undoubtedly do not compare with an annealed single crystal since the nature of production of evaporated screens would probably produce imperfections such as holes.

It was found, however, that crystals could be darkened to the point where they contained several times 10^{18} (*F*-centers/cm^3) by using soft x-rays from a tube with a beryllium window. This concentration of *F*-centers should produce a measurable difference in density. As a result of the experiments it was found that the crystals changed density upon irradiation with x-rays, and that this decrease in density was in reasonable agreement with that predicted from the concentration of *F*-centers as measured optically.

II. GENERAL PROCEDURE

As mentioned above, the change in density of the potassium chloride was obtained by determining the difference in suspension temperature between a colored and an uncolored crystal. The suspension liquid was 1,3-dibromopropane which has the same density as potassium chloride at a convenient temperature around 15°C. The method of "crystal suspension" has been developed by C. A. Hutchison, H. L. Johnston, D. A. Hutchison,[2] and others. After the change in density had been determined, the concentration of *F*-centers was determined by measuring the absorption coefficient of the crystal at the maximum of the *F* band for KCl. The measurement of the absorption coefficient and the calculation of the *F*-center concentration from this will be discussed later.

III. EXPERIMENTAL DETAILS

A. General Precautions

It was found in preliminary experiments that crystals which had been exposed to air during and after the cutting process did not yield reproducible density values. Consequently, great care had to be taken throughout the handling of the crystals in order to prevent them from being exposed to the atmosphere. Any moisture on the crystals or in the liquid would cause hydrolysis of the liquid. The resulting HBr acts as a catalytic agent causing an ion exchange between the KCl and the $BrCH_2CH_2CH_2Br$, the Cl^- ion being replaced by a Br^- ion with a resulting change in the density of the crystal. The 1,3-dibromo-propane also had to be free of HBr or Br_2 which might result from heating or decomposition due to light.

B. Preparation of Single Crystals of Potassium Chloride

A single crystal of potassium chloride, approximately three centimeters in diameter and five centimeters long, was grown from a melt of potassium chloride (C. P. Baker's Analyzed) by the method developed by Kyropolus.[3] The crystal was slowly cooled to room temperature.

Since the crystals could not be exposed to air while cutting them, the crystals were cut inside a box which could be filled with helium and was fitted with rubber gloves and a glass top. The crystals could be cut inside this box. The helium used was dried by passing it through a liquid nitrogen trap. In addition, the box contained phosphorus pentoxide as a drying agent to remove moisture entering through the rubber gloves.

The large crystal was cut into approximately one-centimeter cubes. These cubes were placed in a quartz tube containing helium, which was

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[2] D. A. Hutchison and H. L. Johnston, J. Am. Chem Soc. 62, 3165 (1940); Phys. Rev. 62, 32 (1942); D. A. Hutchison, Phys. Rev. 66, 144 (1944); J. Chem. Phys. 10, 383 (1945); H. L. Johnston and C. A. Hutchison, J. Chem. Phys. 8, 869 (1940).

[3] S. Kyropolus, Zeits. f. anorg. allgem. Chemie 154, 308 (1926).

then sealed. The tube with the crystals was placed in an annealing oven (Leeds and Northrup Micromax control). The rate of rise of the temperature was 4.2°C/min. The temperature was held constant at a point 56°C below the melting point for eight hours. The crystals were cooled at a rate of 3°C/min.

After removal from the annealing oven the tube with the crystals was again placed in the "glove box" containing helium. From a large crystal several small crystals were cleaved to a size of about 3×3×0.5 mm. One of the crystals was irradiated with x-rays while the rest were to serve as control specimens. At least one control crystal was cut from a place adjacent to the one to be darkened.

The penetration of the x-rays which are effective in coloring the crystal is of the order of 0.05 mm (see Fig. 1). This is computed from $I=I_0e^{-\mu x}$ where I is the intensity of the incident x-rays, μ is the absorption coefficient for x-rays of a wave-length believed effective for coloring the crystal, and x is the distance from the surface of the crystal. For $I/I_0=1/e$, and using $\mu=185/\text{cm}$, this gives $x=0.05$ mm. Crystals of this thickness could not be cleaved; it was therefore desirable to irradiate the crystal from both sides. Since the crystal could not be exposed to air, it was necessary to construct a radiation tube which would permit this and yet not reduce the intensity of the x-rays appreciably. In addition, the tube should be flat so that the crystal could be brought near the window of the x-ray tube where the intensity of the beam would be high. A satisfactory tube for holding the crystal while being irradiated was constructed by placing a piece of 9-mm Pyrex tubing over a copper strip 0.6 mm×7 mm×150 mm. The glass was heated and then pulled lengthwise, putting a skin of glass over the copper strip. The copper was dissolved with nitric acid, leaving a thin walled glass tube having a rectangular cross section. One end of the tube was sealed and to the other end was connnected a cap made from a "no lube" platinized tapered joint. A small arm was connected to the tube to hold the control crystals where they wouldn't be exposed to the x-rays. Also a small bulb was attached in which phosphorus pentoxide was placed as a drying agent.

After cleaving, the crystals were placed in the radiation tube which contained helium. The crystal to be colored was exposed to 50-kv x-rays with a beam current of 15 ma, the exposure time being a variable. The irradiation tube was placed directly in front of the beryllium window. After darkening the crystal, the tube was placed back in the "glove box" in which the crystals were transferred to the tube containing the suspension liquid, without exposure to the air.

C. Preparation of the Suspension Liquid

1,3-dibromo-propane, obtained from the Eastman-Kodak Company, was used for the suspension liquid. This liquid has a suitable density and temperature coefficient.[4] However, as mentioned above, care has to be taken to insure that the liquid is free of water, HBr, and Br_2, which may cause the crystal to react with the liquid.

The 1,3-dibromo-propane was treated with concentrated sulfuric acid in a separatory funnel. This process was repeated until the 1,3-dibromo-propane separated from the sulfuric acid as a clear liquid. The 1,3-dibromo-propane was then washed with a saturated solution of sodium bicarbonate, after which it was washed with distilled water and then dried over $CaSO_4$. The liquid was vacuum distilled and stored over $CaSO_4$ with a drop of mercury to precipitate any HBr or Br_2 formed.

D. Description of Vessel Containing Suspension Liquid and Crystals

The vessel containing the suspension liquid and the crystals was constructed so that the liquid could be distilled into it without exposure to air. The crystals also had to be transferred to the liquid without exposure to air. It was further

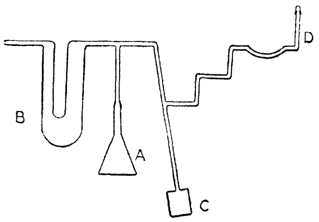

FIG. 2. Crystal suspension apparatus.

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[4] Density KCl at 20°C = 1.987 g/ml. Density 1,3-dibromo-propane at 20°C = 1.979 g/ml.

Table I.

Thickness of crystal mm	Total radiation time hrs.	F-centers cm^3 by optical measurement	F-centers cm^3 from density measurement
0.518	17	5.94×10^{17}	$12.3\ \times10^{17}$
0.420	17	6.40×10^{17}	$11.6\ \times10^{17}$
0.543	17	5.27×10^{17}	$10.2\ \times10^{17}$
0.417	$8\frac{1}{2}$	6.48×10^{17}	$9.0\ \times10^{17}$
0.433	$8\frac{1}{2}$	7.62×10^{17}	$10.1\ \times10^{17}$
0.388	$8\frac{1}{2}$	5.62×10^{17}	$12.6\ \times10^{17}$
0.545	$4\frac{1}{4}$	2.25×10^{17}	3.63×10^{17}
0.458	$2\frac{1}{8}$	1.25×10^{17}	—
0.528	$2\frac{1}{8}$	1.17×10^{17}	—

desirable to evacuate the crystals for about twenty minutes before immersing in the liquid so that any surface gases on the crystals would be removed. All this could be satisfactorily accomplished with the vessel shown in Fig. 2.

It was also found necessary to shield the crystals from electrostatic charges on the surface of the glass. The electrostatic forces caused by these charges were appreciable because of the small size of the crystals which had to be used. Shielding was obtained by lining the inside of the glass vessel with a platinum mesh through which the crystals could still be observed.

E. Procedure for Immersion of Crystals and the Distillation of the Liquid

The 1,3-dibromo-propane was placed in the distilling flask (A), Fig. 2, with some $CaSO_4$ ("Drierite" brand). The distillation was made at room temperature. Application of heat would cause decomposition of the liquid forming Br_2 which would produce the aforementioned reaction with KCl. The distillate was caught in the U tube (B) which was immersed in liquid nitrogen. After distillation the flask (A) was removed. The liquid from the U tube could then be poured into the vessel (C), which contained the crystals. A drop of mercury was also introduced to inhibit reaction. Helium was then let into the system through a liquid nitrogen trap. The tube (D) with the cap on it was projected into the "glove box" which contained the crystals in a helium atmosphere. The crystals were removed from the radiation tube and placed in the tube (D), after which the cap was replaced. The system was then evacuated for about twenty minutes, during which time the crystals were heated to 100°C to remove surface gases and moisture which might have been present. After the crystals were immersed in the liquid, the evacuation was continued for another ten minutes. Helium was finally introduced into the tube until atmospheric pressure was reached, and all connections were sealed. All the operations with the colored crystal were performed in the dark to prevent bleaching.

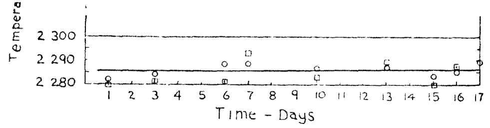

Fig. 3. Suspension temperatures of non-irradiated KCl crystals. Lower curve—comparison of suspension temperatures of thin plate of KCl (□) and cube of KCl (○). Upper curve—suspension temperatures of quartz float.

F. Determination of Suspension Temperatures

The temperature bath consisted of an insulated tank with windows for observing the crystals. Light entering the box was filtered with amber glass to prevent possible decomposition of the liquid. The temperature was manually controlled by allowing ice water to enter the tank. Temperatures were measured with a Beckmann thermometer. In spite of all precautions the 1,3-dibromo-propane was not quite homogenous. This caused the suspension temperature to vary with different trials, dependent mainly upon the length of time of evacuation of the crystals, since during this time the more volatile components (apparently isomers) of the liquid could escape. In order to have a correlation between the various trials a quartz float was made similar to the micro floats used in the determination of the concentration of heavy water.[5] The suspension temperature of the quartz float could be adjusted by altering the size of an air bubble in it so that it would be on the scale of the Beckmann thermometer in the neighborhood of the suspension temperature of the crystals. Corrections for slight changes in density of the liquid with time could be made by the use of the quartz float. The quartz float also proved valu-

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[5] See, for instance, M. Randall and F. B. Longtin, Ind. Eng. Chem. **7**, 44 (Jan. 15, 1939).

able in the work in case a reaction started to occur, since then it was possible to determine whether it was the liquid, the crystal, or both, which were changing. If a reaction did occur it would generally proceed quite rapidly, with the crystal getting more dense. However, if a reaction did not occur within a few days, the liquid and crystals remained stable as long as measurements were continued, in some cases for as long as one month.

IV. PRELIMINARY EXPERIMENTS

As was pointed out previously, crystals had to be cleaved to a thickness of about 0.4 mm in order that they could be colored throughout. This, however, brought up the question as to whether the density of the crystal might be changed by cleaving such a thin piece. Also the liquid might not completely penetrate holes in the surface of the crystal, or other surface effects might exist, in which case the density would depend upon the amount of surface area of the crystal. To test these possible effects, various size crystals were cleaved, some large cubes, others thin plates. It was found that to the degree of accuracy of the measurements no difference in density existed between a thin plate and a large cube (see Fig. 3).

V. RESULTS OF CHANGE IN DENSITY MEASUREMENTS

A number of crystals were irradiated for varying lengths of time. The change in suspension temperature for a crystal about 0.5 mm thick which had been exposed to x-rays for $8\frac{1}{2}$ hours was about 0.09°C, which corresponds to a change in density of 1.4×10^{-4} g/cm^3. Increasing the length of time that the crystal was irradiated above this did not change the density further, indicating that saturation had been attained in this time. Decreasing the time of irradiation decreased the change in density. The results obtained for different crystals for various radiation times are given in Table I. A typical experiment is represented in Fig. 4.

VI. OPTICAL DETERMINATION OF *F*-CENTER CONCENTRATION

The concentration of *F*-centers was computed from the absorption coefficient of each crystal

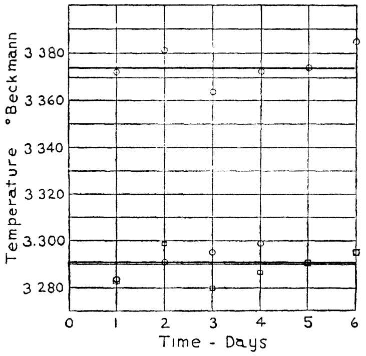

FIG. 4. Suspension temperatures of colored and uncolored KCl crystals. Upper curve—crystal irradiated $17\frac{1}{2}$ hours with x-rays. Lower curve—(○) uncolored crystal No. 1; (□) uncolored crystal No. 2.

measured at the maximum of the *F*-band for KCl using the equation developed by Smakula.[6]

$$n_0 = 18mn'\alpha_m W/\pi e^2 h(n'+2)^2 f,$$

n_0 = number of *F*-centers per unit volume,
m = mass of electron,
e = charge of electron,
n' = index of refraction of crystal,
α_m = absorption coefficient at maximum of *F* band,
W = width at half-maximum of *F* band[1],
f = oscillator strength of absorbing center = 0.81 for KCl,
h = Planck's constant.

A diagram of the optical system used in the measurement of the absorption coefficient is shown in Fig. 5. The image of the filament of a lamp which was controlled by a voltage regulator was projected on the entrance slit of a prism monochromator after which it was focused on the crystal. The crystal was mounted so that it could be quickly moved in or out of the light beam. After passing through the crystal the light fell on a photo-cell. The photoelectric current was amplified by an FP54 tube used in a DuBridge and Brown[7] circuit. The dark current was compensated by a similar photo-cell in opposition to the other.

VII. COMPUTATION OF NUMBER OF *F*-CENTERS FROM CHANGE IN DENSITY MEASUREMENTS

The computation of the number of *F*-centers from the change in density was based on the assumption that there is one *F*-center for each pair of missing ions—a pair consisting of a

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[6] A. Smakula, Zeits. f. Physik **59**, 603 (1930).
[7] L. A. DuBridge and H. Brown, Rev. Sci. Inst. **4**, 532 (1933).

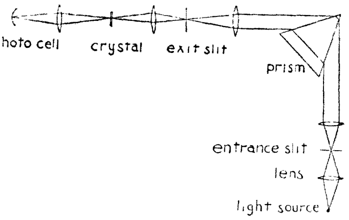

FIG. 5. Diagram of optical system for measuring *F*-center concentration.

potassium ion and a chlorine ion. This assumption is in general agreement with the behavior of crystals darkened by x-rays, in contrast to those subjected to additive coloring.[1] In addition, theoretical calculations[8] show that pairs are more mobile than isolated vacancies, and further, that the isolated vacancies would not have had sufficient time to migrate distances which have been observed in the length of time necessary to produce the coloration. On this basis the number of *F*-centers may be computed as follows:

$$\Delta\rho = -\rho\Delta v = -\rho n v_0,$$

where $\Delta\rho$ is the change in the density of KCl, Δv is the change in volume per unit volume of the crystal due to the migration of the ions from the interior to the surface of the crystal, n is the number of pairs of ions per cm^3 which migrate to the surface, v_0 is the volume of a pair of ions. v_0 may be computed from the molecular weight M of KCl, the density of KCl, and Avogadro's number N:

$$v_0 = \frac{M}{\rho N}.$$

Now,

$$n = -\frac{\Delta\rho}{\rho v_0} = -\frac{N}{M}\Delta\rho.$$

Also,

$$-\Delta\rho = \rho(\alpha-\beta)\Delta t,$$

where α and β are the volume expansion coefficients of liquid and KCl, and ρ their common density at the suspension temperature, and Δt the change in suspension temperature due to the coloring of the crystal. Inserting this value for $\Delta\rho$, one obtains

$$n = \frac{N\rho}{M}(\alpha-\beta)\Delta t$$

Upon substituting the numerical values ($N = 6.02 \times 10^{23}$, $M = 74.6$, $\rho = 1.989$, $\alpha = 8.89 \times 10^{-4}$, and $\beta = 1.13 \times 10^{-4}$), we obtain $n = 1.24 \times 10^{19} \Delta t$(ion pairs/cm^3) or *F*-centers/cm^3.

This calculation does not allow for the possibility of a change in density resulting from an alteration of the lattice constants of the crystal caused by the missing ions. It is believed that this change is small; however, experiments to verify this are planned.

VIII. COMPARISON BETWEEN CHANGE IN DENSITY WITH THE *F*-CENTER CONCENTRATION

Table I gives a comparison of the number of *F*-centers per cm^3 in the crystal, as computed from the change in suspension temperature, with the number of *F*-centers per cm^3 as determined from the optical measurements. It can be seen that the *F*-center concentration reaches a saturation value after about 8½ hours of exposure to x-rays. The *F*-center concentration calculated from optical measurements is less than that obtained from the change in density. This is to be expected for several reasons. First, in the calculation of the absorption coefficient, monochromatic light is assumed. Secondly, since the amount of light transmitted through the crystal is of the order of 0.1 percent, a small amount of stray light can affect the results appreciably, reducing the computed number of *F*-centers. Thirdly, some bleaching will occur, since even to make a measurement of the absorption coefficient it is necessary to expose the crystal to light in the *F*-band. The significant fact, however, is that there is a correlation between the values in the two columns in Table I, giving strong support to the hypothesis that the *F*-centers are vacancies with trapped electrons which are responsible for the change in density.

It should be noted that the density measurements and also the optical measurements give the *average* number of *F*-centers per cm^3 in the crystal. The maximum number of *F*-centers per cm^3 may be considerably greater than this since the crystal is not uniformly colored. One may obtain a rough approximation, neglecting diffusion, for the number of *F*-centers per cm^3 by assuming that the concentration falls of exponentially according to

$$n = n_0 e^{-\mu x},$$

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[8] G. Dienes, thesis, Carnegie Institute of Technology.

where n is the concentration of F-centers, μ is the absorption coefficient of the x-rays, and x is the distance from the surface of the crystal. Figure 1 shows the concentration of F-centers calculated in this manner as a function of x for the first crystal appearing in Table I. The average ordinate in Fig. 1 (shown dashed) gives the experimentally measured concentration $\bar{n}$. The value of n_0 can be obtained from

$$2\int_0^d n_0 e^{-\mu x}dx = \bar{n}d,$$

where d is the thickness of the crystal. This gives

$$n_0 = \mu d/2(1-e^{-\mu d})\bar{n}.$$

For

$$\mu = 185\ \text{cm}^{-1},\quad d = 0.0518\ \text{cm},\quad n_0 = 4.8\bar{n}.$$

Thus the maximum concentration of F-centers may be around five times the value given in Table I.

IX. CONCLUDING REMARKS

F-centers were first observed about a half-century ago. Their nature has been seriously considered for over ten years. The exigencies of war particularly accelerated the study of the problem. Despite the enormous amount of experimental and theoretical work, their very nature still remained uncertain. As a result of these density measurements, the theory that the F-center is an electron occupying the position of a missing negative ion in the crystal lattice has been greatly strengthened. As a further result it has been found that the vacancies in which the electrons become trapped are largely produced during the process of irradiation.

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A Study of the High Frequency Fundamental Bands in the Spectrum of AsH_3 and AsD_3

VIRGINIA MARIE MCCONAGHIE AND HARALD H. NIELSEN
Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio

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An analysis has been carried out on the fundamental bands ν_1 and ν_2 (Dennison's notation), in the infra-red spectrum of AsH_3. This analysis has made possible the evaluation of the reciprocals of inertia, B, and the Coriolis coupling coefficient, ζ_2. These are found to be $B'' = 3.723$ cm^{-1}, $B'(\nu_1) = 3.682$ cm^{-1}, $B'(\nu_2) = 3.69$ cm^{-1} and $\zeta_2 = -0.0602$. The harmonic vibration frequencies have been computed after the method of Dennison. The values obtained are $\omega_1 = 2209.2$ cm^{-1}, $\omega_2 = 2225.8$ cm^{-1}, $\omega_3 = 973.3$ cm^{-1}, and $\omega_4 = 1012.1$ cm^{-1} for the AsH_3 molecule and $\omega_1 = 1571.2$ cm^{-1}, $\omega_2 = 1582.4$ cm^{-1}, $\omega_3 = 696$ cm^{-1}, and $\omega_4 = 718.6$ cm^{-1} for AsD_3. This information permits the calculation of ζ_2 for AsD_3. A value $\zeta_2 = -0.0383$ is obtained which is in satisfactory agreement with experimental data. For AsD_3 the following B values prevail; $B'' = 1.896$ cm^{-1}, $B'(\nu_1) = 1.883$ cm^{-1}, and $B'(\nu_2) = 1.874$ cm^{-1}. The B'' values obtained enable one to estimate closely that the value of r(As-H) is equal to 1.513A and the H-As-H angle is equal to 89°50′.

I. INTRODUCTION

THE infra-red spectra of AsH_3, AsD_3, PH_3, and PD_3 have been investigated by a number of authors.[1] The only high dispersion measurements on the spectra of these molecules are those by Fung and Barker on PH_3 and those by Lee and Wu on AsH_3. From the foregoing works certain conclusions have been drawn concerning the size and the shape of these molecules by Sutherland, Lee, and Wu.[2] Recently a publication was made by us[3] on the preliminary results of our study of the spectra of AsH_3, AsD_3, and PH_3 under high dispersion, and in this paper we wish to discuss in somewhat greater detail our analysis of the high frequency funda-

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[1] R. Robertson and J. J. Fox, Proc. Roy. Soc. **A120**, 128 (1928); L. W. Fung and E. F. Barker, Phys. Rev. **45**, 238 (1934); G. B. B. M. Sutherland and G. K. T. Conn, Nature **138**, 641 (1936); E. Lee and C. K. Wu, Trans. Faraday Soc. **35**, 1 (1939).

[2] G. B. B. M. Sutherland, E. Lee, and Cheng-Kai Wu, Trans. Faraday Soc. **35**, 1373 (1939).

[3] V. M. McConaghie and H. H. Nielsen, Proc. Nat. Acad. Sci. **34**, 455 (1948).