



## Spectroscopic observation of the b 1+X3 transition of AsH

M. Arens and W. Richter

Citation: The Journal of Chemical Physics **93**, 7094 (1990); doi: 10.1063/1.459432 View online: http://dx.doi.org/10.1063/1.459432 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/93/10?ver=pdfcov Published by the AIP Publishing

### Articles you may be interested in

Laser spectroscopy in a pulsed jet of AIH: Ionizationdetected ultraviolet absorption spectra of the transitions C 1+-X 1+ and b 3-X 1+ J. Chem. Phys. **97**, 883 (1992); 10.1063/1.463192

Rotational analysis of the B2+-X2+ transition of BaOH and BaOD J. Chem. Phys. **84**, 698 (1986); 10.1063/1.450566

The b 1+X 3 transition in PH: A measurement of the term energy, bond length, and vibrational frequency of a phosphinidene metastable J. Chem. Phys. **80**, 5926 (1984); 10.1063/1.446698

The a 3+ X 1+ and b 3 X 1+ band systems of SiO and the a 3+ X 1+ band system of GeO observed in chemiluminescence J. Chem. Phys. **63**, 2810 (1975); 10.1063/1.431713

Relative vibrational intensities for the B 1+X 1+ transition in carbon monoxide J. Chem. Phys. **60**, 4830 (1974); 10.1063/1.1680989



# Spectroscopic observation of the $b^{1}\Sigma^{+} \rightarrow \widetilde{X}^{3}\Sigma^{-}$ transition of AsH

M. Arens

I. Physikalisches Institut, Rheinisch-Westfälische Technische Hochschule Aachen, 5100 Aachen, Federal Republic of Germany

W. Richter

Institut für Festkörperphysik, TU Berlin, 1 Berlin 12, Federal Republic of Germany

(Received 13 March 1990; accepted 30 July 1990)

Emission lines of the  $b^{1}\Sigma^{+} \rightarrow \tilde{X}^{3}\Sigma^{-}$  transition of AsH radicals have been detected in the fluorescence of a dc-glow-discharge of arsine in hydrogen. From measurements of line positions of the (0,0), (1,1), and (2,2) *Q* branches and the (0,0) *P* and *R* branches, the molecular constants of the  $b^{1}\Sigma^{+}$  state were determined:  $T_{e} = 14\,178.0\,\mathrm{cm}^{-1}$ ,  $B_{0} = 7.2467\,\mathrm{cm}^{-1}$ ,  $D_{0} = 3.1528\cdot10^{-4}\,\mathrm{cm}^{-1}$ ,  $\omega_{e} = 2213\,\mathrm{cm}^{-1}$ ,  $\omega_{e}x_{e} = 47.5\,\mathrm{cm}^{-1}$ ,  $r_{e} = 152.937\,\mathrm{pm}$ .

#### I. INTRODUCTION

Simple hydride radicals often play an important role in radical chemistry, e.g., AsH and PH for the metal-organic vapor phase epitaxy (MOVPE) of GaAs and InP and related compounds. To get insight in the decomposition of arsine in a dc-glow-discharge (plasma-assisted MOVPE),<sup>1</sup> the emission in the frequency range of 12 000–25 000 cm<sup>-1</sup> was investigated.

The open-shell  $\sigma^2 \pi^2$  electronic configuration of diatomic hydrides involving group V elements gives rise to the low lying  $\tilde{X}^3 \Sigma^-$ ,  $a^1 \Delta$ , and  $b^1 \Sigma^+$  states. The excited configuration  $\sigma \pi^3$  produces the  $\tilde{A}^3 \Pi$  and the  $c^1 \Pi$  states (see also Fig. 3 below). While both NH (Ref. 2) and PH (Refs. 3-5) were widely studied by spectroscopic methods and most of the transition energies between the low-lying states have been measured, less information is available for the AsH radical.

The  $\tilde{A}{}^{3}\Pi_{i} \rightarrow \tilde{X}{}^{3}\Sigma^{-}$  electronic transitions of AsH and AsD had been studied during the flash photolysis of arsine.<sup>6,7</sup> They provided the first data on these radicals. Far infrared laser magnetic resonance spectroscopy<sup>8</sup> and infrared diode laser spectroscopy<sup>9</sup> yielded more accurate values of the vibronic and rotational constants for the electronic ground state  $\tilde{X}{}^{3}\Sigma^{-}$  than the earlier study. In recent years potential energy curves, spectroscopic constants, electric dipole moments, zero-field splittings and radiative lifetimes have been calculated for various electronic states of AsH (Refs. 10–12).

In the present work we report on the observation of emission lines due to the  $b \, {}^{1}\Sigma^{+} \rightarrow \widetilde{X} \, {}^{3}\Sigma^{-}$  transition in an AsH<sub>3</sub> glow-discharge. The data allow the determination of the molecular constants of the  $b \, {}^{1}\Sigma^{+}$  state and a comparison with the calculated values is made.

#### **II. EXPERIMENTAL**

The AsH radicals were produced by decomposing arsine (AsH<sub>3</sub>) diluted in hydrogen in a parallel-plate dc-glowdischarge. The discharge reactor had a cross section of 18  $cm^2$  and the total flow rate was 118 standard cm<sup>3</sup> per minute corresponding to an average velocity of 20 cm/s. The total pressure was held at 500 Pa while the partial pressure of arsine was 50 Pa. The emitted radiation was collected in the direction of the electric field and dispersed with a Spex 1403 monochromator fitted with two 1800 groove/mm gratings. A resolution of  $0.1 \text{ cm}^{-1}$  could be obtained with slit widths of 20  $\mu$ m. The optical signal was detected by a cooled RCA C31034 photomultiplier. The output pulses of the photomultiplier are processed with an amplifier Ortec 570 and discriminator Ortec 550 and recorded with a microcomputer. Signal levels in the order of 50000 counts per second were observed for the strongest peak while the noise was approximately 2 counts per second. Wavelengths were calibrated using emission lines of a Ne lamp.

#### **III. RESULTS AND ANALYSIS**

Figure 1 shows the spectrum observed around 14 200 cm<sup>-1</sup> taken with a resolution of 1.5 cm<sup>-1</sup>. It is assigned to the  $b^{1}\Sigma^{+} \rightarrow \tilde{X}^{3}\Sigma^{-}$  transition with the typical O-, S-, and Q-type branches. The assignment was made by the following reasons: (i) Other possible transitions like  $a^{1}\Delta \rightarrow \tilde{X}^{3}\Sigma^{-}$  should show more branches and lower intensity. (ii) Theoretical calculations<sup>10,11</sup> yielded energy values for the b state





TABLE I. Line positions for the <sup>o</sup>P and <sup>S</sup>R rotational branches of the  $b^{1}\Sigma^{+} \rightarrow \tilde{X}^{3}\Sigma^{-}$  (v',v'') = (0,0) transition in AsH. The spectrum was recorded with a resolution of 1.5 cm<sup>-1</sup>. The error of line positions is 0.5 cm<sup>-1</sup>. The values in the last row are the fitted positions.

$\Delta N \Delta J_{J}$ .	λ	$\tilde{\nu}_{ m vac}$	$\tilde{\nu}_{ m calc}$
•	(Å)	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
<sup>o</sup> P <sub>2</sub>	7050.74	14 179.0	14 179.02
$^{O}P_{3}$	7061.45	14 157.5	14 157.47
<sup>0</sup> P <sub>4</sub>	7073.34	14 133.7	14 133.76
°Ps	7085.97	14 108.5	14 108.71
<sup>0</sup> P <sub>6</sub>	7098.95	14 082.7	14 082.84
<sup>о</sup> Р <sub>7</sub>	7112.27	14 056.4	14 056.50
<sup>0</sup> P <sub>8</sub>	7125.76	14 029.8	14 029.91
°P,	7139.34	14 003.1	14 003.21
<sup>0</sup> P <sub>10</sub>	7152.97	13 976.4	13 976.53
°P <sub>11</sub>	7166.71	13 949.6	13 949.92
<sup>s</sup> R <sub>o</sub>	6974.77	14 333.5	14 333.50
$SR_1$	6964.08	14 355.5	14 355.42
$SR_2$	6952.31	14 379.8	14 379.68
<sup>s</sup> R,	6939.87	14 405.6	14 405.47
<sup>s</sup> R₄	6926.98	14 432.4	14 432.27
SR,	6913.81	14 459.8	14 459.74
SR6	6900.45	14 487.8	14 487.65
${}^{S}R_{7}$	6887.10	14 515.9	14 515.86
<sup>S</sup> R <sub>8</sub>	6873.61	14 544.4	14 544.28
$SR_{9}$	6860.17	14 572.9	14 572.82

in the range from 14 500 cm<sup>-1</sup> to 17 000 cm<sup>-1</sup>. Spectroscopic data of the  $\tilde{A} {}^{3}\Pi_{i} \rightarrow \tilde{X} {}^{3}\Sigma^{-}$  transition,<sup>6</sup> evaluated under the assuption that  $b {}^{1}\Sigma^{+}$  is responsible for the  $\Lambda$  doubling, gave a value of 13 000  $\pm$  1000 cm<sup>-1</sup> for  $b {}^{1}\Sigma^{+}$ . These values are in good agreement with the experimentally determined position. In contrast much lower values of  $6500 \pm 1000$  cm<sup>-1</sup> (Ref. 6) and in the range from 8709 cm<sup>-1</sup> to 9968 cm<sup>-1</sup> (Refs. 10 and 11) are obtained for the  $a {}^{1}\Delta$ . (iii) By assigning the measured line positions to the

TABLE II. Measured and calculated line positions of the AsH  $b^{1}\Sigma^{+} \rightarrow \tilde{X}^{3}\Sigma^{-} Q$  (O,O) transition. The error of line positions is  $\pm 0.1$  cm<sup>-1</sup>.

$\Delta^{N}\Delta J_{J}$ .	λ	$\tilde{\nu}_{vac}$	$\tilde{v}_{calc}$
	(Å)	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
°Q1	7041.559	14 197.52	14 197.53
$^{Q}Q_{2}$	7041.465	14 197.71	14 197.71
$^{Q}Q_{3}$	7041.326	14 197.99	14 197.99
°Q4	7041.148	14 198.35	14 198.36
°Q,	7040.910	14 198.83	14 198.82
°Q,	7040.632	14 199.39	14 199.38
°Q7	7040.305	14 200.05	14 200.04
°Q.	7040.938	14 200.79	14 200.80
°Q.	7039.502	14 201.67	14 201.66
<sup>Q</sup> Q <sub>10</sub>	7039.036	14 202.61	14 202.63
<sup>Q</sup> Q <sub>11</sub>	7038.491	14 203.71	14 203.70



FIG. 2. High resolution (0.1 cm  $^{-1}$ ) spectrum of the (0,0)  $^{o}Q$  branch from Fig. 1.

 $b^{1}\Sigma^{+} \rightarrow \tilde{X}^{3}\Sigma^{-}$  transition they can be reproduced with excellent agreement, as shown in Tables I and II.

In detail, Fig. 1 shows the central Q-type branch with maximum at 14 198 cm<sup>-1</sup> with remarkably high intensity and besides this the O-type P branch and the S-type R branch on the low and high frequency sides, respectively. They are assigned to the (0,0) vibrational band of the  $b^{1}\Sigma^{+} \rightarrow \tilde{X}^{3}\Sigma^{-}$  transition of AsH. The Q-type branches of the (1,1) and (2,2) vibrational bands can also be seen with maxima at 14 239 and 14 283 cm<sup>-1</sup> but with lower intensity. Table I lists the line positions for the  ${}^{O}P$  and  ${}^{S}R$  branches.

A spectrum with higher resolution  $(0.1 \text{ cm}^{-1})$  of the (0,0) *Q*-type branch is shown in Fig. 2. The observed lines can all be assigned to the  ${}^{Q}Q$  branch and are listed in Table II.

Because of the lower intensity of the  $^{O}P$ ,  $^{S}R$  branches and the higher vibrational bands and the large frequency range it was not possible to record high resolution spectra of these features with sufficient signal-to-noise ratio.

The line positions were modeled using the expressions<sup>6</sup>

$$F_1(N) = F_2(N) + B(2N+3) - (\lambda + \gamma/2)$$
$$- [f(N+1)]^{1/2}$$

with J = N + 1,

$$F_2(N) = BN(N+1) - DN^2(N+1)^2$$

with J = N,

$$F_3(N) = F_2(N) - B(2N-1) - (\lambda + \gamma/2) + [f(N-1)]^{1/2}$$

with J = N - 1,

with

$$f(N) = (2B - \gamma)^2 \cdot N(N+1) + (\lambda - B + \gamma/2)^2$$
  
for the rotational levels of the ground state  $\tilde{X}^3 \Sigma^-$  and  
 $F(N) = T_0 + B_0 \cdot N(N+1) - D_0 \cdot N^2 (N+1)^2$ 

for the  $b^{1}\Sigma^{+}$  state.

article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: J. Chem. Phys. Vol. 93, No. 10, 15 November 1990



FIG. 3. Electronic energy level diagram for the AsH radical. Solid lines originate from experimentally observed levels including that one studied in the present paper. Dashed lines indicate calculated levels (Refs. 6 and 9) which have not yet been observed.

For the ground state levels, all constants were taken from Refs. 8 and 9 and are listed in Table III.  $T_0$ ,  $B_0$ , and  $D_0$ were fitted with a least-squares method to the line positions with weights of  $(1/0.1)^2$  for the  ${}^{Q}Q$  branch and  $(1/0.5)^2$  for the  ${}^{O}P$  and  ${}^{S}R$  branches to account for the different resolution in Figs. 1 and 2. The values of  $\omega_e$  and  $\omega_e x_e$  were determined from the positions of the Q-type branches of the (1,1)and (2,2) vibrational bands. With these values  $T_e$  was calculated. The constants for the b state of AsH obtained in this way are listed in Table III.

The  $T_e$  value here obtained is higher than expected from spectroscopic observations of the  $\tilde{A} \, {}^{3}\Pi_{i} \rightarrow \tilde{X} \, {}^{3}\Sigma^{-}$  transition and lower than the values from theoretical calculations [14 500 cm<sup>-1</sup> (Ref. 10) and 15 295 cm<sup>-1</sup> (Ref. 11) as the lowest given energy value for this state]. The estimated molecular constants agree well with the calculated ones: Both the measured  $\omega_e$  and  $r_e$  turn out to be slightly higher than the calculated 2197, respectively, 2176 cm<sup>-1</sup> and 152.2, respectively, 152.6 pm (Refs. 10 and 11).  $B_0$  obtained here might be compared to the value for  $B_e$  of 7.276 cm<sup>-1</sup> given in Ref. 11. The difference of the two values is in the usual order.

TABLE III. Molecular constants of the AsH radical (units are cm<sup>-1</sup> unless stated otherwise). The values in parentheses denote  $3\sigma$  and apply to the last digits of the constants.

	<i>b</i> <sup>1</sup> Σ <sup>+</sup>	$\tilde{X}^{3}\Sigma^{-}$ (Refs. 8 and 9)
T <sub>e</sub>	14 178.0 (5)	0
<b>B</b> <sub>0</sub>	7.246 71 (84)	7.200 8996
$10^4 \times D_0$	3.1529 (642)	3.280
λ		58.8236
γ		- 0.270 67
$v_0 (v = 1)$	2118	2076.874
ω <sub>e</sub>	2213	2175
$\omega_{a} \mathbf{x}_{a}$	47.5	49
r <sub>e</sub>	152.9366 (89) pm	152.315 pm

#### **IV. SUMMARY**

The  ${}^{O}P$ ,  ${}^{S}R$ , and  ${}^{Q}Q$  branches of the (0,0) vibrational band and the Q-type branches of the (1,1) and (2,2) vibrational bands of the  $b {}^{1}\Sigma^{+} \rightarrow \tilde{X} {}^{3}\Sigma^{-}$  transition of AsH have been observed. These measurements allowed the determination of rotational and vibrational constants of the b state. Figure 3 summarizes the present knowledge of the electronic energy levels of AsH.

#### ACKNOWLEDGMENT

Apparative and financial support from the Deutsche Forschungsgemeinschaft (Ba 724/2) is gratefully acknowledged.

- <sup>1</sup>H. Heinecke, A. Brauers, H. Lüth, P. Balk, J. Cryst. Growth 77, 241 (1986).
- <sup>2</sup>J. Masanet, A. Gilles, and C. Vermeuil, J. Photochem. 3, 417 (1974/75).
- <sup>3</sup>F. Legay, Can. J. Phys. 38, 797 (1960).
- <sup>4</sup>A. T. Droege and P. C. Engelking, J. Chem. Phys. 80, 5926 (1984).
- <sup>5</sup>W. J. Balfour and A. E. Douglas, Can. J. Phys. 46, 2277 (1968).
- <sup>6</sup>R. N. Dixon and H. M. Lamberton, J. Mol. Spectrosc. 25, 12 (1968).
- <sup>7</sup>N. Basco and K. K. Yee, Spectrosc. Lett. 1, 17 (1968).
- <sup>8</sup>K. Kawaguchi and E. Hirota, J. Mol. Spectrosc. 106, 423 (1984).
- <sup>9</sup>F. R. Anacona, P. B. Davies, and S. A. Johnson, Mol. Phys. 56, 989 (1985).
- <sup>10</sup> K. Balasubramanian and V. Nannegari, J. Mol. Spectrosc. 138, 482 (1989).
- <sup>11</sup>T. Matsushita, C. M. Marian, R. Klotz, and S. D. Peyerimhoff, Can. J. Phys. 65, 155 (1987).
- <sup>12</sup>L. G. M. Petterson and S. R. Langhoff, J. Chem. Phys. 85, 3130 (1986).