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Rotational lines of AsH and AsD radicals in their $X^{3}\Sigma^{-}$ ground state have been observed in the submillimetre-wave region for the first time. The AsH radical was generated by dc-glow discharge in pure AsH₃ gas, and the AsD radical was generated by the reaction of arsenic powder with a mixture of D₂ and O₂ gases in a dc-glow discharge. Three rotational transitions of AsH with hyperfine structure (*N*,*J* = 0,1–1,0 2,1–1,1 3,2–2,2) were measured in the frequency region 120–338 GHz, and five transitions (*N*,*J* = 0,1–1,0 2,1–1,0 2,2–1,1 4,3–3,3 5,4–4,4) of AsD in the region 173–440 GHz. The molecular constants, including the rotational constants, the spin–rotation coupling constant with the centrifugal distortion term and hyperfine coupling constants associated with the arsenic, hydrogen and deuterium nuclei, were precisely determined by least-squares fitting to the observed spectral lines. Using the results of both AsH and AsD, the Born–Oppenheimer equilibrium bond length was derived, where the adiabatic correction was taken into account: $r_e^{BO} = 1.522 370 (86) \text{ Å}.$

Simple hydride molecules have a relatively small number of rotational transitions in the submillimetre-wave region. Recently, we showed that microwave (MW) spectroscopic measurements, even for a small number of rotational transitions, made it possible to determine their particular hyperfine structure with high precision.^{1,2} We extended this spectroscopic study to another hydride, AsH, in its X ${}^{3}\Sigma^{-}$ ground electronic state. The first spectroscopic investigation of AsH and AsD was made in 1968 by Dixon and Lamberton, who observed the A ${}^{3}\Pi_{i}$ -X ${}^{3}\Sigma^{-}$ transitions in the UV region and determined the rotational constants, spin-spin coupling constants and spin-rotation coupling constants of AsH and AsD in the X ${}^{3}\Sigma^{-}$ state and the effective rotational constants and spin-orbit coupling constants of both radicals in the A ${}^{3}\Pi_{i}$ state.³ 16 years later, in addition to the above parameters, the hyperfine coupling constants of AsH of the X ${}^{3}\Sigma^{-}$ state were determined using far-IR laser magnetic resonance spectroscopy (FIR LMR) by observation of the transitions indicated in Fig. 1.4 The molecular constants of AsH in the vibrationally excited state (v = 1) were given in a successive study by IR diode laser spectroscopy.⁵ In 1990, the b ${}^{1}\Sigma^{+}-X$ ${}^{3}\Sigma^{-}$ transition of AsH was observed in emission, and the molecular constants of the b ${}^{1}\Sigma^{+}$ state were derived.⁶ Recently, the vibrational dependence of several parameters, including the hyperfine coupling constant, was determined by observation of the v = 2-1 and 3-2 hot bands of AsH using IR LMR spectroscopy.7 Several experimental investigations of AsH have been carried out to date whereas, until recently, no investigation of AsD had been undertaken since Lindgren reported the re-analysis of the UV spectroscopic data measured by Dixon and Lamberton.⁸ The recent study of the a ${}^{1}\Delta$ -X ${}^{8}\Sigma^{-1}$ (v = 0-0, 1-1, 2-2) transitions in emission of AsH and AsD in the near-IR (NIR) region using a Fourier-transform spectrometer led to the determination of molecular constants of AsH and AsD in the X $^3\Sigma^-$ and a $^1\Delta$ states, 9 but the hyperfine coupling constants of AsD are still unknown.



Fig. 1 Rotational energy levels of the AsH(left) and AsD(right) radical in the ground electronic $X^{3}\Sigma^{-}$ state. The solid lines which connect the two different energy levels represent the transitions observed in this study, while the dashed lines represent the transitions observed by FIR LMR in ref. 4.



frequency/MHz

Fig. 2 Submillimetre-wave lines of AsD radical: the N, J = 1,2-0,1, $F_1 = 2.5-1.5$, F = 3.5-2.5, 2.5-1.5 transitions and mixed transition of F = 1.5-0.5, 1.5-1.5 and 2.5-2.5 observed by dc-glow discharge (170 mA) of a mixture of D₂(25 mTorr) and O₂(1 mTorr) gas over arsenic powder. The integration time was 20 s. Vertical lines represent the calculated frequencies and intensities.

The spectroscopic constants of AsH, including equilibrium bond length, dipole moment, zero-field splitting and vibrational frequency, have been studied by several quantum chemical calculations. $^{10-13}$

The purpose of the present study was to observe the rotational transitions of AsH and AsD in the millimetre and submillimetre wave region, and to determine the detailed molecular constants of the radicals more precisely than previously.

Experimental

The spectral lines of AsH and AsD were observed by a 100 kHz source-modulated millimetre and submillimetre-wave spectrometer combined with a free-space absorption cell, 2 m in length, at the Institute for Molecular Science.¹ The AsH radical was initially produced by dc-glow discharge (200 mA) in H₂ gas (25 mTorr) and O₂ gas (1 mTorr) over arsenic powder at a cell temperature of -130 to ca. -100 °C, a method similar to those given in ref. 4 or 7. The prediction of the AsH lines was based on the molecular constants determined by FIR LMR⁴ and IR LMR.⁷ Several lines which indicated paramagnetism were detected in the region 310.9-311.1 GHz on a CRO display. They were easily assigned to the N,J = 0,1-1,0 transition of AsH. A more efficient method of production for AsH was then used, namely a dc-glow discharge (170 mA) in pure AsH₃ gas (25 mTorr) and the N,J = 2,1-1,1 and 3,2-2,2 transitions were observed in the

Table 1Observed and calculated transition frequencies of the AsH(X ${}^{3}\Sigma^{-}$) radical (MHz)

N',J'-N,J	$F'_1 - F_1$	F'-F	v _{obs} ^a	Δv^b
0,1–1,0	0.5-1.5	0.0-1.0	310 923.601(3)	-0.840^{c}
	0.5–1.5	1.0–2.0	210.02(480(5)	0 1000
	0.5-1.5	1.0–1.0	310 920.489(3)	-0.482
	1.5-1.5 1.5-1.5	2.0–2.0 2.0–1.0	310 935.385(4)	0.367 ^d
	1.5–1.5 1.5–1.5	1.0-1.0 1.0-2.0	310 950.955(5)	-0.004^{e}
	2.5-1.5	3.0-2.0	311 036.609(8)	0.014 ^e
	2.5–1.5 2.5–1.5	2.0-1.0	311 055.055(8)	-0.010
2,1–1,1	2.5-1.5	2.0-1.0	119 991.564(8)	-0.006
	2.5-1.5	3.0-2.0	119 994.592(12)	0.005
	1.5-0.5	2.0-1.0	120 268.736(24)	0.009
	1.5-0.5	1.0 - 0.0	120 285.952(13)	0.006
	2.5-2.5	2.0-2.0	120 412.059(8)	0.012
	2.5-2.5	3.0-3.0	120 429.467(6)	-0.038
	0.5–1.5	1.0 - 2.0	120 784.176(23)	0.016
	1.5–2.5	1.0 - 2.0	120 917.898(24)	0.009
	1.5–2.5	2.0-3.0	120 938.945(24)	-0.013
3,2–2,2	3.5–2.5	3.0–2.0	337 864.171(28)	-0.022
	3.5–2.5	4.0-3.0	337 891.046(26)	0.021
	2.5–1.5	2.0–1.0	338 000.127(41)	0.037
	2.5-1.5	3.0–2.0	338 022.173(15)	-0.045
	3.5–3.5	3.0-3.0	338 043.512(17)	-0.019
	3.5–3.5	4.0-4.0	338 073.372(21)	0.031
	1.5-0.5	1.0 - 0.0	338 121.296(57)	-0.009
	2.5-2.5	2.0-2.0	338 145.878(25)	-0.045°
	2.5–2.5	3.0-3.0	338 170.379(15)	0.012
	1.5–1.5	1.0–1.0	338 220.329(41)	-0.006
	1.5–1.5	2.0-2.0	338 240.878(32)	0.024
	0.5-0.5	1.0–1.0	338 283.843(22)	-0.014
	2.5-3.5	2.0-3.0	338 325.135(31)	-0.127^{c}
	2.5-3.5	3.0-4.0	338 352.611(24)	-0.072^{c}
	0.5–1.5	1.0–2.0	338 379.904(26)	-0.012
	1.5-2.5	2.0-3.0	338 389.004(29)	0.001

^{*a*} Values in parentheses indicate standard deviation of the frequency measurement and apply to the last digits of the frequencies. ^{*b*} Residuals in the least-squares fit. $\Delta v = v_{obs} - v_{calc}$. ^{*c*} Not included in the least-squares fit, because of the overlap with other lines. ^{*d*} Unresolved line. When the separations between components are larger than the linewidth of about 0.6 MHz, the averaged frequency does not correspond well with an observed one where the observed frequency was not included in the least-squares fit. ^{*e*} Unresolved line. The calculated frequencies were obtained by averaging the frequencies of components weighted in proportion to relative intensities.

	Table 2 Observed and ca		s of the AsD($X^{\circ}\Sigma^{\circ}$) fadical (MHZ)	
N',J'-N,J	$F'_1 - F_1$	F'-F	v _{obs} ^a	Δv^{o}
0,1–1,0	1.5–1.5 1.5–1.5 1.5–1.5 1.5–1.5	2.5–1.5 1.5–1.5 1.5–0.5 1.5–2.5	189 711.792(12)	-0.726 ^c
	$ \begin{array}{r} 1.5-1.5 \\ 0.5-1.5 \\ 0.5-1.5 \\ 2.5-1.5 \\ \end{array} $	0.5–0.5 J 0.5–1.5 1.5–1.5 3.5–2.5	189 727.920(19) 189 729.080(13) 189 781.206(2)	0.012 0.000 0.005
	2.5–1.5 2.5–1.5	2.5–1.5 2.5–2.5	189 782.798(3)	-0.022^{d}
	2.5–1.5 2.5–1.5 2.5–1.5	1.5–0.5 1.5–1.5 1.5–2.5	189 783.875(6)	0.005 ^d
1,2–0,1	2.5–2.5 2.5–2.5	3.5–3.5 2.5–1.5	380 979.400(7)	-0.127°
	2.5–2.5 2.5–2.5	1.5–1.5 2.5–2.5	380 980.657(7)	0.009 ^d
	2.5–2.5 2.5–2.5	2.5–3.5 1.5–2.5	380 982.094(30)	0.063 ^c
	0.5-0.5	1.5-1.5	381 002.349(19)	-0.163^{e}
	0.5-0.5	1.5-0.5	381 003.625(15) 381 005 138(16)	-0.059
	1.5-0.5	1.5-1.5	381 007.755(13)	-0.001^{d}
	0.5-0.5	0.5-0.5	381 009.071(17)	-0.011
	1.5-0.5 0 5-1 5	0.5-0.5 1 5-2 5	381 010.296(24)	0.094 ^e
	0.5 1.5	1.5 - 2.5 1.5 - 1.5	381 019.276(15)	-0.271°
	0.5–1.5 1.5–1.5 0.5–1.5 1.5–1.5	0.5–1.5 2.5–1.5 0.5–0.5 2.5–2.5	381 022.211(9)	0.019 ^d
	1.5-1.5 1.5-1.5	1.5-1.5 1.5-0.5	381 024.076(26)	-0.234 ^c
	$1.5-1.5 \\ 1.5-1.5 \\ 1.5-1.5$	$\left. \begin{array}{c} 0.5-1.5\\ 1.5-2.5\\ 0.5-0.5 \end{array} \right\}$	381 025.113(17)	-0.103 ^c
	2.5–1.5 2.5–1.5 2.5–1.5	3.5–2.5 2.5–1.5 1.5–0.5	381 048.854(4) 381 050.675(4)	$0.012 \\ -0.037$
	2.5–1.5 2.5–1.5 2.5–1.5	1.5-1.5	381 051.816(12)	0.019 ^d
	3.5–2.5 3.5–2.5	4.5–3.5 3.5–2.5	381 065.274(2) 381 066.580(3)	-0.036 0.049
	3.5-2.5	2.5-1.5	381 067.856(20)	0.231 ^c
	3.5-2.5	2.5–2.5	381 068.935(11)	0.324 ^e
2,2–1,1	1.5-0.5	2.5-1.5	439 581.387(18)	-0.001
	1.5-0.5	1.5-0.5	439 586.449(30)	-0.108^{e}
	1.5-0.5	0.5-0.5 3.5-2.5)	439 387.809(27)	0.002
	2.5–1.5 2.5–1.5	2.5–1.5	439 662.932(7)	-0.834 ^c
	0.5-0.5	1.5-1.5	439 677.050(17)	0.510 ^e
	$0.5-0.5 \\ 0.5-0.5$	1.5-0.5 0.5-1.5	439 680.053(14)	0.404 ^c
	1.5–1.5 1.5–1.5 1.5–1.5	2.5-2.5 1.5-1.5 0.5-0.5	439 810.154(13)	-0.372 ^c
	3.5–2.5 3.5–2.5	2.5–1.5 3.5–2.5	439 908.570(11) 439 909.707(14)	-0.025 0.008
	3.5–2.5 3 5–2 5	2.5-2.5	439 911.365(17)	0.015 ^d
	2.5-2.5	1.5–1.5	440 089.058(35)	-0.005
	2.5–2.5	2.5-2.5	440 090.636(19)	0.042
	2.5–2.5 2.5–2.5	3.5–3.5 (1.5–2.5)	440 092.565(18)	-0.035^{d}

Table 2 Observed and calculated transition frequencies of the AsD(X ${}^{3}\Sigma^{-}$) radical (MHz)

N',J'-N,J	$F'_1 - F_1$	$F'\!\!-\!\!F$	$v_{\rm obs}{}^a$	Δv^b
4,3-3,3	4.5-4.5	5.5-5.5	173 032.745(14)	-0.007
	4.5-4.5	4.5-4.5	173 028.979(26)	-0.012
	3.5-3.5	4.5-4.5	173 106.988(30)	0.026
	3.5-3.5	3.5-3.5	173 103.537(36)	0.090 ^e
	2.5-2.5	3.5-3.5	173 165.091(52)	-0.007
5,4-4,4	5.5-5.5	6.5-6.5	279 595.963(27)	-0.003
· ·	5.5-5.5	5.5-5.5	279 591.404(15)	0.019
	5.5-5.5	4.5-4.5	279 587.497(18)	-0.012
	4.5-4.5	5.5-5.5	279 682.040(9)	0.006
	4.5-4.5	4.5-4.5	279 677.625(27)	0.006
	4.5-4.5	3.5-3.5	279 674.013(24)	0.007
	3.5-3.5	4.5-4.5	279 752.814(32)	-0.032
	3.5-3.5	3.5-3.5	279 748.428(22)	0.014
	3.5-3.5	2.5-2.5	279 744.942(43)	-0.023
	2.5-2.5	3.5-3.5	279 808.184(12)	-0.088^{e}
	2.5-2.5	2.5-2.5	279 803.445(29)	0.018

 Table 2 (Continued)

^{*a*} Values in parentheses indicate standard deviation of the frequency measurement and apply to the last digits of the frequencies. ^{*b*} Residuals in the least-squares fit. $\Delta v = v_{obs} - v_{calc}$. ^{*c*} Unresolved line. When the separations between components are larger than the linewidth of *ca*. 0.6 MHz, the averaged frequency does not correspond well to an observed one where the observed frequency was not included in the least-squares fit. ^{*d*} Unresolved line. The calculated frequencies were obtained by averaging the frequencies of components weighted in proportion to relative intensities. ^{*e*} Not included in the least-squares fit, because of the overlap with other lines.

regions 119.9-121.0 GHz and 337.7-338.4 GHz, respectively. Production of the AsD radical occurred in a dc-glow discharge of D_2 gas and O_2 gas over arsenic powder at -150 to ca. -120 °C, but some very weak lines could not be observed above -140 °C. The prediction of the AsD lines was based on the molecular constants determined by reanalysing UV spectroscopic data⁸ and on the hyperfine coupling constants estimated from those of AsH, since information on the molecular constants of AsD determined by NIR was not available when this study began. Six lines were detected in the region 189.7-189.8 GHz by integrating the absorption signals and were assigned to the N,J = 0,1-1,0 transition. The N,J = 1,2-0,12,2-1,1 5,4-4,4 and 4,3-3,3 transitions were then observed in the regions 380.9-381.1, 439.5-440.1, 279.5-279.9 and 173.0-173.2 GHz, respectively. Fig. 2 shows an example of the observed spectral lines, which are relatively strong. Most observed lines of AsD were very weak, except several lines of the N,J = 1,2-0,1 transition. We did not attempt to observe the transitions of AsH and AsD in the vibrationally excited states, because they were expected to be very weak, from the magnitudes of the vibrational energy for $v = 1,2080 \text{ cm}^{-1}$ for AsH⁷ and ca. 1500 cm⁻¹ for AsD, whose levels could be populated at excitation temperatures of 3000 and 2200 K, respectively. The transitions of AsH and AsD observed in this study are illustrated in Fig. 1. All observed lines of AsH and AsD are listed in Tables 1 and 2, respectively.

Table 3 Molecular constants of the AsH and AsD radicals (MHz)^a

	AsH	AsD
Bo	215882.657(53)	109975.426(15)
D_0	10.0363(26)	2.5810(39)
λ	1764360 ^b	1763014 ^b
$\lambda_{\rm D}$	1.529^{b}	1.199(21)
γ	-8207.647(47)	-4179.69(18)
γ _D	1.649^{b}	0.392(15)
$b_{\rm F}({\rm As})$	-14.097(25)	-13.039(31)
c(As)	-478.801(58)	-478.621(67)
$b_{\rm F}({\rm H,D})$	-49.045(75)	-7.511(48)
$c(\mathbf{H}, \mathbf{D})$	13.08(14)	1.96(11)
$C_{I}(As)$	0.471(17)	0.283(12)
eQq(As)	-99.45(14)	-98.39(16)
eOq(D)		0.20(17)

^{*a*} The numbers in parentheses represent three times the standard deviation in units of the last significant digits. ^{*b*} Fixed to the values of ref. 9.

Analysis

The observed data for AsH and AsD were fitted to a conventional Hamiltonian, appropriate for a two nuclear spin molecule in a triplet sigma state, of the form

$$H = H_{\rm rot} + H_{\rm ss} + H_{\rm sr} + H_{\rm hfs}(As) + H_{\rm hfs}(H \text{ or } D) \qquad (1)$$

where H_{rot} is the rotational Hamiltonian, H_{ss} , the spin-spin interaction term and H_{sr} , the spin-rotation interaction term. $H_{\rm hfs}({\rm As})$ and $H_{\rm hfs}({\rm H~or~D})$ are the magnetic dipole and electric quadrupole hyperfine interaction terms. The matrix elements were calculated by the standard procedure using Hund's case (b) basis function with the coupling scheme J = N + S, $F_1 =$ J + I(As) and $F = F_1 + I(H \text{ or } D)$. Unlike NH and PH, AsH has a much larger spin-spin coupling constant than the rotational constant, so that AsH closely approximates Hund's case (c) when J is small.⁴ In fact, the eigenvectors of N,J = 0,1 and 2,1 have nearly the same magnitude when the Hamiltonian is diagonalized. Consequently, caution was taken to assign several components of the hyperfine structure for the transitions concerned and the program used to calculate energy levels was modified to select the eigenvalue of appropriate energy necessarily in the case of N,J = 0,1.

The unresolved lines were included in the fit by averaging frequencies of the individual components concerned, which had been weighted in proportion to their relative intensities when fitting the data. The 25 observed lines of AsH and 38 lines of AsD were used in the least-square fits and the corresponding molecular constants determined are listed in Table 3. The standard deviations of the fits are 24 kHz for AsH and 27 kHz for AsD, which are comparable to the frequency measurement errors, as shown in Tables 1 and 2. The spin-spin coupling constant, λ , and the centrifugal distortion terms, $\lambda_{\rm D}$ and $\gamma_{\rm D}$, of AsH were fixed to the values determined by NIR spectroscopy,9 because only three rotational transitions, N,J = 0,1-1,0 2,1-1,1 3,2-2,2 were measured in the present study. Moreover, λ and γ indicated strong correlation, even when the other centrifugal distortion term was fixed. Therefore, the value of λ could not but be fixed. λ of AsD was similarly fixed to the value derived from NIR spectroscopic data.9 We note that the centrifugal distortion terms, λ_D and γ_D , of AsD depend on the magnitude of λ , independent of how they have been determined. An attempt was made to determine the nuclear spin-rotation coupling constants of the hydrogen or deuterium of AsH and AsD, but it was found that these values were smaller than their uncertainties in the least-square fit.

Table 4 Comparison of present and previously determined parameters for AsH (MHz)^a

	MW (this study)	NIR^b	IR LMR ^c	FIR LMR ^d
B ₀	215882.657(53)	215877.3(27)	215884.5(14)	215877.54(23)
D_0	10.0363(26)	9.950(18)	10.041(48)	9.834(11)
λ	1764360 ^e	1764360(45)	1764354(90)	1763488(56)
λ	1.529 ^e	1.529(720)	5.0(37)	
γ້	-8207.647(47)	- 8202.3(18)	-8195.4(72)	-8114.5(60)
γ _D	1.649 ^e	1.649(180)	1.68(15)	
$b_{\rm F}({\rm As})$	-14.097(25)		-12.0(51)	-11.5(14)
c(As)	-478.801(58)		-478.9(81)	-478.2(39)
$b_{\rm F}({\rm H})$	-49.045(75)			-49.80(66)
$c(\mathbf{H})$	13.08(14)			12.5(18)
$C_{\rm I}({\rm As})$	0.471(17)			
eQq(As)	-99.45(14)		-95.6(39)	-97.6(72)

^{*a*} Values in parentheses are 3*s*. ^{*b*} Ref. 9. ^{*c*} Ref. 7. ^{*d*} Ref. 4. ^{*e*} Fixed.

Table 5 Comparison of present and previously determined parameters for AsD (MHz)^a

	MW (this study)	NIR^b	UV ^e	UV ⁴
$B_{0} \\ D_{0} \\ \lambda \\ \lambda_{D} \\ \gamma$	$\begin{array}{c} 109975.426(15)\\ 2.5810(39)\\ 1763014^{e}\\ 1.199(21)\\ -4179.69(18)\end{array}$	$\begin{array}{c} 109971.73(81)\\ 2.560(27)\\ 1763014(27)\\ 1.08(18)\\ -4179.1(36)\end{array}$	$\begin{array}{c} 109987.9(90)\\ 2.690(63)\\ 1763110(270)\\ 3.0(27)\\ -4422(54)\end{array}$	110018(145) 2.64(45) 1763619(1349) - 4406(270)
$\gamma_{\mathbf{D}}$	0.392(15)	0.402(27)		

^{*a*} Values in parentheses are 3*σ*. ^{*b*} Ref. 9. ^{*c*} Ref. 8. ^{*d*} Ref. 3. ^{*e*} Fixed.

Therefore, these values were fixed to be zero in the final analyses.

Results and Discussion

Comparison of molecular constants

As shown in Table 3, the nuclear spin-rotation coupling constant of AsH, C_{I} (As), and the hyperfine coupling constants of AsD including C_{I} (As), were determined for the first time. The hyperfine coupling constants for the As nucleus in AsH and AsD show marginal agreement. In particular, the Fermi contact terms of As, $b_{\rm F}$ (As), differ by 7.5%. However, this corresponds to a change of 0.007% in the s-character of the unpaired electron around the As nucleus. This small change may be reasonable, considering the difference between the bond length of AsH and that of AsD in the ground vibrational state. The molecular constants of AsH and AsD that we have determined are compared with previously determined values in Tables 4 and 5. As can be seen in Table 4, the uncertainties of molecular parameters of AsH in the present study are one or two orders of magnitude smaller than those in ref. 4, 7 and 9, as are those of AsD, as shown in Table 5. For AsH, the results are essentially the same as those using IR LMR and NIR, but there are differences between several parameters determined by MW and FIR LMR. The differences for λ and γ may occur because the centrifugal distortion terms, $\lambda_{\rm D}$ and $\gamma_{\rm D}$, were not taken into account in the latter study. However, the Fermi contact terms, $b_{\rm F}({\rm As})$ and $b_{\rm F}({\rm H})$, in this study are marginally different from those given by FIR LMR, because the hyperfine coupling constants of the As nucleus and the H nucleus were determined discretely in the two step leastsquares analysis in ref. 4. For AsD, the results of this study are consistent with the NIR results, however, each rotational constant, B_0 , is slightly different.

Equilibrium bond distance

The internuclear distances, r(As-H) and r(As-D), can be calculated, because the precise rotational constants of AsH and AsD were obtained in the present study. The rotation-vibration coupling constant, α_e , of AsH, 6348.8(65) MHz, was cited from ref. 7 and used to convert B_0 to B_e . The second-

order rotation–vibration coupling constant, γ_e , of AsH, 1.4(17) MHz,⁷ could be neglected, because the correction value, $\gamma_e(v + 1/2)^2$, is smaller than the error in α_e for v = 0. α_e of AsD was obtained from¹⁴

$$\alpha_{\rm e}({\rm AsD}) = \alpha_{\rm e}({\rm AsH})[\mu({\rm AsH})/\mu({\rm AsD})]^{3/2}$$
(2)

where μ is the reduced mass of AsH or AsD. The B_e values obtained were used to determine r_e for both AsH and AsD. The Equilibrium structural parameters are listed in Table 6. The uncertainties in B_e and r_e are almost solely due to the large uncertainties in α_e . It is obvious that the r_e of AsH, 1.523 137(11) Å and AsD, 1.522 753(8) Å, show a discrepancy beyond their uncertainties, which is indicative of a breakdown of the Born–Oppenheimer approximation. In order to derive r_e^{ad} , higher-order corrections, the electron-slipping correction and the Dunham correction, must be taken into consideration.

The electron-slipping correction was calculated using:15

$$B_{\rm e} + \delta_1 = B_{\rm e}(1 - g_{\rm xx}/1836) = B_{\rm e}(1 - g_{\rm r}) \tag{3}$$

where g_{xx} and g_r are the rotational g-factors given by the nuclear magneton or Bohr magneton, respectively. The g_r value of AsH was taken from the FIR LMR study, to be 0.000 620(78).⁴ Unfortunately, the value g_r of AsD is not available. Therefore, it was calculated using the following

Table 6 Equilibrium structural parameters of AsH and AsD in the $X\,{}^{3}\Sigma^{-}$ state^a

	AsH	AsD	
B _e /MHz	219057.1(32)	111121.5(11)	
$r_{e}/Å$	1.523137(11)	1.522753(8)	
δ_1/MHz^b	-135.8(171)	-34.7(43)	
δ_2/MHz^c	8.8	2.2	
$\overline{B_{\rm c}^{\rm ad}}/{\rm MHz}$	218930.1(174)	111089.0(44)	
$r_{\rm e}^{\rm ad}/{\rm \AA}$	1.523579(61)	1.522975(30)	
$r_{\rm e}^{\rm BO}/\rm{\AA}^d$	1.522370(86)		
$d_{\rm H}^{\rm ad}/{ m \AA}^d$	1.46	(17)	

^{*a*} The numbers in parentheses represent three times the standard deviation in unit of the last significant digits. ^{*b*} The electron slipping correction. ^{*c*} The Dunham correction. ^{*d*} Derived from r_e^{ad} . equation¹⁵ and the value g_{xx} value of AsH,

$$g_{xx} = \frac{m_{\rm p}}{I_{\rm e}} \left\{ \sum_{i} Z_{i} z_{i}^{2} - \frac{2}{m_{\rm e}} \sum_{n} \frac{|\langle n | L_{\rm x} | 0 \rangle|^{2}}{W_{\rm n}(r_{\rm e}) - W_{\rm 0}(r_{\rm e})} \right\}$$
(4)

where m_e and m_p are the masses of an electron and a proton, respectively, I_e is the inertia moment at equilibrium structure, Z_i is the atomic number of nucleus *i*, and z_i is the distance between nucleus *i* and the centre of mass. Assuming that the second term in the parentheses of eqn. (4) for AsD is equal to that of AsH, g_{xx} of AsD was calculated to be 0.000312(39) × 1836. Thus, δ_1 values calculated were -135.8(171) MHz for AsH and -34.7(43) MHz for AsD.

The Dunham correction was calculated using:¹⁵

$$B_{e} + \delta_{2} = B_{e} \left\{ 1 - \left(\frac{B_{e}^{2}}{\omega_{e}^{2}} \right) \left[\omega_{e}^{2} \left(\frac{\gamma_{e}}{4B_{e}^{3}} \right) + 16a_{1} \left(\frac{-\omega_{e} x_{e}}{3B_{e}} \right) - 8a_{1} - 6a_{1}^{2} + 4a_{1}^{3} \right] \right\}$$
(5)

where the anharmonic potential constant, $a_1 = (-\alpha_e \omega_e / 6B_e^2) - 1$, γ_e is the second-order rotation-vibration coupling constant. The second term of eqn. (5) was neglected because of its small contribution. The vibrational parameters, ω_e and $\omega_e x_e$, of AsD were derived from:¹⁴

$$\omega_{\rm e}({\rm AsD}) = \omega_{\rm e}({\rm AsH})[\mu({\rm AsH})/\mu({\rm AsD})]^{1/2}$$
(6)

$$\omega_{e} x_{e}(AsD) = B_{e}(AsD)[-\alpha_{e}(AsD)\omega_{e}(AsD)/6B_{e}(AsD)^{2} + 1]^{2}$$

$$\omega_{\rm e} x_{\rm e} (\rm{AsH}) [\mu(\rm{AsH})/\mu(\rm{AsD})]$$
(7)

Using values of the vibrational parameters, $\omega_{\rm e}({\rm AsH}) = 2155.503 \ {\rm cm}^{-1}$ and $\omega_{\rm e} x_{\rm e}({\rm AsH}) = 39.2227(26) \ {\rm cm}^{-1}$, δ_2 was calculated to be 8.8 MHz for AsH and 2.2 MHz for AsD. Thus the adiabatic rotational constants, $B_{\rm e}^{\rm ad}$, of AsH and AsD were obtained. The uncertainties in $B_{\rm e}^{\rm ad}$ and $r_{\rm e}^{\rm ad}$ are mainly due to the large uncertainties in $g_{\rm r}$.

The converted adiabatic equilibrium distances, r_e^{ad} , of AsH and AsD still show a discrepancy beyond their uncertainties. The Born–Oppenheimer equilibrium distance, r_e^{BO} , can be derived from r_e^{ad} of AsH and AsD using:¹⁶

$$r_{e}^{\rm ad} = r_{e}^{\rm BO} [1 + m_{e} (d_{a}^{\rm ad} / M_{a} + d_{\rm b}^{\rm ad} / M_{\rm b})]$$
(8)

where $m_{\rm e}$, $M_{\rm a}$ and $M_{\rm b}$ are the masses of an electron, nucleus a and nucleus b, respectively, and $d_{\rm a}^{\rm ad}$ and $d_{\rm b}^{\rm ad}$ are the adiabatic correction factors of nuclei a and b. Since data for normal (AsH) and only one substituted isotope species are available (AsD), the adiabatic correction of the arsenic nucleus with much larger mass in eqn. (8) could be neglected. $r_{\rm e}^{\rm B0}$ was determined to be 1.522 370(86) Å and $d_{\rm H}^{\rm ad}$ 1.46(17). The value of $r_{\rm e}^{\rm B0}$, 1.522 Å, which Kawaguchi and Hirota estimated by simply transferring the ratio $r_{\rm e}^{\rm B0}/r_0$ of PH to AsH⁴ is found to be close to the present value.

Spin-Rotation coupling constants

Hensel *et al.* estimated the theoretically derived spin-rotation coupling constant γ of AsH using second-order perturbation theory, and stated that the theoretical value, -8892 MHz, was consistent with the experimental value of -8195.4(72) MHz.⁷ The experimental γ value of AsD, -4179.68(18) MHz, was compared with its theoretical value -4546 MHz, calculated from the rotational constant determined in this study, spin-orbit coupling constant A = -617.39 cm⁻¹,³ and $E_{3\pi}$ $- E_{3\pi}$ = 29 880.65 cm⁻¹.³ Additionally, the ratios γ (AsD)/ γ (AsH) = 0.5092 and B_0 (AsD)/ B_0 (AsH) = 0.5094 are nearly the same; this agreement is consistent with the statement that the spin-rotation coupling constant γ is mainly due to the second-order contribution from low-lying excited states.

Hyperfine structure

The ratios between the magnetic hyperfine coupling constants associated with hydrogen and deuterium of AsH and AsD, $b_{\rm F}({\rm D})/b_{\rm F}({\rm H}) = 0.1532(17)$ and $c({\rm D})/c({\rm H}) = 0.150(12)$, are equal to the ratio of the nuclear g factors of proton and deuteron, 0.153 506 1, which is calculated using the magnetic moments of proton and deuteron with their corresponding nuclear spins, $\mu_{\rm H} = 2.792\,845\,6\,\mu_{\rm N}$ and $\mu_{\rm D} = 0.857\,437\,6\,\mu_{\rm N}$,¹⁷ where $\mu_{\rm N}$ is the nuclear magneton.

Second-order perturbation theory gives an expression for the nuclear spin-rotation coupling constant, C_I , by considering the interaction of the nuclear magnetic moment of a nucleus with electrons and other nuclei in the molecule.¹⁴ In the case of a diatomic molecule with nuclei I and J, C_I is given by,

$$C_{I} = 4hB \sum_{n} \frac{a_{0n} |\langle 0 | L_{x} | n \rangle|^{2}}{E_{n} - E_{0}} - 4\pi B \frac{\mu_{I}}{I_{I}} \frac{q_{J}}{cr_{J}}$$
(9)

where a_{0n} is the matrix element of the nuclear spin-orbit interaction between the ground state, $|0\rangle$, and the excited electronic state, $|n\rangle$, I_1 , the nuclear spin of I, μ_1 , nuclear magnetic moment, c, velocity of light, r_J , the internuclear distance and q_J the net charge of the nucleus J plus the electrons in closed shells around it. Because the spin density and the s character of the unpaired electron orbital around the As nucleus were calculated at 96% and -0.1%, respectively,⁴ the unpaired electrons mainly occupy the $p\pi$ orbital of As. Therefore, the first term of eqn. (9) can be estimated. Assuming the pure precession approximation, and that the dominant contribution is only due to A ${}^{3}\Pi_{i}$

$$C_I \approx Bh \, \frac{a_{\Sigma\Pi} L (L+\mathrm{I})}{E_{3_{\Pi}} - E_{3_{\Sigma^-}}} \tag{10}$$

 C_I (As) for AsH or AsD was calculated to be 0.402 and 0.205 MHz respectively, using 29 880.65 cm⁻¹ for $E_{3\pi} - E_{3\Sigma^-}$ and 834.1 MHz for the anisotropic hyperfine parameter $a_{\Sigma\Pi}$.¹⁸ These values are comparable with the observed values, 0.471(17) MHz for AsH and 0.283(12) MHz for AsD.

Summary

This microwave spectroscopic study presents precise molecular constants for AsH and AsD radicals; in addition, the Born–Oppenheimer equilibrium bond length has been derived. Their experimental spin–rotation and nuclear spin– rotation coupling constants are consistent with the values estimated using second-order perturbation theory.

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References

- 1 S. Saito and M. Goto, Astrophys. J., 1993, 410, L53.
- 2 M. Goto and S. Saito, Chem. Phys. Lett., 1993, 211, 443.
- 3 R. N. Dixon and H. M. Lamberton, J. Mol. Spectrosc., 1968, 25, 12.
- 4 K. Kawaguchi and E. Hirota, J. Mol. Spectrosc., 1984, 106, 423.
- 5 J. R. Anacona, P. B. Davies and S. A. Johnson, *Mol. Phys.*, 1985, 56, 989.
- 6 M. Arens and W. Richter, J. Chem. Phys., 1990, 93, 7094.
- K. D. Hensel, R. A. Hughes and J. M. Brown, J. Chem. Soc., Faraday Trans., 1995, 91, 2999.
 B. Lindgren, Phys. Scr., 1975, 12, 164.
- 9 M. Beutel, K. D. Setzer, O. Shestakov and E. H. Fink, J. Mol. Spectrosc., 1996, **178**, 165.
- 10 L. G. H. Petersson and S. R. Langhoff, J. Chem. Phys., 1986, 85, 3130.

- T. Matsushita, C. H. Harian, R. Klotz and S. D. Peyerimhoff, *Can. J. Phys.*, 1987, **65**, 155. 11
- K. Balasburamanian and V. Nannegari, J. Mol. Spectrosc., 1989, 12 138, 482.
- 13
- M. Klobukowski, Chem. Phys. Lett., 1991, 183, 417. C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, 14 Dover, New York, 1975.
- W. Gordy and R. L. Cook, Microwave Molecular Spectra, Inter-15 science, New York, 1970.
- 16 J. K. G. Watson, J. Mol. Spectrosc., 1973, 45, 99.
- International Union of Pure and Applied Chemistry, Quantities, 17 Units, and Symbols in Physical Chemistry, ed. I. Mills, T. Cvitas, K. Homann, N. Kallay and K. Kuchitsu, Blackwell Scientific Publications, Oxford, 1988.
- 18 J. R. Morton and K. F. Preston, J. Magn. Reson., 1978, 30, 577.

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