

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

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

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.

A Study of the High Frequency Fundamental Bands in the Spectrum of AsH₃ and AsD₃

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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 AsH₃. 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 $B'' = 3.723 \text{ cm}^{-1}$, $B'(\nu_1) = 3.682 \text{ cm}^{-1}$, $B'(\nu_2) = 3.69 \text{ cm}^{-1}$ and $\zeta_2 = -0.0602$. The harmonic vibration frequencies have been computed after the method of Dennison. The values obtained are $\omega_1 = 2209.2 \text{ cm}^{-1}$, $\omega_2 = 2225.8 \text{ cm}^{-1}$, $\omega_3 = 973.3 \text{ cm}^{-1}$, and $\omega_4 = 1012.1 \text{ cm}^{-1}$ for the AsH₃ molecule and $\omega_1 = 1571.2 \text{ cm}^{-1}$, $\omega_2 = 1582.4 \text{ cm}^{-1}$, $\omega_3 = 696 \text{ cm}^{-1}$, and $\omega_4 = 718.6 \text{ cm}^{-1}$ for AsD₃. This information permits the calculation of ζ_2 for AsD₃. A value $\zeta_2 = -0.0383$ is obtained which is in satisfactory agreement with experimental data. For AsD₃ the following B values prevail; $B'' = 1.896 \text{ cm}^{-1}$, $B'(\nu_1) = 1.883 \text{ cm}^{-1}$, and $B'(\nu_2) = 1.874 \text{ cm}^{-1}$. The B'' values obtained enable one to estimate closely that the value of $r(\text{As-H})$ is equal to 1.513A and the H-As-H angle is equal to 89°50'.

I. INTRODUCTION

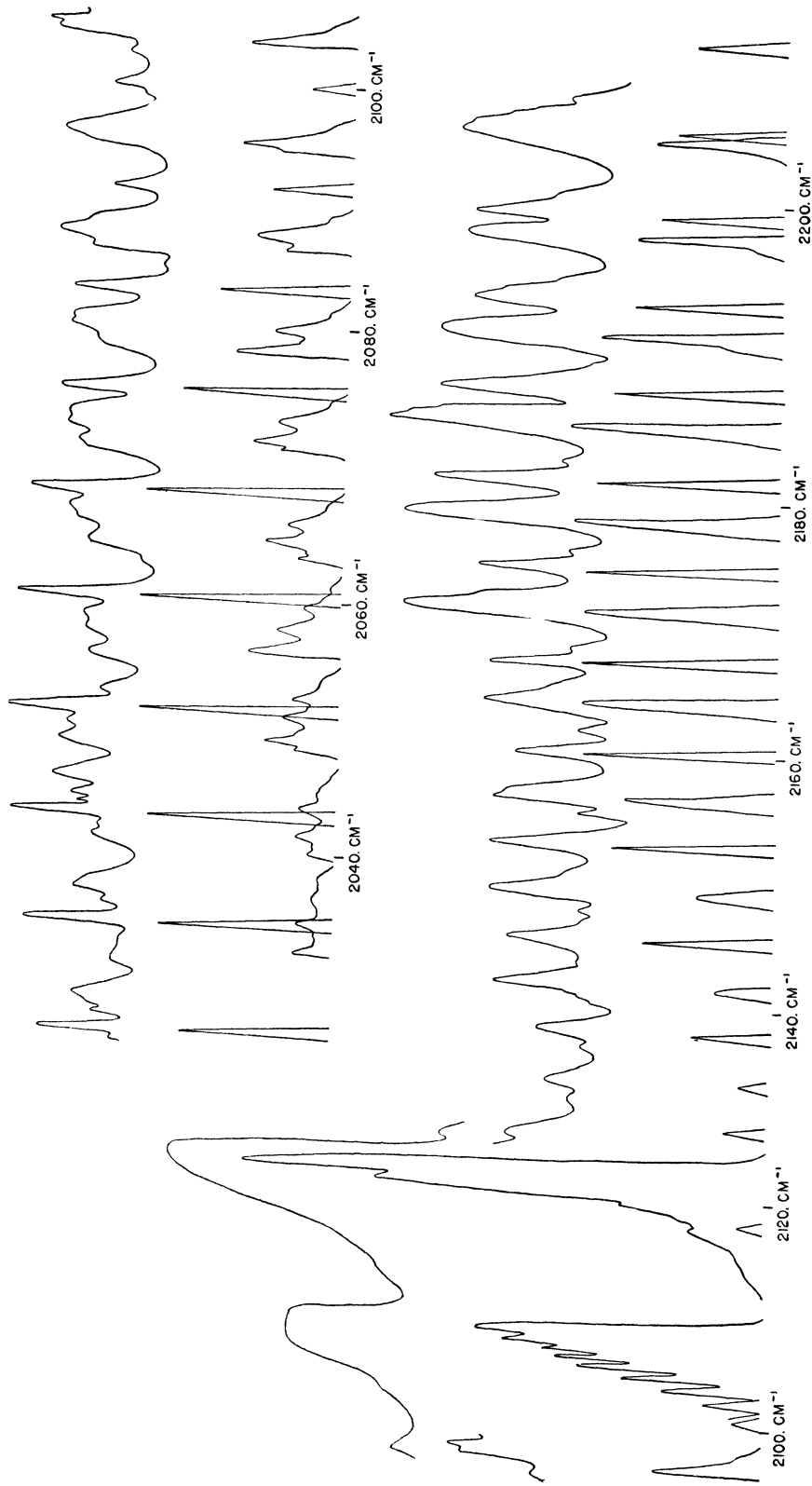
THE infra-red spectra of AsH₃, AsD₃, PH₃, and PD₃ have been investigated by a number of authors.¹ The only high dispersion measurements on the spectra of these molecules are those by Fung and Barker on PH₃ and those by Lee and Wu on AsH₃. From the foregoing

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).

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 us³ on the preliminary results of our study of the spectra of AsH₃, AsD₃, and PH₃ under high dispersion, and in this paper we wish to discuss in somewhat greater detail our analysis of the high frequency funda-

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).

FIG. 1. Experimental and calculated absorption curves for AsH_3 .

mental bands in the spectrum of AsH₃ and AsD₃ and the conclusions we have drawn from this analysis.

II. EXPERIMENTAL DETAILS

The two regions which we shall concern ourselves with here lie, respectively, near 2116 cm⁻¹ and 1523 cm⁻¹ for AsH₃ and AsD₃. The measurements were made with an absorption cell 24-cm long and a gas pressure of 30 mm Hg in both cases. The windows were of sodium chloride. The measurements were made using the vacuum prism-grating spectrograph described elsewhere,⁴ which was equipped with a replica grating made by Wood with 7200 lines per inch. The data, recorded automatically, were taken with slit widths equivalent to a frequency interval of 0.3 cm⁻¹. The data have been redrawn and are shown as the upper curves in Figs. 1 and 2, respectively, for the two molecules AsH₃ and AsD₃. In Tables I and II are given the positions in cm⁻¹ of the principal absorption lines in the two absorption regions.

III. DISCUSSION AND ANALYSIS OF THE BANDS

These bands have, in each case, been interpreted to comprise the fundamental bands ν_1 and ν_2 , using the notation of Dennison.⁵ The frequency ω_1 is a vibration where the electric moment oscillates along the axis of symmetry. The band is, therefore, a parallel band. The structure consists, for such a band, of a group of component bands (one for each value of K , $K \leq J$), each containing a Q branch and P and R branches. The former is a line at the center of the component band, the other two branches consisting of a set of nearly equally spaced lines on the low and high frequency sides, respectively, of the Q line. These component bands fall almost exactly on top of each other, so that the general appearance of the band is rather simple, i.e., a strong central Q branch and a group of nearly equally spaced P and R lines which lie

on the low and high frequency sides of the Q branch.

The frequency ω_2 is a twofold degenerate oscillation where the electric moment alternates normally to the axis of symmetry. Such a band is known as a perpendicular band and consists also of a group of component bands (one on each side of the center for each value of K , $K \leq J$) each having P , Q , and R branches. The Q branches are, in this case, separated from each other by a frequency interval of about $2[(1-\zeta) \times C - B]$, where C and B are the reciprocals of inertia $h/8\pi^2 c I_{zz}$ and $h/8\pi^2 c I_{xx}$ and ζ is the Coriolis coupling coefficient. The perpendicular band is, therefore, likely to present a considerably more complicated appearance than the parallel type band.

In Fig. 1 we have, therefore, identified the sharp set of lines with the parallel band. Neglecting any splitting for different values of K , the combination relations

$$R(J-1) - P(J+1) = 4B''(J + \frac{1}{2}), \quad (1a)$$

$$R(J) - P(J) = 4B'(J + \frac{1}{2}), \quad (1b)$$

and

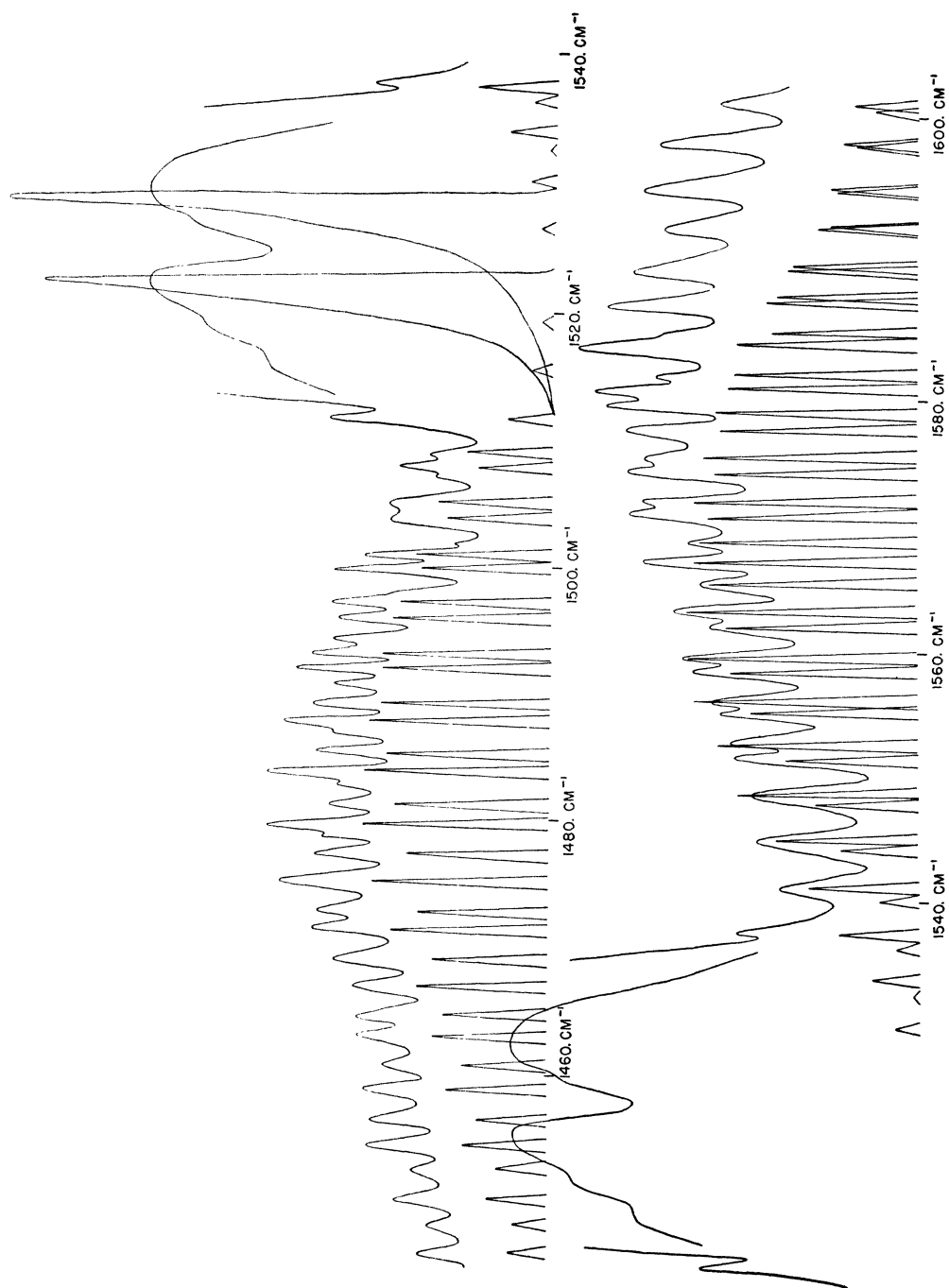
$$R(J-1) + P(J) = 2\nu + 2(B' - B'')J^2 \quad (1c)$$

have been applied to the lines in the band. When the values $R(J-1) - P(J+1)$ and $R(J) - P(J)$ are plotted against $4(J + \frac{1}{2})$, values for B in the initial and final states are obtained by determining the slopes of the resulting straight lines. The values obtained are $B'' = 3.723$ cm⁻¹ and $B' = 3.682$ cm⁻¹, respectively. When the values (1c) are plotted against $2J^2$, the value of the band center, ν_1 , is obtained by reading the intercept, and the slope gives a value for $B' - B''$. For ν_1 we obtain 2116.1 cm⁻¹ and the slope gives $B' - B''$ equal to -0.04 /cm⁻¹. This value for $B' - B''$ is in satisfactory agreement with the value obtained by taking the difference between the magnitudes B' and B'' obtained above.

In Fig. 2, it will be seen that the two sets of lines appear almost equally sharp. By analogy, however, we assume that the band of lower frequency is ν_1 , and we have identified the lines associated with it by means of asterisks. When the combination relations (1) are applied to these line positions, the following are obtained: $B'' = 1.896$ cm⁻¹, $B' = 1.883$, $\nu_1 = 1523.1$ cm⁻¹, and $B'' - B' = 0.013$ cm⁻¹.

⁴ E. E. Bell, R. H. Noble, and H. H. Nielsen, Rev. Sci. Inst. **18**, 48 (1947).

⁵ D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940). In the notation of Gerhard Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), these are the frequencies ν_1 and ν_2 . We use the notation of Dennison because so much of the literature concerning the XY_3 molecular model is written in that notation.

FIG. 2. Experimental absorption curves for AsD_3 .

The values B'' obtained are, of course, those for B in the normal state of the molecule and not the quantities B_e obtained when the molecule is in equilibrium. The magnitudes of B'' will differ only very slightly from those of B_e , however, and we shall henceforth use the approximation $B_e = B''$ in our calculations. From the quantities B_e we may compute the values of the moments of inertia, $I_{zz}^{(e)}$, for the two molecules, $I_{zz}^{(e)}$ being one of the two equal moments of inertia. We obtain $I_{zz}^{(e)} = 7.517 \times 10^{-40}$ g for AsH_3 and $I_{zz}^{(e)} = 14.76 \times 10^{-40}$ g cm^2 for AsD_3 . These are sufficient to determine the shape and size of the pyramid, since it may readily be shown that for the pyramidal XY_3 molecular model

$$I_{zz}^{(e)} = [3mr^2/2(1+3m/M)] \times \{2 - [1 - (3m/M)] \sin^2\beta\}, \quad (2)$$

in which m and M are the masses of the X and Y atoms, respectively, r is the $X-Y$ distance in the molecule, and β is the angle between the distance r and the axis of symmetry of the molecule. Using the two values $I_{zz}^{(e)}$ given above and assuming r and β to be the same for AsH_3 and AsD_3 , we obtain $r = 1.513 \text{ \AA}$ and $\beta = 54^\circ 39'$. We may now evaluate $I_{zz}^{(e)}$ and $C_e = (h/8\pi^2 c I_{zz}^{(e)})$. For these we arrive at $I_{zz}^{(e)} = 7.641 \times 10^{-40}$ g cm^2 for AsH_3 and $I_{zz}^{(e)} = 15.282 \times 10^{-40}$ g cm^2 since $I_{zz}^{(e)}$ may be shown to be

$$I_{zz}^{(e)} = 3mr^2 \sin^2\beta. \quad (3)$$

These lead immediately to $C_e = 3.663 \text{ cm}^{-1}$ and $C_e = 1.831 \text{ cm}^{-1}$, respectively.

We now turn our attention to the second set of lines in Fig. 1 which, we shall assume, must be ascribed to the band ν_2 . It is convenient at this point to write down the relations which state the frequency positions of the lines we may expect to observe in a perpendicular band. When the transitions $\Delta J = 0$, $\Delta K = \pm 1$ are observed, we obtain the relation

$$\omega = \nu_2 - (C'' - B'') + J(J+1)(B' - B'') + K^2[C' - B' - C'' + B''] \pm 2K[(1-\xi)C'' - B'']. \quad (4)$$

When the transitions are $\Delta J = \pm 1$, $\Delta K = \pm 1$ one

⁶ The centrifugal distortion terms have been omitted since the graphs resulting when $R(J-1) - P(J+1)$ and $R(J) - P(J)$ are plotted against $4(J + \frac{1}{2})$ are straight lines.

TABLE I. Observed positions of lines of ν_1 for AsH_3 ν $VAC(\text{cm}^{-1})$.

R_1	2130.7	P_2	2100.9
R_2	2138.1	P_3	2093.2
R_3	2145.1	P_4	2085.4
R_4	2152.2	P_5	2077.9
R_5	2159.3	P_6	2070.0
R_6	2166.3	P_7	2062.2
R_7	2172.9	P_8	2054.1
R_8	2179.4	P_9	2045.9
R_9	2186.1	P_{10}	2037.8
R_{10}	2192.5	P_{11}	2029.8
R_{11}	2198.8	P_{12}	2021.3
R_{12}	2204.6	P_{13}	2012.2
R_{13}	2210.5	P_{14}	2004.4
R_{14}	2216.8	P_{15}	1995.4
R_{15}	2223.1		
R_{16}	2229.7		
R_{17}	2237.9		

obtains

$$\omega = \nu_2 - (C'' - B'') + J^2(B' - B'') + K^2[C' - B' - C'' + B''] \pm 2K[(1-\xi)C'' - B''] \pm J(B' + B''). \quad (5)$$

The transitions $\Delta J = \pm 1$, $\Delta K = \mp 1$ are less important and will not be considered here.

The data indicate that the perpendicular band ν_2 resembles much a parallel type band in appearance. The strong central line near 2123 cm^{-1} would then be the result of the Q branches of each component bands piling up at nearly the same frequency position. We take this to mean that the quantity $[(1-\xi)C'' - B'']$ in (4) and (5) is nearly equal to zero.

If this quantity is small, the lines on the high and low frequency sides of the center will group themselves in branches corresponding to a transition $J \rightarrow J \pm 1$, each bunch consisting of J com-

TABLE II. Observed positions of lines of ν_1 for AsD_3 ν $VAC(\text{cm}^{-1})$.

R_3	1537.1	P_3	1511.9
R_4	1541.4	P_4	1507.7
R_5	1545.3	P_5	1503.7
R_6	1549.4	P_6	1499.7
R_7	1553.8	P_7	1496.0
R_8	1556.3	P_8	1492.0
R_9	1560.1	P_9	1488.0
R_{10}	1563.5	P_{10}	1483.7
R_{11}	1567.3	P_{11}	1479.6
R_{12}	1571.0	P_{12}	1475.4
R_{13}	1574.4	P_{13}	1471.5
R_{14}	1577.8	P_{14}	1467.0
R_{15}	1580.7	P_{15}	1463.2
R_{16}	1584.0	P_{16}	1459.0
R_{17}	1587.4	P_{17}	1454.7
R_{18}	1590.6	P_{18}	1450.4
R_{19}	1593.4	P_{19}	1446.1
R_{20}	1596.4		

ponents. One sees from the data on the high frequency side that the component lines remain always very close together and give no indication of resolution. On the low frequency side this is not true. The component lines are spread out over a considerable distance giving a diffuse, partially resolved appearance. We interpret this to mean that neither of the two terms $-2K[(1-\zeta) \times C'' - B'']$ nor $K^2[C'' - B'' - C' + B']$, though small, can be regarded as entirely negligible. It is assumed, moreover, that on the high frequency side the two terms have opposite signs, thereby tending to nullify their effect upon each other. Evidently, these terms will have the same sign on the low frequency side and their effects will be additive. A slight amount of trial and error will show that best agreement with experiment is obtained if the absolute values of the above terms are equal to each other for values of K equal approximately to $K=12$. From the fact that the effects of the two terms approximately nullify each other at this point on the high frequency side and from the magnitude of the spread of the components of the corresponding line on the low frequency side, we have estimated that $[(1-\zeta)C'' - B''] \approx 0.16 \text{ cm}^{-1}$ and $[B'' - C'' - B' + C'] \approx 0.02 \text{ cm}^{-1}$. Evidently some latitude exists in the above choice, but the latitude is, nevertheless, surprisingly small. We estimate the above values to fit our data accurately to within 5 percent.

We must now decide on the sign to be attached to the terms $[(1-\zeta)C'' - B'']$ and $[B'' - C'' - B' + C']$. This is not determined convincingly by the data of the high and low frequency sides of the band, since positive and negative values of the former quantity with corresponding values for the second term can be found which give satisfactory agreement with experiment. The choice is made, however, when we take into account that the Q branch converges on the high frequency side and diverges on the other side. This can be so only if both the above terms are positive, i.e., $[(1-\zeta)C'' - B''] = 0.16 \text{ cm}^{-1}$ and $[B'' - C'' - B' + C'] = -0.02 \text{ cm}^{-1}$. With the previously determined magnitudes for B'' and C'' we evaluate ζ to be equal to $\zeta = -0.0607$.

With these values it is found that rather satisfactory agreement with experiment is had if B' is taken to be 3.69 cm^{-1} . A plot of the band has

been made by drawing each transition as a triangle of which the altitude is proportional to the calculated intensity of the line and of which the base is drawn about twice as wide as the equivalent slit width in wave numbers. The close-lying components are then added together to give a resultant absorption pattern. These composite "lines" have been drawn in the lower half of Fig. 1. To complete the picture, the intensities of the parallel transitions have also been calculated. Since it has been assumed that here the K splitting may be neglected, the components for a given line J have been added together and the resultant line is shown as a triangle proportional in height to the calculated intensity and with a base about twice as wide as the frequency interval subtended by the slit. To obtain the best agreement it is necessary to make the proportionality constant multiplying the intensities of ν_2 about 50 percent greater than the proportionality constant multiplying the intensities of ν_1 . We believe the agreement between the computed absorption pattern and the measured pattern to be in reasonably good agreement.

It is desirable to have some verification that the analysis of this region is a reasonably accurate one. To make such a verification we shall test the data on ν_2 for the molecule AsD_3 and see if the structure of that band is consistent with our analysis of ν_2 for AsH_3 . As we have noted, the lines on both sides of the center of ν_2 for the molecule AsD_3 remain quite sharp. This can be so only if the quantity $[(1-\zeta_2)C'' - B'']$ for the AsD_3 molecule is much smaller than the same quantity for AsH_3 and provided the quantity $[B'' - C'' - B' + C']$ can be regarded as negligible. We have no way of estimating accurately what the value $B'' - C'' - B' + C'$ may be for AsD_3 but, since B'' and C'' have been determined, the magnitude $[(1-\zeta_2)C'' - B'']$ may be estimated if it is possible to calculate ζ_2 for AsD_3 . This is indeed possible,⁷ but to arrive at an accurate estimate it is necessary to know the values of the harmonic frequencies ω_2 and ω_4 and not merely the band centers ν_2 and ν_4 . Dennison⁵ has shown how one may proceed to correct for the anharmonicity in such molecules as AsH_3 and AsD_3 where all the vibration frequencies transform with about the same factor. We shall not

⁷ W. H. Shaffer, J. Chem. Phys. 9, 607 (1941).

here discuss his method except to say that it depends upon the observance of the Teller-Redlich product rule, $(4I_{zz}\mu'/I_{zz}'\mu) = (\omega_2\omega_4)^2/(\omega_2'\omega_4')^2$, and a second relation which is derived from a knowledge of how ζ_2 depends upon the potential energy constants α , β , and γ ⁸ in Dennison's notation. The primed quantities in the foregoing relate to the isotopic molecule and $\mu = 3mM/(3m+M)$. Using the method of Dennison we obtain $\omega_2 = 2225.8$ cm⁻¹, $\omega_4 = 1012.1$ cm⁻¹ for AsH₃, and $\omega_2' = 1528.4$ cm⁻¹ and $\omega_4' = 718.6$ cm⁻¹ for AsD₃. In making this determination we have made use of the value ν_4' for AsD₃ given in the work of Lee and Wu.¹ With these values for ω_2 , ω_4 , ω_2' , and ω_4' it is possible to compute what will be the value of ζ_2 for the AsD₃ molecule by using Shaffer's relations⁷ or by Dennison's⁵ method. For ζ_2' we have calculated the value $\zeta_2' = -0.0270$. With this quantity we have determined $[(1-\zeta_2')C''-B'']$ to be 0.0053 cm⁻¹ for the AsD₃ molecule, which is less than 1/30 the value for this quantity for the AsH₃ molecule. A hypothetical absorption pattern has been computed for AsD₃ in the same manner as for the AsH₃ molecule using the above determination for $[(1-\zeta_2')C''-B'']$ and regarding $[B''-C''-B'+C']$ to be entirely negligible. The pattern embracing ν_1 and ν_2 is shown in Fig. 2 below the experimental curve. The curve accounts for all the measured lines in a satisfactory manner except for three or four which we believe must be due to a weak superimposed band.

As one further verification that the model here proposed for the AsH₃ molecule is a satisfactory one, we have made the following calculation. It seems reasonable to assume that in this molecule the valence force field approximation is a rather satisfactory one. On the basis of the valence force field assumption, Lechner⁹ has derived the relation

$$4\lambda_2\lambda_4 = (f/m)(6d/m)[2/(1+3\cos^2\beta)] \times [p+(2-p)\cos^2\beta], \quad (6)$$

where $p = (3m+M)/M$ (M and m being the masses of the arsenic and hydrogen atoms, f and d the valence force constants) and where $\lambda_i = 4\pi^2c^2\omega_i'^2$ (ω_i being one of the normal fre-

⁸ The constants α , β and γ are, respectively, equal to the constants $(I_{zz}^{(e)}/2I_{zz}^{(e)})^2n_1$, $(I_{zz}^{(e)}/2I_{zz}^{(e)})n_2$ and n_3 in Shaffer's notation.

⁹ F. Lechner, Sitz. ber. Akad. Wiss. Wien **141**, 633 (1932).

TABLE III. Vibration frequencies and constants for the AsH₃ and AsD₃ molecules.

	AsH ₃	AsD ₃	
ν_1 (cm ⁻¹)	2116.1	1523.1	
ν_2	2123.0	1529.3	
ν_3	904.4-906.9	660.0	(1)
ν_4	1003.	714	(1)
ω_1	2209.2	1571.2	
ω_2	2225.8	1582.4	
ω_3	973.3	696.3	
ω_4	1012.1	718.6	
α (10 ⁶ dynes/cm)	2.768	2.768	
β	1.665	1.665	
γ	1.204	1.204	
a	3.6221	3.6221	
b	2.2076	2.2076	
c	0.6851	0.6851	

quencies). Since f , d , and β will be the same for AsH₃ and AsD₃, one quickly verifies that

$$(\lambda_2\lambda_4/4\lambda_2'\lambda_4')[p+(2-p)\cos^2\beta]/ [p'+(2-p')\cos^2\beta]. \quad (7)$$

Using the ω_2 and ω_4 given above, one obtains for β the value $\beta = 54^\circ 15'$.

We shall also make a calculation to determine values for the harmonic frequencies ω_1 and ω_3 . We shall make up a method rather similar to that devised by Dennison⁵ to determine ω_2 and ω_4 in NH₃. We shall assume, as did Dennison, that one may write $\nu_i = \omega_i(1+\alpha_i)$ for AsH₃ and $\nu_i' = \omega_i'(1+\omega_i'\alpha_i/\omega_i) \approx \omega_i'(1+\nu_i'\alpha_i/\nu_i)$. We have also the product relation $(\omega_1\omega_3/\omega_1'\omega_3')^2 = (m'\mu'/m\mu)$. One more relation is required before the ω_i may be calculated. We obtain it in the following manner.

It is observed that for AsD₃ the convergence of the P and R lines in the band ν_1 is somewhat greater than for ν_2 , i.e., $(B''-B')_{\nu_1} > (B''-B')_{\nu_2}$. It has been established⁷ that a Coriolis interaction may exist between the two frequencies ω_1

TABLE IV. Rotational constants and dimensions of the AsH₃ and AsD₃ molecules.

	AsH ₃	AsD ₃
B'' (cm ⁻¹)	3.723	1.896
$B'(\nu_1)$	3.682	1.883
$B'(\nu_2)$	3.69	1.874
C''	3.663	1.831
	-0.0602	-0.0383
$I_{zz}^{2(e)}$ (g-cm ² × 10 ⁴⁰)	7.517	14.760
$I_{zz}^{(e)}$	7.641	15.282
r_0 (Å)	1.513	1.513
h_0	0.93	0.93
$\angle\beta$	54°39'(54°14')	54°39'
$\angle\alpha$	89°50'	89°50'

and ω_3 . The effect of this interaction would be to decrease B' for ν_1 and to increase B' for ν_2 . Since these frequencies are of about the same magnitude and the motions correspond to displacements along the AS-H bonds in both cases, but to no change in the bond angle we shall assume that the convergence in both instances is the same except for the Coriolis contribution. Inspection of the quantities α_1 and α_2 in reference 7 will then show that the Coriolis contribution $2\omega_2^2\xi_{12}^2/(\omega_2^2-\omega_1^2) \approx 2\omega_1^2\xi_{12}^2/(\omega_2^2-\omega_1^2) \approx 2\nu_1^2\xi_{12}^2/(\nu_2^2-\nu_1^2) = 0.03$. In this relation ξ_{12} is the Coriolis coupling coefficient between ω_1 and ω_2 . From this relation $|\xi_{12}|$ may be computed to be $\xi_{12} = 0.01$. We shall make the approximation of setting ξ_{12} equal to zero. Shaffer's expression for ξ_{12} then makes it possible to derive the relation

$$\mu(\omega_1^2 + \omega_3^2) - \mu'(\omega_1'^2 + \omega_3'^2) = \left[\frac{(C-1)}{2C}\omega_1^2 + \frac{(C+1)}{2C}\omega_3^2 \right] (\mu - \mu'/2), \quad (8)$$

where the primes refer to the isotopic molecule, $\mu = 3mM/(3m+M)$ and $C = [(k_1/\mu) - (k_3/m)]$. Equation (8) supplies the additional relation required to evaluate ω_1 and ω_3 . We have obtained the following values for these: $\omega_1 = 2209.2 \text{ cm}^{-1}$, $\omega_3 = 973.3 \text{ cm}^{-1}$, $\omega_1' = 1571.2 \text{ cm}^{-1}$, and $\omega_3' = 696.3 \text{ cm}^{-1}$. These values of ω_1 and ω_3 are probably less reliable than those obtained for ω_2 and ω_4 , because the double minimum effect of the poten-

tial energy makes it more difficult to take the anharmonicity satisfactorily into account for ω_3 . The separation of the components of ω_3 is only about 2.5 cm^{-1} and, since one may expect the doubling in the normal state to be quite negligible, the doubling of the first excited state must be about 2.5 cm^{-1} . Since this splitting is rather small (especially when compared to the splitting in the case of NH_3), this method of approximating to the frequencies ω_1 and ω_3 is, nevertheless, probably quite good.

The constants of the harmonic portion of the potential energy function have also been evaluated. They are $\alpha = 2.768 \times 10^5$, $\beta = 1.665 \times 10^5$, $\gamma = 1.204 \times 10^5 \text{ dynes/cm}$, and $a = 3.622 \times 10^5$, $b = 2.2076 \times 10^5$, $c = 0.6851 \times 10^5$ in Dennison's notation. The last three of these are, respectively, equivalent to the constants k_1 , k_3 , and k_2 in Shaffer's notation. In Tables III and IV are summarized the information obtained concerning the size, shape, and structure of the AsH_3 molecule from a study of the fundamental bands ν_1 and ν_2 . In a later paper we hope then to give a discussion of the structure of the bands ν_3 and ν_4 in the spectra of AsH_3 and AsD_3 .

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Infra-Red Bands in the Spectrum of Difluoromethane

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Eight absorption bands have been observed in the infra-red spectrum of CH_2F_2 . Seven of these are believed to be fundamental bands and have been identified as follows; the symmetry species of the band being given in parentheses: $\omega_1(A_1) = 2949 \text{ cm}^{-1}$, $\omega_2(A_1) = 1116 \text{ cm}^{-1}$, $\omega_4(A_1) = 528.6 \text{ cm}^{-1}$, $\omega_6(B_1) = 3015.2$, $\omega_7(B_1) = 1176.1 \text{ cm}^{-1}$, $\omega_8(B_2) = 1089.7 \text{ cm}^{-1}$ and $\omega_9(B_2) = 1435.4 \text{ cm}^{-1}$. A band of species B_1 is observed at 2945 cm^{-1} . It is identified as $\omega_5 + \omega_9$ and from this it is inferred that $\omega_5(A_2) = 1510.6 \text{ cm}^{-1}$. Rotational constants for the normal state are found to be $B'' = 0.354 \text{ cm}^{-1}$ and $C'' - B'' = 1.303 \text{ cm}^{-1}$. From these values the values $r_0(\text{C}-\text{F}) = 1.32 \text{ \AA}$ and $\angle(\text{F}-\text{C}-\text{F}) = 107^\circ$ are obtained assuming that $r_0(\text{C}-\text{H}) = 1.094 \text{ \AA}$ and $\angle(\text{H}-\text{C}-\text{H}) = 110^\circ$.

I. INTRODUCTION

THE infra-red spectra of a considerable number of pentatomic molecules, in particular molecules of the type XY_4 (i.e., CH_4 ,

SiH_4 , GeH_4 , etc.) and the XYZ_3 type (i.e., CH_3F , CH_3Cl , etc.), have been investigated under high dispersion. With the exception of the spectrum of CH_2D_2 which was resolved by