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Microwave Spectra and Molecular Constants of Arsine and Stibine*

Paul Helminger, Edward L. Beeson, Jr.,† and Walter Gordy
Department of Physics, Duke University, Durham, North Carolina 27706

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Millimeter and submillimeter wave rotational transitions have been measured for different isotopic species of arsine and stibine from which accurate values of the rotational constants, including centrifugal stretching constants, nuclear quadruple and nuclear magnetic coupling constants, were obtained. Results (in Mc/sec) are for $^{75}\mathrm{AsH_3}$, $B_0 = 112\,470.59 \pm 0.03$, $D_J = 2.925 \pm 0.003$, $D_{JK} = -3.718 \pm 0.004$, $eqQ = -162.63 \pm 0.03$, $C_N = 0.106 \pm 0.003$, $C_K = 0.028 \pm 0.014$; for $^{75}\mathrm{AsD_3}$, $B_0 = 57\,477.60 \pm 0.02$, $D_J = 0.741 \pm 0.002$, $D_{JK} = -0.928 \pm 0.003$, $eqQ = -164.75 \pm 0.03$, $C_N = 0.051 \pm 0.003$, $C_K = 0.069 \pm 0.015$; for $^{121}\mathrm{SbH_3}$, $B_0 = 88\,038.99 \pm 0.03$, $D_J = 1.884 \pm 0.004$, $D_{JK} = -2.394 \pm 0.015$, $eqQ = 460.31 \pm 0.10$, $C_N = 0.245 \pm 0.006$, $C_K = 0.247 \pm 0.030$; for $^{123}\mathrm{SbH_3}$, $B_0 = 88\,022.51 \pm 0.03$, $D_J = 1.884 \pm 0.004$, $D_{JK} = -2.365 \pm 0.015$, $eqQ = 586.65 \pm 0.11$, $C_N = 0.130 \pm 0.005$, $C_K = 0.165 \pm 0.030$; for $^{121}\mathrm{SbD_3}$, $B_0 = 44\,694.92 \pm 0.03$, $D_J = 0.473 \pm 0.004$, $D_{JK} = -0.598 \pm 0.009$, $eqQ = 465.32 \pm 0.10$, $C_N = 0.127 \pm 0.006$, $C_K = 0.162 \pm 0.030$; for $^{123}\mathrm{SbD_3}$, $B_0 = 44\,678.81 \pm 0.03$, $D_J = 0.476 \pm 0.004$, $D_{JK} = -0.589 \pm 0.010$, $eqQ = 593.06 \pm 0.11$, $C_N = 0.063 \pm 0.005$, $C_K = 0.044 \pm 0.030$.

INTRODUCTION

In 1955, measurements of the $J = 0 \rightarrow 1$ rotational transitions of arsine[1] and stibine[2] in both normal and deuterated forms were reported. Because of the small dipole moment, $0.20D$ for arsine and $0.11D$ for stibine, and because of the multiple nuclear quadrupole splitting of the lines, higher rotational transitions could not be measured with the millimeter wave spectrometers then available. Since that time, considerable improvement in the sensitivity and accuracy of microwave spectrometers for the shorter millimeter wave region has been made in our laboratory. This improvement has made possible a considerably more accurate remeasurement of the $J = 0 \rightarrow 1$ transition, and a first measurement of higher rotational transitions from which the centrifugal distortion constants can be evaluated and corrections of B_0 for these distortions can be made. In addition, significant improvement is achieved in the values of the magnetic and nuclear quadrupole coupling constants and of the molecular structural parameters. These improved values for the various isotopic species are reported here. Recently, the submillimeter wave spectra of the similar molecules, ammonia and phosphine, were reported.[3]

Infrared measurements of the rotational constants of arsine[4] and stibine[5] have been made, but because of lower resolution these are less accurate than the ones reported here. No hyperfine constants could be obtained from the infrared observations. Microwave measurements in the centimeter wave region for the asymmetric forms of mixed H and D isotopic species were made by Loomis and Strandberg[6] in 1951.

EXPERIMENTAL OBSERVATIONS

The observations were made with harmonic energy from OKI 30V11 and 55V11 klystrons, with a crystal harmonic multiplier of the same general design as that used earlier.[7] A bombarded silicon crystal from Bell Telephone Laboratories was employed in the multiplier. Detection of the lower-frequency lines was accomplished with a silicon crystal detector such as that described previously,[7] but most of the submillimeter lines reported here were detected with an indium-antimonide detector operated at temperatures less than 2 °K. The latter detector, obtained from Mullard Limited, proved to be the more sensitive one in the shorter millimeter regions. The absorption cells consisted of glass cylinders 30 or 72 in. long and 4 in. diam, equipped with Teflon windows through which the millimeter wave radiation was focused by a combination of metallic horns and Teflon lenses. Frequency measurements were made with a frequency standard continuously monitored by the broadcast signals of station WWVB. Lines of the $J=0\rightarrow 1$ transition, except for SbD_3, and the stronger components of the higher transitions were displayed and measured on the oscilloscope with a video spectrometer. Figure 1 illustrates the signal-to-noise ratio of the $J=1\rightarrow 2$ lines of AsD_3 obtainable on the oscilloscope with the indium-antimonide detector. The $J=0\rightarrow 1$ transition of SbD_3, and weaker components of the $J=1\rightarrow 2$ transition of SbD_3 and AsH_3, were observed with a recording spectrometer which employed a phase-lock-in detector with source-frequency modulation.

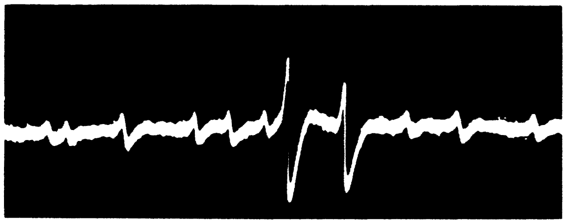

FIG. 1. Cathode-ray trace of the $J=1\rightarrow 2$, $K=0$ and $K=1$ transitions of AsD_3, showing hyperfine structure due to ^{75}As nuclear coupling.

RESULTS ON AsH_3 AND AsD_3

The observed frequencies of AsH_3 are listed in Table I, and those of AsD_3 in Table II. Calculated frequencies are given to show the degree of consistency of the results. The calculated frequencies were obtained according to theory for the rotational spectra of symmetric-top molecules,[8] with the centrifugal stretching effects evaluated to first order and the nuclear quadrupole hyperfine structure to second order; second-order quadrupole effects for arsine were generally on the order of experimental error in line measurement. The rotational constants and nuclear coupling constants obtained from this fitting of the calculated to the observed frequencies are given in Table III. Nuclear magnetic coupling terms calculated according to the expression

$$E_M = \tfrac{1}{2}\left[C_N + (C_K - C_N)K^2/J(J+1)\right] \times \left[F(F+1) - I(I+1) - J(J+1)\right] \qquad (1)$$

were required to give an accurate fitting of the lines. The resulting magnetic coupling constants are also listed in Table III.

Because they have fewer hyperfine components, and because they fall at lower frequencies where the spectrometer sensitivity is greater and the Doppler broadening less, the $J=0\rightarrow 1$ lines are measured with greater precision than are those of the higher J transitions. Consequently, the nuclear quadrupole coupling constants and values for C_N listed in Table III were derived entirely from the hyperfine structure of the $J=0\rightarrow 1$ transition. These constants were then used in a least-squares fit for prediction of all measured line frequencies. The results on higher J transitions were required, of course, for evaluation of the centrifugal distortion constants D_J and D_{JK}, which had not been obtained before. The frequencies of the $J=0\rightarrow 1$ transition were measured to an estimated accuracy of ±0.05 Mc/sec, approximately ten times that of the earlier measurement.

Unfortunately, the precise rotational constants cannot be used to give more accurate values of the ground-state structures of arsine because there is only one stable isotope (^{75}As) of arsinic. The differences between the effective structures of the normal and deuterated forms are too great to permit a useful derivation of the structures from deuterium substitution. In the earlier work,[1] the angles H-As-H and D-As-D were assumed to be 91°50′ and 91°30′, respectively, and the distances were calculated to be $d_{AsH} = 1.5192$ Å and $d_{AsD} = 1.5145$ Å. These values are consistent with the present measurements.

RESULTS ON SbH_3 AND SbD_3

The observed and calculated frequencies for

TABLE I. Observed frequencies for $^{75}AsH_3$.

Transition	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
$J=0\to1$, $K=0$: $F=\frac{3}{2}\to\frac{5}{2}$	224 937.78	224 937.78	0.00
$\frac{3}{2}\to\frac{3}{2}$	224 896.85	224 896.85	0.00
$\frac{3}{2}\to\frac{1}{2}$	224 969.88	224 969.88	0.00
$J=1\to2$, $K=0$: $F=\frac{5}{2}\to\frac{7}{2}$	449 792.43	449 792.42	0.01
$\frac{5}{2}\to\frac{5}{2}$	449 751.38	449 751.38	0.00
$\frac{3}{2}\to\frac{3}{2}$	449 821.08	449 821.09	−0.01
$\frac{1}{2}\to\frac{3}{2}$	449 748.06	449 748.06	0.00
$J=1\to2$, $K=1$: $F=\frac{5}{2}\to\frac{7}{2}$	449 813.69	449 813.70	−0.01
$\frac{3}{2}\to\frac{5}{2}$	449 772.90	449 772.88	0.02
$\frac{1}{2}\to\frac{3}{2}$	449 823.85	449 823.86	−0.01

$^{121}SbH_3$ and $^{123}SbH_3$ are compared in Table IV; those for $^{121}SbD_3$ and $^{123}SbD_3$, in Table V. Rotational and hyperfine coupling constants derived from these frequencies are listed in Tables VI. Second-order quadrupole effects for stibine were, in general, slightly greater in magnitude than experimental error in line measurement. As for arsine, values for the nuclear quadrupole coupling constants and the nuclear magnetic interaction terms C_N were derived entirely from hyperfine structure of the $J=0\to1$ transition.

Because of the relatively small difference between the values of B_0 for the two species of either SbH_3 or SbD_3, and because of the wide span and the density of the nuclear quadrupole pattern (the two antimony isotopes have spins $\frac{5}{2}$ and $\frac{7}{2}$), some overlapping of individual lines was encountered in the $J=1\to2$ transition. Only those lines which were completely resolved or, in the case of overlap, were clearly predominant in intensity were used in the fit.

TABLE II. Observed frequencies for $^{75}AsD_3$.

Transition	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
$J=0\to1$, $K=0$: $F=\frac{3}{2}\to\frac{5}{2}$	114 960.55	114 960.54	0.01
$\frac{3}{2}\to\frac{3}{2}$	114 919.24	114 919.23	0.01
$\frac{3}{2}\to\frac{1}{2}$	114 993.30	114 993.29	0.01
$J=1\to2$, $K=0$: $F=\frac{5}{2}\to\frac{7}{2}$	229 890.31	229 890.28	0.03
$\frac{5}{2}\to\frac{5}{2}$	229 848.92	229 848.92	0.00
$\frac{3}{2}\to\frac{3}{2}$	229 919.53	229 919.53	0.00
$\frac{1}{2}\to\frac{3}{2}$	229 845.47	229 845.47	0.00
$\frac{1}{2}\to\frac{1}{2}$	229 886.56	229 886.58	−0.02
$J=1\to2$, $K=1$: $F=\frac{5}{2}\to\frac{7}{2}$	229 900.45	229 900.47	−0.02
$\frac{5}{2}\to\frac{5}{2}$	229 879.68	229 879.68	0.00
$\frac{3}{2}\to\frac{5}{2}$	229 859.26	229 859.24	0.02
$\frac{3}{2}\to\frac{3}{2}$	229 873.77	229 873.82	−0.05
$\frac{1}{2}\to\frac{3}{2}$	229 911.01	229 910.98	0.03
$\frac{1}{2}\to\frac{1}{2}$	229 931.47	229 931.49	−0.02
$J=2\to3$, $K=0$: $F=\frac{7}{2}\to\frac{9}{2}$	344 787.60	344 787.58	0.02
$\frac{5}{2}\to\frac{5}{2}$	344 806.52	344 806.57	−0.05
$\frac{3}{2}\to\frac{5}{2}$	344 777.28	344 777.27	0.01
$\frac{3}{2}\to\frac{3}{2}$	344 818.32	344 818.33	−0.01
$J=2\to3$, $K=1$: $F=\frac{7}{2}\to\frac{9}{2}$	344 795.53	344 795.60	−0.07
$\frac{7}{2}\to\frac{7}{2}$	344 764.52	344 764.48	0.04
$\frac{5}{2}\to\frac{5}{2}$	344 799.51	344 799.48	0.03
$\frac{3}{2}\to\frac{3}{2}$	344 815.70	344 815.66	0.04
$J=2\to3$, $K=2$: $F=\frac{7}{2}\to\frac{9}{2}$	344 819.66	344 819.66	0.00
$\frac{5}{2}\to\frac{7}{2}$	344 778.44	344 778.43	0.01
$\frac{3}{2}\to\frac{5}{2}$	344 807.80	344 807.81	−0.01
$\frac{1}{2}\to\frac{3}{2}$	344 848.96	344 848.96	0.00

It should be noted that our results indicate a negative value for the stretching constant D_{JK} for both arsine and stibine. These results are consistent with the negative values for D_{JK} found in previous work on group-V hydrides.[3]

MOLECULAR STRUCTURE OF STIBINE

From the new rotational constants, it is possible to obtain molecular structural parameters for stibine which are more accurate than those previously obtained. Sufficient data are available for calculation of the averaged ground-state structures[8] and the substitution structures. The former, sometimes called the effective structures, are obtained from simultaneous solution of the moment-of-inertia equations for two isotopic species. Nevertheless, because of differences in zero-point vibrational energy, the structural parameters for the two isotopic species are not exactly the same, as they are assumed to be in this method. The differences are most pronounced for light atoms for which the zero-point vibrations are large. The bonds to H and D differ noticeably in length. Hence, we have employed the B_0 value for $^{121}SbH_3$ and that for $^{123}SbH_3$ to obtain the effective ground-state structures for SbH_3, and that for $^{121}SbD_3$ and for $^{123}SbD_3$ to obtain the effective structures for SbD_3. The resulting values, shown in Table VII, are reasonable. As expected, the Sb-H distance is slightly greater than that for Sb-D. However, the accuracy of this value is limited to three figures because of the fact that the Sb atom is near the center of gravity and the difference in mass between ^{121}Sb and ^{123}Sb causes only a small difference in the B_0 values, ~16 Mc/sec. In the previous work, this difference in B_0 could not be measured with sufficient accuracy for meaningful ground-state structures to be determined.

TABLE III. Calculated constants for $^{75}AsH_3$ and $^{75}AsD_3$.

	$^{75}AsH_3$	$^{75}AsD_3$
B_0 (Mc/sec)	112 470.59 ± 0.03	57 477.60 ± 0.02
D_J (Mc/sec)	2.925 ± 0.003	0.741 ± 0.002
D_{JK} (Mc/sec)	−3.718 ± 0.004	−0.928 ± 0.003
eqQ (Mc/sec)	−162.63 ± 0.03	−164.75 ± 0.03
C_N (Mc/sec)	0.106 ± 0.003	0.051 ± 0.003
C_K (Mc/sec)	0.028 ± 0.014	0.069 ± 0.015

TABLE IV. Measured frequencies of $^{121}SbH_3$ and $^{123}SbH_3$.

Transition	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
$^{121}SbH_3$			
$J=0\rightarrow 1,\ K=0:\ F=\frac{5}{2}\rightarrow\frac{7}{2}$	176 048.04	176 048.04	0.00
$\frac{5}{2}\rightarrow\frac{5}{2}$	176 143.85	176 143.85	0.00
$\frac{5}{2}\rightarrow\frac{3}{2}$	176 005.15	176 005.15	0.00
$J=1\rightarrow 2,\ K=0:\ F=\frac{7}{2}\rightarrow\frac{9}{2}$	352 086.44	352 086.40	0.04
$\frac{7}{2}\rightarrow\frac{7}{2}$	352 174.07	352 174.06	0.01
$\frac{5}{2}\rightarrow\frac{5}{2}$	352 054.33	352 054.40	−0.07
$\frac{5}{2}\rightarrow\frac{3}{2}$	351 987.99	351 988.02	−0.03
$\frac{3}{2}\rightarrow\frac{5}{2}$	352 193.11	352 193.11	0.00
$\frac{3}{2}\rightarrow\frac{3}{2}$	352 126.70	352 126.72	−0.02
$\frac{3}{2}\rightarrow\frac{1}{2}$	352 067.23	352 067.17	0.06
$J=1\rightarrow 2,\ K=1:\ F=\frac{7}{2}\rightarrow\frac{9}{2}$	352 077.99	352 077.89	0.10
$\frac{7}{2}\rightarrow\frac{7}{2}$	352 121.17	352 121.19	−0.02
$\frac{5}{2}\rightarrow\frac{7}{2}$	352 170.31	352 170.38	−0.07
$\frac{5}{2}\rightarrow\frac{5}{2}$	352 157.94	352 158.01	−0.07
$\frac{3}{2}\rightarrow\frac{3}{2}$	352 056.18	352 056.10	0.08
$\frac{3}{2}\rightarrow\frac{1}{2}$	352 026.11	352 026.13	−0.02
$^{123}SbH_3$			
$J=0\rightarrow 1,\ K=0:\ F=\frac{7}{2}\rightarrow\frac{9}{2}$	176 008.61	176 008.61	0.00
$\frac{7}{2}\rightarrow\frac{7}{2}$	176 121.17	176 121.17	0.00
$\frac{7}{2}\rightarrow\frac{5}{2}$	175 974.06	175 974.06	0.00
$J=1\rightarrow 2,\ K=0:\ F=\frac{9}{2}\rightarrow\frac{11}{2}$	352 017.66	352 017.64	0.02
$\frac{9}{2}\rightarrow\frac{9}{2}$	352 115.64	352 115.69	−0.05
$\frac{7}{2}\rightarrow\frac{7}{2}$	351 993.62	351 993.59	0.03
$\frac{5}{2}\rightarrow\frac{7}{2}$	352 140.70	352 140.71	−0.01
$J=1\rightarrow 2,\ K=1:\ F=\frac{9}{2}\rightarrow\frac{9}{2}$	352 052.66	352 052.70	−0.04
$\frac{7}{2}\rightarrow\frac{9}{2}$	352 109.96	352 109.91	0.05
$\frac{7}{2}\rightarrow\frac{7}{2}$	352 104.87	352 104.81	0.06
$\frac{5}{2}\rightarrow\frac{7}{2}$	352 031.98	352 031.99	−0.01
$\frac{5}{2}\rightarrow\frac{5}{2}$	352 000.05	352 000.11	−0.06
$\frac{5}{2}\rightarrow\frac{3}{2}$	351 962.34	351 962.35	−0.01

TABLE V. Measured frequencies of $^{121}SbD_3$ and $^{123}SbD_3$.

Transition	Oberserved frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
$^{121}SbD_3$			
$J=0\rightarrow 1,\ K=0:\ F=\frac{5}{2}\rightarrow\frac{7}{2}$	89 365.02	89 365.02	0.00
$\frac{5}{2}\rightarrow\frac{5}{2}$	89 462.30	89 462.30	0.00
$\frac{5}{2}\rightarrow\frac{5}{2}$	89 322.39	89 322.39	0.00
$J=1\rightarrow 2,\ K=0:\ F=\frac{7}{2}\rightarrow\frac{9}{2}$	178 754.85	178 754.91	−0.06
$\frac{7}{2}\rightarrow\frac{7}{2}$	178 844.11	178 844.09	0.02
$\frac{5}{2}\rightarrow\frac{7}{2}$	178 746.83	178 746.81	0.02
$\frac{5}{2}\rightarrow\frac{5}{2}$	178 723.16	178 723.13	0.03
$\frac{3}{2}\rightarrow\frac{5}{2}$	178 863.06	178 863.04	0.02
$\frac{3}{2}\rightarrow\frac{3}{2}$	178 796.19	178 796.22	−0.03
$J=1\rightarrow 2,\ K=1:\ F=\frac{7}{2}\rightarrow\frac{9}{2}$	178 738.98	178 739.02	−0.04
$\frac{7}{2}\rightarrow\frac{7}{2}$	178 783.36	178 783.33	0.03
$\frac{5}{2}\rightarrow\frac{7}{2}$	178 832.65	178 832.67	−0.02
$\frac{5}{2}\rightarrow\frac{5}{2}$	178 820.53	178 820.57	—0.04
$\frac{3}{2}\rightarrow\frac{5}{2}$	178 751.10	178 751.15	−0.05
$\frac{3}{2}\rightarrow\frac{3}{2}$	178 717.74	178 717.61	0.13
$^{123}SbD_3$			
$J=0\rightarrow 1,\ K=0:\ F=\frac{7}{2}\rightarrow\frac{9}{2}$	89 326.29	89 326.29	0.00
$\frac{7}{2}\rightarrow\frac{7}{2}$	89 440.39	89 440.39	0.00
$\frac{7}{2}\rightarrow\frac{5}{2}$	89 291.91	89 291. 91	0.00
$J=1\rightarrow 2,\ K=0:\ F=\frac{9}{2}\rightarrow\frac{11}{2}$	178 687.49	178 687.51	−0.02
$\frac{9}{2}\rightarrow\frac{9}{2}$	178 787.03	178 787.02	0.01
$\frac{7}{2}\rightarrow\frac{9}{2}$	178 672.89	178 672.92	−0.03
$\frac{7}{2}\rightarrow\frac{7}{2}$	178 663.48	178 663.60	−0.12
$\frac{7}{2}\rightarrow\frac{5}{2}$	178 599.87	178 599.81	0.06
$\frac{5}{2}\rightarrow\frac{7}{2}$	178 812.16	178 812.08	0.08
$\frac{5}{2}\rightarrow\frac{5}{2}$	178 748.31	178 748.28	0.03
$J=1\rightarrow 2,\ K=1:\ F=\frac{9}{2}\rightarrow\frac{11}{2}$	178 666.55	178 666.60	−0.05
$\frac{9}{2}\rightarrow\frac{9}{2}$	178 716.23	178 716.24	−0.01
$\frac{7}{2}\rightarrow\frac{9}{2}$	178 773.72	178 773.64	0.08
$\frac{7}{2}\rightarrow\frac{7}{2}$	178 768.89	178 768.81	0.08
$\frac{5}{2}\rightarrow\frac{7}{2}$	178 694.87	178 694.90	−0.03
$\frac{5}{2}\rightarrow\frac{3}{2}$	178 624.88	178 624.94	−0.06

From the four isotopic species it is possible to obtain both structural parameters, bond length and bond angle, by use of the isotopic substitution method. As was shown by Costain,[9] this method gives values ranging between the effective ground-state values and the equilibrium values. Since the equilibrium values are independent of zero-point vibrational effects, they are also independent of isotopic substitution. Therefore, the substitution values are less sensitive to zero-point vibration, and hence to isotopic substitution, than are the effective values for the ground rotational state. Although we have used isotopic combinations involving D or H to obtain the substitution structures listed in Table VII, the values differ only in the fourth figure. As expected, the substitution values obtained are in all instances less than the averaged ground-state values.

Methods for calculation of the various kinds of molecular structural parameters, together with a discussion of their differences, are given in a recent monograph by Gordy and Cook.[8]

NUCLEAR QUADRUPOLE COUPLING

The nuclear quadrupole coupling constants *eQq* for the stable isotopes of As and Sb are improved

TABLE VI. Calculated constants for stibine.

Molecule	B_0 (Mc/sec)	D_J (Mc/sec)	D_{JK} (Mc/sec)	eqQ (Mc/sec)	C_N (Mc/sec)	C_K (Mc/sec)
$^{121}SbH_3$	88 038.99 ± 0.03	1.884 ± 0.004	− 2.394 ± 0.015	460.31 ± 0.10	0.245 ± 0.006	0.247 ± 0.030
$^{123}SbH_3$	88 022.51 ± 0.03	1.884 ± 0.004	− 2.365 ± 0.015	586.65 ± 0.11	0.130 ± 0.005	0.165 ± 0.030
$^{121}SbD_3$	44 694.92 ± 0.03	0.473 ± 0.004	− 0.598 ± 0.009	465.32 ± 0.10	0.127 ± 0.006	0.162 ± 0.030
$^{123}SbD_3$	44 678.81 ± 0.03	0.476 ± 0.004	− 0.589 ± 0.010	593.06 ± 0.11	0.063 ± 0.005	0.044 ± 0.030

TABLE VII. Molecular dimensions of stibine.

Isotopic species	Bond distance (Å)	Bond angle
Effective ground-state structure		
$^{121}\mathrm{SbH}_3$, $^{123}\mathrm{SbH}_3$	1.7102	91° 42′
$^{121}\mathrm{SbD}_3$, $^{123}\mathrm{SbD}_3$	1.7075	91° 42′
Substitution structure		
$^{121}\mathrm{SbD}_3$: $^{123}\mathrm{SbD}_3$, $^{121}\mathrm{SbH}_3$	1.7039	91° 35′
$^{123}\mathrm{SbD}_3$: $^{121}\mathrm{SbD}_3$, $^{123}\mathrm{SbH}_3$	1.7039	91° 35′
$^{121}\mathrm{SbH}_3$: $^{123}\mathrm{SbH}_3$, $^{121}\mathrm{SbD}_3$	1.7032	91° 29′
$^{123}\mathrm{SbH}_3$: $^{121}\mathrm{SbH}_3$, $^{123}\mathrm{SbD}_3$	1.7032	91° 29′

in accuracy by a factor of 10 over the previous values. Unfortunately, the new values cannot yet be used to advantage for giving more precise information about the molecular bonding or about the nuclear moment Q. The difficulty in interpretation comes mainly from the uncertainty in the atomic coupling per p electron in the group-V elements.[10] There is an additional complication because d-orbital hybridization, as well as s-orbital hybridization, occurs in the bonding orbitals of both As and Sb. As evidence for this, the nuclear quadrupole coupling, according to the best estimates of the eQq per p electron, indicates an s contribution of 12% to the bonding orbital of As in arsine and an s contribution of about 19% of Sb in stibine, whereas the nearly right-angle bonds in these molecules seem to indicate almost pure p bonding orbitals. Reconciliation of the bond angles and nuclear coupling can be achieved with spd-hybrid orbitals, but the required proportions are uncertain because of effects of ionic character, and because of approximations in the atomic coupling per p electron. A recent treatment of the molecular quadrupole coupling of group-V elements is given by Gordy and Cook.[8]

It is interesting to note from Tables III and VI that the nuclear quadrupole couplings of As and Sb are definitely larger in the deuterated species. This effect is not as easily understood as are the shorter bond lengths of the deuterated species, which can be ascribed to the smaller zero-point vibrations of the deuterium in a Morse-type potential field. The coupling differences reveal a definite alteration in the electronic structure of the molecule by the isotopic substitution.

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Symmetry-Adapted Pair Correlations in Ne, F^-, Ne^+, and F†

A. W. Weiss
National Bureau of Standards, Washington, D. C. 20234

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The superposition-of-configurations method has been used to calculate, a single pair at a time, the pair correlation energies for Ne, Ne^+, F^-, and F. The approach is essentially a symmetry-adapted variation of Nesbet's formulation of the Bethe-Goldstone scheme for the atomic correlation problem, and the aim of this research was to test the usefulness of the method for predicting such physically observable quantities as ionization potentials and electron affinities. The calculations predict an ionization potential for neon of 21.52 eV, compared with a 21.56-eV experimental value, and a fluorine electron affinity of 3.47 eV, for which the experimental value is 3.45 eV.

INTRODUCTION

This paper reports the results of *ab initio* calculations of the correlation contributions to the binding energy of the final electron in the ground state of the 10-electron atoms Ne and F^-, i.e., the ionization potential of neon and the electron affinity of fluorine. The total correlation energies of both

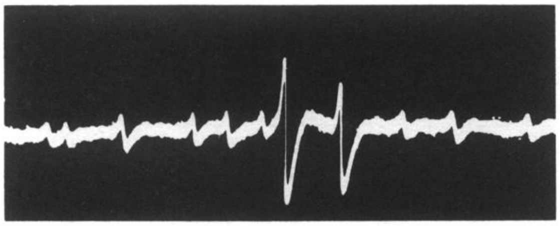

FIG. 1. Cathode-ray trace of the $J=1\rightarrow 2$, $K=0$ and $K=1$ transitions of AsD_3, showing hyperfine structure due to ^{75}As nuclear coupling.