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Submillimeter-wave spectrum of the AsH_2 radical in the 2B_1 ground electronic state

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The pure rotational spectrum of the AsH₂ radical in its ${}^{2}B_{1}$ ground electronic state was observed for the first time by microwave spectroscopy. The AsH₂ radical was generated in a free-space cell by dc-glow discharge of a mixture of H₂ and O₂ gases over arsenic powder. Fifty-five fine and hyperfine components of six rotational transitions were measured in the frequency region of 304– 374 GHz, and were analyzed by least-squares methods. Molecular constants, including the rotational constants, the centrifugal distortion constants, the spin-rotation coupling constant incorporating the centrifugal distortion term, and the hyperfine coupling constants associated with the arsenic and hydrogen nuclei, were precisely determined. The bonding in AsH₂ was discussed on the basis of the hyperfine coupling constants, first determined in the present study. © 1998 American Institute of *Physics*. [S0021-9606(98)03337-6]

I. INTRODUCTION

Dihydrides of the group V elements furnish a series of fundamental bent triatomic free radicals in molecular spectroscopy. The NH₂ (Ref. 1) and PH₂ (Ref. 2) radicals have been extensively studied and well characterized by various high-resolution molecular spectroscopic methods in the region from optical to microwave, whereas the dihydride of the third row element As, AsH₂, has been studied so far only in the optical region. The first spectroscopic investigation of AsH₂ and AsD₂ in the gas phase was carried out in 1966 by Dixon and his collaborators³ who observed $\tilde{A}^{2}A_{1} - \tilde{X}^{2}B_{1}$ transitions of both species in the visible region using flash photolysis of arsine. Later they determined the rotational constants, centrifugal distortion constants, and spin-rotation coupling constants of AsH₂ in both electronic states.⁴ The same bands generated by ArF laser photolysis were also studied in emission, and the vibrational structure of both electronic states was analyzed in 1986.⁵ Jackel and Gordy studied the ESR spectrum of AsH₂, but did not report hyperfine coupling constants.⁶ Spectroscopic constants of AsH₂, including its equilibrium bond length, vibrational frequency, and dipole moment, were predicted by several quantum chemical calculations.^{7–9}

The hyperfine coupling constants provide information as to the nature of the chemical bonding, which has not been systematically available for the arsenic bearing hydrides. Therefore we studied AsH_2 by microwave spectroscopy and determined detailed molecular constants including the hyperfine coupling constants.

II. EXPERIMENT

Spectral lines of AsH_2 were observed by using a frequency-modulated microwave spectrometer combined with a 2 m free-space absorption cell.¹⁰ The submillimeter-

wave radiation was supplied by a tripler or a quadrupler driven by millimeter-wave klystrons. Production of AsH₂ was similar to that of AsH.¹¹ The radical was produced by dc-glow discharge (130–150 mA) of a mixture of H₂ gas (25 mTorr) and O₂ gas (1 mTorr) over arsenic powder at a cell temperature of -120 to -100 °C. The addition of a small amount of oxygen gas was essential to the production of gaseous AsH₂. dc-glow discharge in AsH₃ was also employed for the production of the radical, but there was no significant change in the intensity of the signal, and so this method was discarded.

Spectral line frequencies of AsH₂ were predicted using the molecular constants reported by the optical spectroscopic study.⁴ Several lines which indicated paramagnetism were detected in the region of 326.1-326.3 GHz and 351.0-351.5 GHz by time-averaging observations of 40 s. They were assigned to the $N_{KaKc} = 1_{11} - 0_{00}$ J = 1.5-0.5 and J = 0.5-0.5 transitions, respectively. Successively, five Q branch transitions were detected mainly in the 300 GHz region: 2_{11} - 2_{02} , J=2.5-2.5 and J=1.5-1.5, $2_{21}-2_{12}$, J=2.5-2.5 and J $=1.5-1.5, 3_{21}-3_{12}, J=3.5-3.5$ and $2.5-2.5, 3_{31}-3_{22}, J$ =3.5-3.5, and 4_{41} - 4_{32} , J=4.5-4.5. Figure 1 shows an example of the observed spectral lines which are relatively strong. Most of the observed lines of AsH₂ were very weak and could not be seen on the CRO display. The averaging time of one observation was 40-320 s. Each line frequency was determined by averaging five or six pairs of upward and downward frequency sweep measurements. The observed line frequencies are listed in Table I.

III. ANALYSIS

The ground electronic state of the AsH₂ radical has ${}^{2}B_{1}$ symmetry. Since AsH₂ has two identical hydrogen nuclei(I = 1/2), symmetric rotational levels of (*KaKc*) = (even even) or (odd odd) are combined with the antisymmetric hydrogen nuclear spin function of $I(H)=I(H_{1}) + I(H_{2})=1$, whereas the (eo) or (oe) levels are combined

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FIG. 1. Submillimeter-wave lines of an AsH₂ radical: the N_{KaKc} = 3₃₁-3₂₂, J=7/2-7/2, F_1 =5-5, F=5-5, 4-4, and 6-6 transitions observed by dc-glow discharge (130–150 mA) of a mixture of H₂(25 mTorr) and O₂(1 mTorr) gas over arsenic powder. The integration time was 80 s. Vertical lines represent the calculated frequencies and intensities.

with the symmetric nuclear spin function of I(H)=0. Therefore the fine-structure level is split into 12 hyperfine sublevels by I(As)=3/2 and I(H)=1 for the symmetric rotational level, and into four hyperfine sublevels by I(As) for the antisymmetric rotational level.

The observed data of AsH_2 were fitted to a conventional Hamiltonian, appropriate for an asymmetric top molecule in a doublet electronic state with two nuclear spins, of the form

$$H = H_{\text{rot}} + H_{\text{sr}} + H_{\text{hfs}}(\text{As}) + H_{\text{hfs}}(\text{H}),$$

where $H_{\rm rot}$ is the rotational Hamiltonian with its centrifugal distortion effect and $H_{\rm sr}$ is the spin-rotation interaction term with the centrifugal distortion effect. $H_{\rm hfs}({\rm As})$ comprises the magnetic dipole and electric quadrupole hyperfine interaction terms and $H_{\rm hfs}({\rm H})$ refers to magnetic dipole hyperfine terms. The matrix elements were calculated by the standard procedure using the basis function with the coupling scheme of J=N+S, $F_1=J+I({\rm As})$, and $F=F_1+I({\rm H})$.^{12,13}

In the initial analysis, the rotational constants and the spin-rotation coupling constants determined by Dixon et al.⁴ were used. The hyperfine coupling constants were estimated from those of AsH (Ref. 11) and the ratios between those of monohydride and dihydride of other group V elements, N (Refs. 14 and 1) and P.^{15,16} The predicted hyperfine coupling constants were as follows; the Fermi contact term $a_F(As)$ = -21 MHz, the magnetic dipole coupling constants $T_{aa}(As) = T_{bb}(As) = 300 \text{ MHz}$, the electric quadrupole cou- $\chi_{aa}(As) = 11 \text{ MHz}$ pling constants and $\chi_{hh}(As)$ = -125 MHz. These were useful for the assignment of the observed rotational transitions, but were not helpful to the assignment of the hyperfine structure of the low J transitions, $N_{KaKc} = 1_{11} - 0_{00}$ J = 1.5 - 0.5, J = 0.5 - 0.5and N_{KaKc} $=2_{11}-2_{02}$ J=1.5-1.5. Therefore $T_{aa}(As)$, $T_{bb}(As)$, χ_{aa} (As), and χ_{bb} (As) were determined using antisymmetric rotational transitions (I=0) in the first instance. The constant of $a_F(As)$ could not be determined from the observed hyperfine structure because this parameter does not affect ΔF_1 =0 transitions of Q branches. The low J transitions, N_{KaKc} $=1_{11}-0_{00}$, J=1.5-0.5 and J=0.5-0.5, could be assigned with changing $a_F(As)$ by trial and error.

Unresolved lines were included in the fit by averaging frequencies of the individual components which had been weighted in proportion to their relative intensities when fitting the data. The 48 observed lines of AsH₂ were used in the least-squares fit and the corresponding molecular constants determined are listed in Table II. The standard deviation of the fit is 28 kHz, which is comparable to the frequency measurement errors, as shown in Table I. The centrifugal distortion constants Δ_N and δ_N were fixed to the values calculated from centrifugal distortion constants $\tau_{aaaa}, \tau_{bbbb}, \tau_{aabb},$ and au_{abab} which were determined by electronic spectroscopy.⁴ Centrifugal distortion terms of the spinrotation coupling constants Δ_N^s , Δ_{NK}^s , and Δ_K^s were fixed to the values derived using symmetric top approximation.¹⁷ The other centrifugal distortion terms δ_N^s and δ_K^s were fixed at zero.

An initial analysis gave residuals of several hundreds of kHz in the fit. Inclusion of the nuclear spin-rotation coupling constants for As reduced the standard deviation of the fit from 553 to 28 kHz. An attempt was made to determine the nuclear spin-rotation coupling constants of the hydrogen, but it was found that these values were smaller than their uncertainties in the least-squares fit. Therefore these values were set to zero in the final analysis.

IV. DISCUSSION

The molecular constants determined in the present study are compared with previously reported values in Table II. Rotational constants and the spin-rotation coupling constants of the present study agree with those determined by the optical spectroscopic study.⁴ However, the precision of molecular parameters is significantly improved in the present study.

Hyperfine coupling constants of the arsenic and hydrogen nuclei of AsH₂ were determined for the first time in the present study. The determined value of the Fermi contact term of As was far from the value predicted from $a_F(NH_2)/b_F(NH)$ and $a_F(PH_2)/b_F(PH)$, whereas the determined values of other magnetic dipole coupling constants and the electric quadrupole coupling constants of As were close to the predicted values. The Fermi contact terms of the group V nuclei in the atom(${}^{4}S$), monohydride(${}^{3}\Sigma^{-}$), and dihydride(${}^{2}B_{1}$) forms are listed in Table III. The atomic value, A, which is a magnetic dipole interaction constant, includes only a contribution from the Fermi contact term in the case of spherical symmetry, ⁴S. For N and P, the Fermi contact term of the atom and that of the dihydride are positive, but for As the atomic value is negative, whereas the value for AsH₂ is positive. As can be seen in Table III, the values of Fermi contact terms of the respective nuclei vary linearly with the number of the bonded hydrogens. This is considered to be due to two factors. The first is the s character of the unpaired electron, and the second is the spin polarization of the s orbits due to the 4p unpaired electrons. According to an optical interference spectroscopic study of As(I), the spin polarization contribution, a_{CP}^{10} , was evaluated to -36(6) MHz.²¹ Therefore the spin polarization contribution is considered to decrease with an increase of the number of the bonded hydrogens, that is to say, with a decrease the

TABLE I. Observed and calculated transition frequencies for an \mbox{AsH}_2 radical(MHz).

F'_{1} - F_{1}	F-F	$ u_{ m obs}{}^{ m a}$	$\Delta \nu^{ m b}$
$N_{K_{1}K_{2}} = 1_{11} - 0_{00}$	J = 1.5 - 0.5		
3-2	4-3	326 258.257(29)	-0.023
3-2	3-2	326 243.817(17)	-0.007
3-2	2-1	326 249.817(22)	0.030
2-1	3-2	326 212.995(13)	-0.005
1-1	1-2	326 207.532(10)	0.030
1-1	2-1	326 187.146(28)	-0.003
0-1	1-1	326 173.002(20)	-0.001
1-1	2-2	326 168.436(22)	-0.028
2-2	3-3	326 124.034(24)	-0.086°
2-2	2-2	326 107.382(25)	0.021
2-2	1-1	326 104.039(13)	-0.056°
$N_{KaKc} = 1_{11} - 0_{00}$	J = 0.5 - 0.5		
2-2	3-3	351 004.801(17)	-0.017
2-2	2-2	350 943.787(18)	-0.002
2-1	2-1	351 101.008(24)	$-0.084^{c,d}$
2-1	1-0		
2-1	3-2	351 093.683(6)	0.009^{d}
2-1	1-1	351 082 370(30)	0.156 ^e
1-2	2-2	351 460 908(13)	-0.005
1-2	1-2	351 418 764(28)	0.003
$N_{K_{1}K_{2}} = 2_{11} - 2_{02}$	I = 2.5 - 2.5	551 110.701(20)	0.025
4-4	5-5	313 170.066(22)	-0.230^{e}
4-4	4-4		00
4-4	3-3	313 167.278(21)	-0.012^{d}
3-3	4-4	313 434.669(27)	-0.212
3-3	3-3	313 439.393(22)	-0.006
2-2	3-3	212 550 227(15)	_0 121 ^{d,e}
2-2	2-2	515 550.557(15)	0.121
2-2	1-1	313 557.204(32)	0.019
$N_{KaKc} = 2_{11} - 2_{02}$	J = 1.5 - 1.5		
3-3	4-4	330 360.461(28)	0.000
3-3	3-3	330 359.143(21)	-0.048
3-3	2-2	330 357.053(19)	0.006
1-2	2-3	329 692.629(28)	0.013
2-1 N -2 2	3-2 I-25-25	529 562.075(25)	0.028
A_{-4}	J = 2.3 - 2.3	336 514 314(15)	0.037
3-3		336 733 122(14)	0.004
2-2		336 874 198(36)	-0.041
1-1		336 957.464(18)	-0.143^{d}
$N_{KaKc} = 2_{21} - 2_{12}$	J = 1.5 - 1.5		
3-3		378 630.565(23)	0.030
2-2		378 101.973(15)	-0.030
$N_{KaKc} = 3_{31} - 3_{22}$	J = 3.5 - 3.5		
5-5	6-6	353 602.002(16)	0.005
5-5	5-5	353 599.436(25)	-0.002
5-5	4-4	353 600.242(20)	-0.042
4-4	5-5	353 705.173(9)	0.028
4-4	4-4	353 698.652(20)	0.012 ^d
4-4	3-3	252 700 20 ((29)	0.001
3-3	4-4	353 790.296(28)	-0.001
3-3	3-3	353 779.640(26)	$-0.147^{d,e}$
3-3 2_2	2-2	353 852 219(23)	-0.201^{e}
$N_{K_{a}K_{a}} = 3_{23} - 3_{12}$	J = 3.5 - 3.5	555 (52.21)(25)	0.201
5-5		304 158.137(12)	0.011
4-4		304 298.804(22)	-0.025
3-3		304 369.710(27)	0.002
2-2		304 398.436(25)	0.012
$N_{KaKc} = 3_{21} - 3_{12}$	J = 2.5 - 2.5	. /	
4-4		310 624.317(13)	0.016
3-3		310 448.651(18)	0.009
2-2		310 275.658(19)	-0.001
1-1		310 140.750(16)	-0.023

TABLE I. (Continued.)

<i>F</i> ₁ '- <i>F</i> ₁	F-F	$ u_{ m obs}{}^{a}$	$\Delta \nu^{\rm b}$
$N_{KaKc} = 4_{41} - 4_{32}$	J = 4.5 - 4.5		
6-6		374 113.946(13)	-0.025
5-5		374 164.208(29)	0.005
4-4		374 217.370(18)	0.025
3-3		374 267.246(28)	-0.004

^aValues in parentheses indicate standard deviation of the frequency measurement and apply to the last digits of the frequencies.

^bResiduals in the least-squares fit. $\Delta \nu = \nu_{obs} - \nu_{calc}$.

^cWeight is 0.1.

^dUnresolved line. The calculated frequencies were obtained by averaging the frequencies of components weighted in proportion to their relative intensities.

^eNot included in the least-squares fit because of the overlap with other lines.

number of unpaired electrons. If the spin polarization contribution is assumed to decrease linearly with an increase of the number of bonding hydrogens in the series of XH_n (n = 0-2) species, then the spin-polarization corrected term is calculated to be 69.8 MHz for AsH₂. The value corresponds to 0.48% *s* character on the unpaired electron orbitals in AsH₂, when compared with that of atomic arsenic.²² The 0.48% *s* character is about one-third of the corresponding

TABLE II. Molecular constants of the AsH₂($X^{2}B_{1}$) radical (MHz).^a

	MW	Visible ^b
Α	226 347.254(94)	226 301(387)
В	214 738.272(27)	214 723(405)
С	108 369.402(29)	108 423(270)
Δ_N	12.57 ^c	12.57 ^d
Δ_{NK}	-31.366(54)	-39.80^{d}
Δ_K	54.050(41)	60.66 ^d
δ_N	5.59 ^c	5.59 ^d
$\delta_{\scriptscriptstyle K}$	-2.8638(20)	-5.01^{d}
ϵ_{aa}	-33 088.39(30)	-31 500(2100)
ϵ_{bb}	-11 858.45(21)	$-12\ 000(2200)$
ϵ_{cc}	89.60(17)	200(2400)
Δ_N^s	2.63 ^e	
Δ^s_{NK}	$-4.93^{\rm e}$	
Δ^s_{KN}	-7.385(73)	
Δ_K^s	15.59 ^e	
δ_N^s	0.0	
δ^s_K	0.0	
$a_F(As)$	57.820(21)	
$T_{aa}(As)$	-287.694(73)	
$T_{bb}(As)$	-322.150(45)	
$\chi_{aa}(As)$	31.21(17)	
$\chi_{bb}(As)$	-140.88(16)	
$C_{aa}(As)$	0.672(19)	
$C_{bb}(As)$	0.471(21)	
$C_{cc}(As)$	0.125(16)	
$a_F(H)$	-50.811(53)	
$T_{aa}(\mathrm{H})$	-0.81(19)	
$T_{bb}(\mathbf{H})$	-3.13(12)	

^aThe numbers in parentheses represent three times the standard deviation in units of the last digits.

^bReference 4.

^cFixed.

^dDerived from the centrifugal distortion constants au_{aaaa} , au_{bbbb} , au_{aabb} , and au_{abab} .

^eFixed to the values derived from the rotational constants, the spin-rotation coupling constants, and centrifugal distortion terms. See text.

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TABLE III. Comparison of the Fermi contact terms of group V element nuclei (MHz). $^{\rm a}$

Х	$A X(^4S)$	$b_F \operatorname{XH}(^{3}\Sigma^{-})$	$a_F \operatorname{XH}_2({}^2B_1)$
Ν	10.450 91(7) ^b	18.832(30) ^c [1.04%]	28.061(52) ^d [1.55%]
Р	55.055 691(24) ^e	128.119(17) ^f [0.96%]	207.25(13) ^g [1.55%]
As	$-66.204(1)^{h}$ -30.2^{k}	$-14.097(25)^{i}$ 9.9 ^k [0.07%]	57.820(21) ^j 69.8 ^k [0.48%]

^aValues in square brackets indicate s character of the unpaired electron.

^bReference 18.

^cReference 14.

^dReference 1. ^eReference 19.

^fReference 15.

^gReference 16.

^hReference 20.

ⁱReference 11.

^jThe present study.

^kSpin-polarization corrected Fermi contact terms.

values of NH_2 and PH_2 as shown in Table III. This suggests a degree of *sp* hybridization of the orbital including the unpaired electron correlated with that of the bonding orbitals.

Table IV shows a comparison of the magnetic dipole coupling constants of the group V element nuclei and the spin densities calculated from the parameters by comparing them with the corresponding atomic values.²² The spin densities of the dihydrides are slightly smaller than those of the monohydrides. This is consistent with the fact that the *s* characters of the unpaired electron of the dihydrides are slightly larger than those of the monohydrides, as shown in Table III. The tendency of the spin densities to increase from NH₂ to AsH₂ is very similar to that of the corresponding monohydrides.

The *s* character of the valence orbital and the ionic character of the bonding orbital can be evaluated from the electric quadrupole coupling constants. Assuming that the valence orbitals of arsenic in the AsH₂ radical are sp^2 -like, they can be expressed as²³

$$\begin{split} \psi_1 &= (1 - 2a_s^2)^{1/2} \psi_s + (2a_s^2)^{1/2} \psi_{py}, \\ \psi_2 &= a_s \psi_s - ((1 - 2a_s^2)/2)^{1/2} \psi_{px} + (1/2)^{1/2} \psi_{py}, \\ \psi_3 &= a_s \psi_s - ((1 - 2a_s^2)/2)^{1/2} \psi_{px} - (1/2)^{1/2} \psi_{py}, \\ \psi_4 &= \psi_{pz}, \end{split}$$

where a_s^2 is the amount of *s* character in each of the equivalent σ As–H bonding orbitals. The equivalent orbitals ψ_2 and ψ_3 form the As–H bonds; ψ_1 has a lone pair of electrons and ψ_4 has an unpaired electron. The axes, *x*, *y*, and *z*, correspond to the principal axes *a*, *b*, and *c*, respectively. From the orbitals $\psi_1 - \psi_4$, the p_x , p_y , and p_z orbital population are found to be

$$n_x = 1 + i_\sigma,$$

 $n_y = 4a_s^2 + (1 + i_\sigma)(1 - 2a_s^2),$
 $n_z = 0.914,$

TABLE IV. Comparison of the magnetic dipole coupling constants of group V element nuclei (MHz).

Х	Ν	Р	As
XH c Spin density	$-68.00(14)^{a}$ 81.6%	-476.843(78) ^b 86.6%	-478.801(58) ^c 95.7%
$\begin{array}{ccc} \mathrm{XH}_2 & T_{aa} \\ & T_{bb} \\ & T_{cc} \\ \mathrm{Spin \ density} \end{array}$	$\begin{array}{c} -43.035(91)^d \\ -44.63(12)^d \\ 87.67 \\ 79.0\% \end{array}$	-300.24(13) ^e -321.86(29) ^e 622.10 84.8%	$\begin{array}{c} -287.694(73)^{\rm f} \\ -322.150(45)^{\rm f} \\ 609.844 \\ 91.4\% \end{array}$

^aReference 14.

^bReference 15.

^cReference 11.

^dReference 1.

^eReference 16. ^fThe present study.

The present study

where i_{σ} is the ionic character of each σ bond when As has a negative charge. The orbital population n_z is cited from the spin density. The electric quadrupole coupling constant is represented as follows

$$\chi_{\alpha\alpha} = (n_{\alpha} - (n_{\beta} + n_{\gamma})/2)eQq_{410}/(1 + c'\epsilon),$$

where c' is the negative charge on the As, i.e., $2i_{\sigma}$. Using values of the quadrupole coupling constant due to one atomic 4p electron, $eQq_{410} = -497$ MHz, obtained from $\langle 1/r^3 \rangle$ =9.102 as reported by Morton and Preston²² for As, the charge screening correction [ϵ =0.15 (Ref. 23)] and the observed quadrupole coupling constants [χ_{aa} =31.21(17)MHz and $\chi_{bb} = -140.88(16)$ MHz], i_{σ} and a_s^2 were calculated to be 0.020 and 0.118, respectively. The derived i_{σ} is close to the theoretical value of 0.015 calculated from Mulliken population analysis of an *ab initio* calculation on AsH₂.⁸ Similarly in the case of AsH₂, the s characters of the σ bond of the AsH radical and AsH₃ were calculated to be 0.149 and 0.114, respectively, using values of the observed eQq of AsH and AsH₃,^{11,24} the spin density of AsH [0.957 (Ref. 11)], and the ionic character i_{σ} cited from Mulliken population analysis.^{25,26} The electric quadrupole coupling constants, the s character, and the ionic character of AsH_n (n=1-3) are shown in Table V. From the above result, the As-H bond character is considered to be nearly the same regardless of the number of bonded hydrogens. The fact that the ionic

TABLE V. Comparison of the electric quadrupole coupling constants, the *s* character of the valence orbital, and the ionic character of bonding orbital of AsH_n (n = 1-3).

	AsH	AsH ₂	AsH ₃
χ_{aa}/MHz		31.21(17) ^a	
χ_{bb} /MHz		$-140.88(16)^{a}$	
eQq/MHz	$-99.45(14)^{b}$		$-162.681(54)^{c}$
a_s^2	0.149	0.118	0.114
i _o		0.020	
i_{σ} (theo.)	0.01 ^d	0.015 ^e	0.03 ^f

^aPresent study.

^bReference 11.

^cReference 24

^eReference 8.

^fReference 26.

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character of the As–H bond is small is reasonable, considering that the difference between the electronegativity of As(2.0) and that of H(2.1) is minimal.

Nuclear spin-rotation coupling constants for the arsenic nucleus $C_{aa}(As)$ and $C_{bb}(As)$ were determined to be 0.672(19) MHz and 0.471(21) MHz, respectively. Using second-order perturbation theory, C_{gg} is derived from the following expression:

$$|C_{gg}| = |\epsilon_{gg}a/A_{so}|.$$

Assuming that the nuclear spin-orbit hyperfine coupling constant $a = (5/4)T_{cc} = 762.3$ MHz and the spin-orbit coupling constant $A_{so} = 617$ cm⁻¹ cited from the value of AsH,²⁷ C_{aa} and C_{bb} are calculated to be 1.36 and 0.49 MHz, respectively. These values are within an order-of-magnitude in agreement with the observed values. The arsenic nuclear spin-rotation coupling constant of AsH, C_I (As), is 0.471(17) MHz,¹¹ and C_N (As) and C_K (As) of AsH₃ are 0.1035(26) and 0.0856(42) MHz, respectively.²⁴ C_{gg} is given by

$$C_{gg} = 4B_{gg} \Sigma a |\langle 0|L_g|n \rangle|^2 / (E_n - E_0),$$

where B_{gg} denotes the rotational constant, L_g the g component of the orbital angular momentum, E_n and E_0 the electronic energy of the excited and ground states, respectively, and $|0\rangle$ and $|n\rangle$ the corresponding wave functions. The values of rotational constants and $E_n - E_0$ of AsH are 215 882.657(53) MHz¹¹ and 29 880.65 cm^{-1.27} A_0 , B_0 , and $E_n - E_0$ of AsH₂ are 226 347.254(94) MHz, 214 738.272(27) MHz, and 19 907 cm^{-1.4} B_0 of AsH₃ is 112 470.5760(45) MHz²⁴ and the theoretical value of the energy difference $E({}^{1}E) - E(X {}^{1}A_1)$ is 44 400 cm^{-1.26} The fact that the nuclear spin-rotation coupling constants of AsH₃ are smaller than those of AsH and AsH₂ is reasonable, considering the small rotational constant and the large energy difference.

In conclusion this microwave spectroscopic study has provided the detailed and precise molecular constants for the AsH₂ radical. From a comparison of the hyperfine coupling constants of AsH_n (n=0-3), the character of the As-H σ bond is nearly the same regardless of the number of bonded hydrogens. However, the change in the number of hydrogen atoms significantly influences the Fermi contact term.

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