

Millimeter Wave Spectra of AsH₃ and AsD₃*

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The $J=0 \rightarrow 1$ rotational transitions of AsH₃ and of AsD₃ have been measured in the one to three millimeter wave region. The B_0 values obtained are, in Mc/sec: 112 468.46 for As⁷⁵H₃ and 57 477.15 for As⁷⁵D₃. The observed nuclear quadrupole coupling, eQq , of As⁷⁵ differs for the two species and is -160.1 ± 0.4 Mc/sec for As⁷⁵H₃ and -165.9 ± 0.4 Mc/sec for As⁷⁵D₃. Detectable As⁷⁵ nuclear magnetic interaction was found with the magnetic coupling constant $A = 0.33$ Mc/sec for AsH₃ and $A = \sim 0.07$ Mc/sec for AsD₃. From a consideration of previous microwave work on AsH₂D and a consideration of the differences in the bond angles in normal and deuterated stibine, the bond angle in AsH₃ is assumed to be $91^\circ 50'$ and that in AsD₃ to be $91^\circ 31'$. These angles with the observed moments of inertia yield the value 1.5192 Å for the As-H length and 1.5145 Å for the As-D length.

INTRODUCTION

PURE rotational transitions of both AsH₃ and AsD₃ have been previously measured in the far infrared region at wavelengths of 0.2 mm and shorter by Stroup, Oetjen, and Bell.¹ In the present work are reported measurements of lower J rotational transitions of the same molecules in the region above one-millimeter wavelength. The rotation vibration spectra of arsine have been investigated in the near infrared region by McConaghie and Nielsen,² and the asymmetric hybrid AsH₂D has been studied with microwave methods in the centimeter wave region by Loomis and Strandberg.³ No previous microwave measurements of AsH₃ nor AsD₃ have been made because the pure rotational spectra of these symmetric forms originate in the shorter millimeter wave region where sensitive measuring techniques have only recently been developed.⁴ The

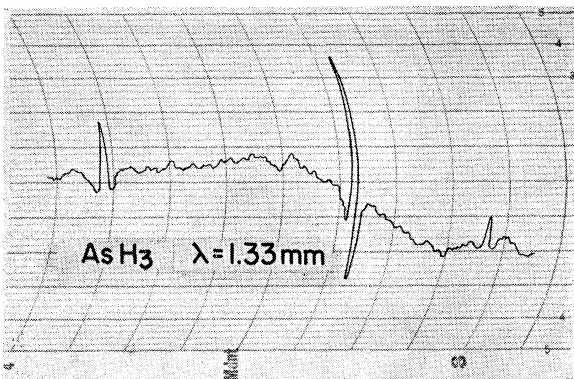


FIG. 1. Recorder tracing of the $J=0 \rightarrow 1$ transition of As⁷⁵H₃ in the region of 225 kMc/sec.

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¹ Stroup, Oetjen, and Bell, *J. Opt. Soc. Am.* **43**, 1096 (1953).

² V. M. McConaghie and H. H. Nielsen, *Phys. Rev.* **75**, 663 (1949).

³ C. C. Loomis and M. W. P. Strandberg, *Phys. Rev.* **81**, 778 (1951).

⁴ W. C. King and W. Gordy, *Phys. Rev.* **90**, 319 (1953); **93**, 407 (1954).

present work reveals observable differences in the molecular dimensions and nuclear couplings of the normal and the deuterated forms.

EXPERIMENTAL METHOD

The spectrometer employed was the same as that referred to in the previous paper on stibine. The fourth harmonic of the klystron power was employed for the AsD₃ measurements and the ninth harmonic for AsH₃.

Arsine was prepared by the action of H₂O on Na₃As. The deuterated arsine was prepared in a similar manner with ²D₂O being substituted for H₂O. The Na₃As was prepared by heating the elements until reaction occurred. All operations were carried out in a previously evacuated system.

EXPERIMENTAL RESULTS

The As⁷⁵ nucleus has a spin of 3/2 and a sizeable electric quadrupole moment. The 0→1 transition is split into three components with intensity ratios 1, 3, and 2. Figure 1 shows a recorder tracing of the 0→1 transition of AsH₃ at 1.33 mm. The lines were also observed on the cathode-ray oscilloscope with the usual video spectrometer but with difficulty. The 0→1 lines of AsD₃ which fall at 2.60 mm were easily observed and measured with the video spectrometer.

Table I gives the observed frequencies and the calculated relative intensities of the lines. Table II lists the B_0 values and moments of inertia, and Table III the nuclear quadrupole couplings derived from the data. As in the Sb coupling for stibine, the nuclear quad-

TABLE I. Observed frequencies with calculated relative intensities.

| Molecule | Transition $J=0 \rightarrow 1$ $F \rightarrow F'$ | Observed frequency in Mc/sec | Relative intensity (theoretical) |
|---------------------------------|---|---------------------------------|--|
| As ⁷⁵ H ₃ | 3/2→1/2 | 224 967.56±0.5 | 33 |
| | 3/2→5/2 | 224 936.78 | 100 |
| | 3/2→3/2 | 224 895.91 | 67 |
| As ⁷⁵ D ₃ | 3/2→1/2 | 114 993.50±0.3 | 33 |
| | 3/2→5/2 | 114 960.57 | 100 |
| | 3/2→3/2 | 114 918.94 | 67 |

TABLE II. Rotational constants.

| Molecule | $\nu_0(J=0 \rightarrow 1)$ in Mc/sec ^a | B_0 in Mc/sec | I_B in 10^{-40} g cm ² |
|----------------------------|--|-------------------------|--|
| As^{75}H_3 | 224 928.22 | 112 468.46 ^b | 7.459 ₀₈ |
| As^{76}D_3 | 114 952.20 | 57 477.15 ^b | 14.595 ₆₆ |

^a The $J=0 \rightarrow 1$ rotational frequency corrected for nuclear perturbations.
^b Obtained from ν_0 measured in the present work with $DJ=2.2$ Mc/sec for AsH_3 and $DJ=0.5$ Mc/sec for AsD_3 as taken from infrared data by Stroup, Oetjen, and Bell [J. Opt. Soc. Am. 43, 1096 (1953)].

rupole coupling of As^{76} is about 5 Mc/sec higher in the deuterated than in the normal arsine. The value obtained by Loomis and Strandberg for AsH_2D , -165 Mc/sec, falls between that which we obtained for AsH_3 and AsD_3 .

It was found necessary to add to the nuclear quadrupole energy a small nuclear magnetic interaction term of the form given in Eq. (2) of the previous paper. The magnetic coupling constant A of As^{75}H_3 , 0.33 Mc/sec, is roughly four times that observed for AsD_3 . The latter is too small to be measured with accuracy.

MOLECULAR STRUCTURE

There is only one stable As isotope, and hence we cannot use the method of isotopic substitution to solve separately for the structures of AsH_3 and AsD_3 . We can of course combine the normal and deuterated forms for the solution, but this will not lead to accurate values because of the effectively different sizes of these two isotopic forms. A more instructive treatment is obtained by making certain reasonable assumptions regarding the bond angles.

From near-infrared data Nielsen⁵ has obtained the value $91^\circ 35'$ for H-As-H angle in AsH_3 . From microwave measurements Loomis and Strandberg³ obtained the value 92° for the bond angle in the hybrid species AsH_2D . The latter value represents, presumably, a mean of the angles H-As-H and H-As-D. It should, therefore, be somewhat closer to the angle H-As-H than to the angle D-As-D. We assume for the H-As-H angle a value of $91^\circ 50'$ which is consistent with the previous microwave and infrared work. From a consideration of the smaller angle (about $20'$ smaller) of the deuterated over the normal forms in phosphine and stibine (see Table V), we assume the angle in AsD_3 to be $91^\circ 30'$, or $20'$ smaller than that in AsH_3 . With these assumptions the As-H and As-D distances were calculated. The results are given in Table IV. It is seen that the effective As-D distance is about 0.005 A shorter than the As-H

TABLE III. Observed nuclear couplings.

| Nucleus | Electric coupling eQq in Mc/sec | Magnetic coupling A in Mc/sec |
|------------------------------------|--------------------------------------|------------------------------------|
| As^{75} in AsH_3 | -160.1 ± 0.4 | 0.33 |
| As^{75} in AsD_3 | -165.9 ± 0.4 | 0.07 |

⁵ H. H. Nielsen, J. Chem. Phys. 20, 759 (1952); 20, 1955 (1952).

TABLE IV. Molecular structures.

| Molecule | Bond angle | Bond length |
|----------------|----------------------------------|----------------------|
| AsH_3 | $91^\circ 50' \pm 20'$ (assumed) | 1.5192 ± 0.002 A |
| AsD_3 | $91^\circ 31' \pm 20'$ (assumed) | 1.5145 ± 0.002 A |

distance, in good agreement with the phosphine and stibine results. The values are compared in Table V.

NUCLEAR COUPLINGS

The nuclear quadrupole coupling per unbalanced p electron in atomic As^{75} has been measured from optical atomic hyperfine structure.⁶ This result allows a simple calculation of the number of unbalanced p electrons in AsH_3 as

$$U_p = eQq(\text{AsH}_3) / (eQq)_{U_p=1} = -160/600 = -0.27.$$

If the bonds were formed with pure p orbitals, there would be electrical symmetry about the As nucleus, the unbalanced p electron charge U_p would be zero, and no quadrupole coupling would be observed. If we assume that the unbalanced p charge indicated by the coupling arises from s hybridization alone with three equivalent directed-valence-bonds, the s hybridization required⁷ for each bond orbital is approximately eight percent. With this type bonding the three equivalent hybridized orbitals would be directed at angles of 97° approximately, whereas the observed bond angle is only $91^\circ 50'$. Evidently the bond orbitals cannot be nearly pure p as indicated by the bond angles alone, nor directed s - p hybrids as is suggested by the coupling alone. If the orbitals are the usual directed valence bond orbitals, the As bonding orbitals must have significant d as well as s character. A similar situation⁸ exists in H_2S where a large asymmetry in the S^{33} coupling is found with a bond angle close to 90° .

It may also be possible to reconcile the bond angles and nuclear couplings in arsine with the nonlocalized molecular orbital treatment.⁸ The $1s$ orbitals of the hydrogens would be combined to form a symmetric

TABLE V. Comparison of structures of phosphine, arsine, and stibine.

| Molecule | Bond angle | Bond length |
|------------------|----------------|-------------|
| PH_3^a | $93^\circ 47'$ | 1.4206 A |
| PD_3^a | $93^\circ 10'$ | 1.4166 A |
| AsH_3^b | $91^\circ 50'$ | 1.5192 A |
| AsD_3^b | $91^\circ 30'$ | 1.5145 A |
| SbH_3^c | $91^\circ 18'$ | 1.7073 A |
| SbD_3^c | $90^\circ 56'$ | 1.7021 A |

^a From Burrus, Jache, and Gordy, Phys. Rev. 95, 706 (1954).

^b Present work.

^c Jache, Blevins, and Gordy (see preceding paper in this issue).

⁶ H. Schuler and M. Marketu, Z. Physik 102, 703 (1936).

⁷ For methods of evaluation see: Gordy, Smith, and Trambarulo, Microwave Spectroscopy (John Wiley and Sons, Inc., New York, 1953), Chap. 7.

⁸ C. A. Burrus and W. Gordy, Phys. Rev. 92, 274 (1953).

and two antisymmetric functions with respect to the figure axis of the molecule. Two pure p orbitals of the As would then be combined with the antisymmetric H functions to form two π molecular orbitals, whereas the third bonding orbital, a σ molecular orbital, would be formed by combination of the symmetric H orbital with a hybridized atomic orbital of the As. This description will be elaborated elsewhere.

The magnetic coupling constant of As^{75}H_3 , 0.33 Mc/sec, is the same as that of $\text{Sb}^{121}\text{H}_3$ while the nuclear g factor of As^{75} , 0.96, is less than that of Sb^{121} , 1.34. This result shows that the molecular magnetic field of AsH_3

at the As nucleus is larger than that of the Sb nucleus in SbH_3 by a factor of 1.40. If the molecular field is generated purely by rotation of the molecule, one might expect this factor to be approximately equal to the ratio of the two B_0 values, or about 1.3. The magnetic coupling constants of deuterated arsine and stibine are too small to be measured with accuracy. They are several times lower than those of the normal species and appear to be reduced by approximately the square of the B_0 ratios from the hydride values.

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Polarization Energy for $3d$ and $4p$ Electrons

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Meshkov has demonstrated the presence of an appreciable polarization energy associated with the combination of a $3d$ and a $4p$ electron in the $3d^2 4p$ configuration of Ti II. He has shown that the mean deviation between theory and experiment is reduced from ± 332 K to ± 249 K when this energy is considered. It is here noted that by use of a modified form of Meshkov's approximation a further reduction to ± 180 K is produced. This modification requires only three adjustable parameters, as compared with the five required in Meshkov's original method. It is suggested that the agreement could be made even better if a breakdown of LS -coupling due to the closeness of three terms in this spectrum were considered.

I. INTRODUCTION AND RESULTS

IN a recent paper, Meshkov has demonstrated the existence of an appreciable polarization energy associated with the combination of a $3d$ and a $4p$ electron in the $3d^2 4p$ configuration of Ti II.¹ His method evaluates the d - p and d - d polarization energy of Ti II by utilizing the experimental data for Ti III in Bacher and Goudsmit's first approximation formula.^{2,3} The parameters of Slater's formulas (more accurately, the differences in value of these parameters in Ti II and Ti III) were evaluated by least squares to get best agreement with the experimental data. His results are reproduced in columns *A* of Table I; the final mean deviation, obtained with five arbitrarily adjustable parameters, is ± 249 K.

Racah also has calculated term values for this configuration, by using a method that accounts for the d - d polarization energy only.^{4,5} He assumes that the total d^2

energy is proportional to the energy of the d^2 parent term in Ti III. The parameters of Slater's formulas that refer to d - p energy, together with the proportionality factor for the d^2 energy, were evaluated by least squares. His results are reproduced in columns *B* of Table I; the final mean deviation, obtained with four adjustable parameters, is ± 332 K. Since this calculation omits d - p polarization energy entirely, the smaller mean deviation obtained in Meshkov's calculation would be due primarily to its inclusion, though his use of an additional adjustable parameter also would help a little.⁶

Meshkov's method accounts for polarization by utilizing experimental data with Bacher and Goudsmit's first approximation, but only a part of the Slater energy is accounted for at the same time. Its main advantage, compared to using Slater's formulas together with the $L(L+1)$ correction,^{3,7} is that it requires fewer adjustable parameters, so that the chance of getting accidental

He regards the energies of the parent term in d^2 as adjustable parameters, so that the number of parameters needed is six. His results are not given in numerical form.

⁶ Racah's calculation *A* in Table I of reference 4 shows that the mean deviation is ± 430 K if neither d - d nor d - p polarization energy is included. Five parameters are used in this calculation.

⁷ In a term $d^n(\beta SL)pS'L'$ the correction would be generalized to the form $(\alpha_d - \alpha_p)L(L+1) + \alpha_p L'(L'+1)$ to include both d - d and d - p polarization effects, so that two additional parameters would be needed. Rigorously, corrections proportional to $S(S+1)$ and $S'(S'+1)$ should be included also, but these seem to have a small effect. However, it should be noted that formula (2) does include these latter corrections.

¹ S. Meshkov, Phys. Rev. **91**, 871 (1953).

² R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

³ R. E. Trees, J. Research Nat. Bur. Standards **53**, 35 (1954), Research Paper 2515. Section 2.2 of this paper discusses the use of a linear approximation [such as Bacher and Goudsmit's first approximation, or the $L(L+1)$ correction] for the polarization energy, and lists other references on this subject. Referred to as A.

⁴ G. Racah, Phys. Rev. **62**, 438 (1942).

⁵ T. Yamanouchi [Proc. Phys.-Math. Soc. Japan **22**, 841 (1940)] has analyzed this configuration by using still another method which would account for the d - d polarization energy.

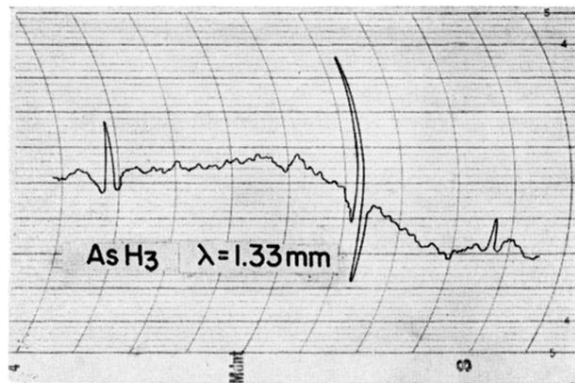


FIG. 1. Recorder tracing of the $J=0 \rightarrow 1$ transition of As^{75}H_3 in the region of 225 kMc/sec.