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Microwave Spectrum of Arsenic Trifluoride in the Excited Vibrational State

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The microwave spectrum of arsenic trifluoride was observed in the excited states of all the normal vibrations. The rotational constant at the equilibrium state was determined, and the equilibrium As–F distance was calculated to be 1.704_4 Å assuming the FAsF angle to be 95°58′. The l-type doubling constant, q_4, and the asymmetry parameter, η, of the As nuclear quadrupole coupling constant were determined in the $v_4=1$ to be 10.24 ± 0.02 MHz and $-0.00_5 \pm 0.01$, respectively.

Kisliuk and Geschwind¹⁾ have measured the $J=2 \leftarrow 1$ transitions of arsenic trifluoride and have determined the ground-state rotational constant, the nuclear quadrupole coupling constant, and the vibration-rotation interaction constants, α_2^B and α_4^B, for a symmetric and a degenerate bending vibration, ν_2 and ν_4. Reichman and Overend²⁾ have analyzed the infrared ν_1 band of arsenic trifluoride and determined the ground-state rotational constant and the α_1^B constant. Mirri³⁾ has obtained the force field of AsF_3 by the combined use of the vibrational frequencies and the centrifugal stretching and Coriolis' coupling constants. On the other hand, Konaka⁴⁾ and Konaka and Kimura⁵⁾ have determined the thermal-average distance, r_g(As—F), by gas-phase electron diffraction and has calculated the zero-point average distance, r_z(As—F). In the present work the microwave spectrum in the excited states of all the normal vibrations was observed to obtain the equilibrium structure of arsenic trifluoride. The l-type doubling transitions in the ν_4 state were also observed to determine the l-type doubling constant and to examine the asymmetry of the quadrupole coupling constant of the As nucleus induced by the degenerate bending vibration, ν_4.

Experimental

A sample of arsenic trifluoride was donated to us by the courtesy of Dr. S. Konaka of Department of Chemistry, Hokkaido University, and it was purified through vacuum distillation. The spectrometer used was of conventional Hughes-Wilson type with 120 kHz sine-wave and square-wave Stark modulators. The spectrum was recorded while pumping the sample through the cell because of decomposition of arsenic trifluoride in the waveguide.

Results

The $J=1 \leftarrow 0$ transitions in the ground vibrational state and four excited vibrational states, ν_1, ν_2, ν_3,

Table 1. Observed frequencies of the $J=1 \leftarrow 0$ transition of AsF_3 (MHz)

State	Assignment	ν_{obsd} a)	Δ b)
Ground	$F=1/2 \leftarrow 3/2$	11 817.21	−0.03
	$5/2 \leftarrow 3/2$	11 770.15	0.05
	$3/2 \leftarrow 3/2$	11 711.14	−0.02
ν_1	$F=1/2 \leftarrow 3/2$	11 807.54	−0.20
	$5/2 \leftarrow 3/2$	11 761.44	0.36
	$3/2 \leftarrow 3/2$	11 702.60	−0.16
ν_2	$F=1/2 \leftarrow 3/2$	11 827.66	−0.19
	$5/2 \leftarrow 3/2$	11 781.04	0.34
	$3/2 \leftarrow 3/2$	11 721.60	−0.15
ν_3	$F=1/2 \leftarrow 3/2$	—	—
	$5/2 \leftarrow 3/2$	11 740.92	−0.26
	$3/2 \leftarrow 3/2$	11 682.60	−0.01
$2\nu_2$	$F=1/2 \leftarrow 3/2$	11 837.70	−0.37
	$5/2 \leftarrow 3/2$	11 792.14	0.68
	$3/2 \leftarrow 3/2$	11 732.90	−0.30

a) Accuracy is ±0.1 MHz. b) Δ = obsd − calcd.

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1) P. Kisliuk and S. Geschwind, *J. Chem. Phys.*, **21**, 828 (1953).

2) S. Reichman and J. Overend, *Spectrochim. Acta*, **26A**, 379 (1970).

3) A. M. Mirri, *J. Chem. Phys.*, **47**, 2823 (1967).

4) S. Konaka, This Bulletin, **43**, 3107 (1970).

5) S. Konaka and M. Kimura, *ibid.*, 1693 (1970).

TABLE 2. MOLECULAR CONSTANTS, B_v, $\alpha_v{}^B$ AND eqQ, OF AsF_3 (MHz)[a)]

State	B_v	$(eqQ)_v$	$\alpha_v{}^B$	
Ground	5879.15 ± 0.02	$-235.7_2\pm0.21$	—	
ν_1	$5874.7_1\pm0.13$	$-233._3\ \pm1.4$	$4.4_4\pm0.15$	$(4.71)^{b)}$
ν_2	$5884.4_5\pm0.12$	$-235._8\ \pm1.3$	$-5.2_9\pm0.14$	$(-5.\pm1.)^{c)}$
ν_3	$5864.5_2\pm0.11$	$-232._2\ \pm1.8$	$14.6_3\pm0.13$	
$2\nu_2$	$5889.9_1\pm0.24$	$-233._1\ \pm2.6$	$10.7_5\pm0.26$	
ν_4	$5879.24^{d)}$	$-235._7\ \pm1.7^{d)}$	$-0.16_5{}^{d,e)}$	$(-0.16\pm0.04)^{c)}$

a) Errors are standard deviations. b) Ref. 2. c) Ref. 1. d) From the $J=5\leftarrow4$ transition. e) In calculating $\alpha_4{}^B$ the ground-state rotational constant of 5879.08 MHz (Table 4) is used, which is determined by using the transitions of $J=2\leftarrow1$ through $5\leftarrow4$.

and $2\nu_2$, were measured. The observed frequencies are listed in Table 1. The rotational constants and the nuclear quadrupole coupling constants were determined using the following equation, Eq. (1):

$$\nu = 2B_v(J+1)+\Delta W_Q{}^{(1)}, \tag{1}$$

where $\Delta W_Q{}^{(1)}$ is the first-order contribution of the quadrupole effect. The vibration-rotation interaction constants were calculated by $\alpha_v{}^B=B_0-B_v$. The molecular constants determined are listed in Table 2. The ν_4 spectra were not resolved from those of the ground state in the $J=1\leftarrow0$ transition, but a hyperfine component $F=11/2\leftarrow9/2$ of the $J=5\leftarrow4$, $K=3$ transition was observed at 58773.09 MHz, which was higher than the ground state line by 1.65 MHz, and thus the $\alpha_4{}^B$ constant was calculated to be -0.16_5 MHz. This is in good agreement with the value of Kisliuk and Geschwind.[1)] On the other hand, the $\alpha_2{}^B$ constant is much improved in accuracy compared with that reported in Ref. 1. Using all the four α^B constants thus obtained the equilibrium rotational constant, B_e, was calculated to be 5893.20 ± 0.30 MHz.

Because both arsenic and fluorine nuclei have only one stable isotope, no isotopic species of arsenic trifluoride are available. It is known that the effect of the intramolecular vibrations on the bond angle is relatively small, and therefore, taking the zero-point average bond angle θ_z(FAsF), 95°58′, obtained by Konaka[4)] as the equilibrium value, the equilibrium length was calculated to be $r_e(\text{As—F})=1.704_4$ Å. If the error in the angle is assumed to be ±1°, that of the bond length is ±0.0013 Å, where the double signs should be taken in the same order.

The l-type doubling transitions in the ν_4 vibrational state were observed for $J=2\leftarrow1$ through $J=5\leftarrow4$. A general expression for the frequencies of the lower and upper doublet components is given for the $J+1\leftarrow J$ transition by [6–8)]

$$\begin{aligned}\nu^\pm &= 2B_4(J+1) \pm q_4(J+1) + (eqQ)_{v_4=1}\\ &\times [\{3/[(J+1)(J+2)]-1\mp(1/2)\eta\}f(I,J+1,F_f)\\ &- \{3/[J(J+1)]-1\mp(1/2)\eta\}f(I,J,F_i)]\end{aligned} \tag{2}$$

where B_4 and q_4 denote the rotational constant and l-type doubling constant, respectively, in the $v_4=1$ state, η (referred to as the asymmetry parameter) the asymmetry in the electric field gradient induced at the arsenic nucleus by the ν_4 mode, and $f(I,J,F)$ Casimir's function. The frequencies of the $K=\pm1$, $l_4=\mp1$ component are given by

$$\begin{aligned}\nu_0 &= 2B_4(J+1) + (eqQ)_{v_4=1}[\{3/[(J+1)(J+2)]-1\}\\ &\times f(I,J+1,F_f)-\{3/[J(J+1)]-1\}f(I,J,F_i)]\end{aligned} \tag{3}$$

By using Eqs. (2) and (3) the following equation is derived.

$$\begin{aligned}\Delta\nu^\pm &= \nu^\pm - \nu_0\\ &= \pm q_4(J+1)\mp(1/2)\eta(eqQ)_{v_4=1}\\ &\times [f(I,J+1,F_f)-f(I,J,F_i)]\end{aligned} \tag{4}$$

The lines of the ground vibrational state and the $K=\pm1$, $l_4=\mp1$ components of the ν_4 vibrational state are overlapped with each other, except for a hyperfine component of the $J=5\leftarrow4$ transition mentioned above. The effect of the l-type resonance[9)] has not been ob-

TABLE 3. OBSERVED FREQUENCIES OF THE l-TYPE DOUBLING TRANSITIONS IN THE ν_4 STATE (MHz)

$J+1\leftarrow J$	$F'\leftarrow F''$	$\nu^-{}_{\text{obsd}}{}^{a)}$	$\nu^-{}_{\text{calcd}}{}^{b)}$	$\Delta\nu^-$
$2\leftarrow1$	$7/2\leftarrow5/2$	23510.52	23510.61	−20.56
	$5/2\leftarrow5/2$	23481.21	23481.00	−20.41
	$5/2\leftarrow3/2$	23451.60	23451.69	−20.56
	$3/2\leftarrow3/2$	23472.77	23472.84	−20.43
	$3/2\leftarrow1/2$	23525.53	23525.60	−20.70
	$1/2\leftarrow1/2$	23555.0	23555.22	−20.70
$3\leftarrow2$	$9/2\leftarrow7/2$	35250.40	35250.34	−30.65
	$7/2\leftarrow5/2$	35235.36	35235.61	−30.96
	$5/2\leftarrow3/2$	35235.36	35235.15	−30.54
	$3/2\leftarrow1/2$	35250.40	23250.88	−30.23
$4\leftarrow3$	$11/2\leftarrow9/2$	—	46994.72	—
	$9/2\leftarrow7/2$	46988.25	46988.83	−41.54
	$7/2\leftarrow5/2$	46985.44	46985.75	−41.29
	$5/2\leftarrow3/2$	46991.10	46991.64	−41.52
$5\leftarrow4$	$13/2\leftarrow11/2$	58740.35	58739.78	−50.82
	$11/2\leftarrow9/2$	58737.01	58737.03	−51.22
	$9/2\leftarrow7/2$	58734.55	58734.41	−50.10
	$7/2\leftarrow5/2$	58737.01	58737.36	−51.56

a) Accuracy is ±0.1 MHz. b) Calculated by using the parameters in Table 4.

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7) R. L. White, *J. Chem. Phys.*, **23**, 249 (1955).

8) J. F. Lotspeich, A. Javan, and A. Engelbrecht, *ibid.*, **31**, 633 (1959).

9) E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, **33**, 460 (1970); E. Hirota, *ibid.*, **37**, 20 (1971); **38**, 195 (1971).

served definitely. In calculating $\Delta\nu^-$ the center frequencies ν_0 of the ν_4 state were estimated by fixing B_4 to 5879.24 MHz, which was obtained from the α_4^B constant and the ground-state B value of 5879.08 MHz, the latter being determined using the $J=2\leftarrow1$ to $5\leftarrow4$ transitions. The observed frequencies of the l-type doubling transitions and $\Delta\nu^-$ are listed in Table 3. The upper components ν^+ are overlapped by the ν_2 satellites and are not resolved clearly because of the broad line width. The frequencies of the l-type doubling transitions were fitted to Eqs. (2) and (4) by a least-squares method, where the centrifugal distortion in the ν_4 state was assumed to be the same as in the ground vibrational state. The constants thus obtained are shown in Table 4. The l-type doubling constant is 10.24 ± 0.02 MHz. The value of the As nuclear quadrupole coupling constant in the ν_4 state was also listed in Table 4. The difference in the hyperfine structure pattern of the ground state and the ν_4 state is hardly noticeable, and electric field gradient at the arsenic nucleus remains almost unaffected by the excitation of the ν_4 vibration. The asymmetry parameter is zero within experimental error.

TABLE 4. MOLECULAR CONSTANTS OBTAINED FROM THE TRANSITIONS OF $J=2\leftarrow1$ TO $J=5\leftarrow4$ (in MHz except for η)a)

	Present	Reference
Ground State		
B_0	5879.08 ± 0.01	5878.97 ± 0.002 b)
eqQ	$-236.1_6\pm0.26$	-236.23 ± 0.005 b)
D_J	$0.0069_9\pm0.00033$	0.00462 ± 0.00002 c)
D_{JK}	$-0.0084_6\pm0.00094$	-0.00618 ± 0.00005 c)
$v_4=1$		
B_4	5879.24 d)	
eqQ	$-235._7\pm1.7$ e)	
q_4	10.24 ± 0.02	
η	$-0.00_5\pm0.01$	

a) Errors are standard deviations. b) Ref. 1. c) Ref. 3. d) Fixed. e) Obtained fixing B_4 to 5879.24 MHz.

The calculation in the present work was carried out at the Computation Center at Kyushu University.