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Direct *l*-Type Doubling Transitions in the $v_4 = 1$ State of AsH_3

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Direct *l*-type doubling transitions $J = 1, 2, 3, 6, 7, 8$ have been measured by microwave spectroscopy in the $v_4 = 1$ state of arsine (AsH_3). From the lowest J transitions the *l*-type doubling constant and the hyperfine constants have been determined. The $J = 6, 7, 8$ transitions appear strongly perturbed by v_2, v_4 Coriolis interactions. © 1985 Academic Press, Inc.

1. INTRODUCTION

Direct *l*-type doubling transitions in the $v_4 = 1$ doubly degenerate state of molecules of the type XH_3 (X = N, P, As, $\cdots$) were, so far, observed for NH_3, ND_3, and PH_3 (*1–4*). As discussed by Oka (*5*), the determination of the splitting constant q_4 provides a valuable means for the parametrization of the molecular potential function.

A C_{3v} molecule splits the rovibrational levels into A_1 and A_2 sublevels when $(K - l)$ is an integer multiple of 3 (here K is used in place of $|k|$). The special case $K = l = 1$ is called *l*-type doubling and $A_1 \leftrightarrow A_2$ transitions are electric dipole moment allowed. In AsH_3 each component of the *l*-type doublet is split further by the quadrupole coupling of the As nucleus.

In the present analysis we have measured the $J = 1, 2, 3, 6, 7, 8$ direct *l*-type doubling transitions in the $v_4 = 1$ state of AsH_3, together with the hyperfine structure (hfs) of $J = 1, 2$ and, partly, of $J = 6, 7, 8$.

The search for the transitions was carried out from 9 to 300 GHz, in three different laboratories, and was based on a recent high-resolution infrared analysis of the v_4 band (*6*).

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2. EXPERIMENTAL DETAILS

The sample of AsH_3 was provided by Matheson, Coleman, and Bell, and was used without further purification.

The $J = 1, 2$ transitions were measured with a computer-controlled Hewlett–Packard microwave spectrometer using Stark modulation, at Bologna.

The $J = 3$ transition was observed with a homemade Stark modulated spectrometer, at Kiel, where the microwave radiation, produced by doubling the frequency of an Oki 30V12 klystron, was fed into a K-band Stark cell. The source was synchronized against a Schomandl ND800 synthesized signal generator. For the search of the $J = 4$ transition source modulation was used instead of Stark modulation. In fact, the shift of the $M = 4$ component is calculated to be only 0.27 MHz at the highest applicable field of 5000 V/cm (*7*), at the time of the experiment.

The $J = 6, 7, 8$ transitions were measured at Gorky with a submillimeter RAD spectrometer using frequency stabilized backward-wave oscillators, with sensitivity increased by the use of a nontunable cavity cell (*8*). The gas pressure was between 0.06 and 0.08 Torr for the $J = 6, 7$ transitions and between 0.13 and 0.15 Torr for the $J = 8$. The self-broadening parameter of AsH_3 in the $v_4 = 1$ state was found to be $\Delta\nu = 3.30$ (30) MHz/Torr (HWHM at T = 300 K) for the $J = 1 \leftarrow 0$ transition.

The frequency measurements are believed to be accurate to 10 kHz for the $J = 1, 2$ transitions and to 50 kHz for the $J = 3$. For the $J = 6, 7, 8$ transitions the standard deviation of the observed frequencies is basically limited by the influence of the wings of neighboring hyperfine quadrupole components on each line, and it is about 300 kHz.

The measured transition frequencies, with their rotational and hfs assignment, are listed in Table I.

3. MICROWAVE SPECTRUM AND RESULTS

The $J = 1, 2, 6, 7, 8$ direct l-type doubling transitions show hfs due to the As quadrupole nucleus. The $J = 1, 2$ transitions are split into a nearly symmetrical multiplet with governing selection rules: $A_1 \leftrightarrow A_2$, $\Delta J = \Delta K = 0$, and $\Delta F = 0, \pm 1$. If the quadrupole splittings were equal for the upper and lower l-type doubling levels with same F the $\Delta F = 0$ transitions would be all superposed. In addition, the $\Delta F = \pm 1$ transitions would produce a symmetrical pattern of less intense satellite lines on both sides of the central line. In this approximation, the level scheme and the corresponding spectrum of the $J = 2$ l-type doubling transition are shown in Fig. 1. Taking into account the effect of the degenerate vibration on the molecular electric field gradient (*9*), the central peak of Fig. 1 splits into four components and the pattern of satellite lines becomes slightly asymmetric. For the $J = 6, 7, 8$ transitions only the $\Delta F = 0$ hfs components were observed, as shown in Fig. 2.

The first-order quadrupole energy of A_1 and A_2 sublevels of the $K = l = 1$ state is accounted for by the expression (*7, 9, 10*):

$$W^{\pm} = \left\{[eqQ + \chi_J J(J+1) + \chi_K K^2]\left[\frac{3K^2}{J(J+1)} - 1 \pm \eta\right] + \chi_d \frac{K^2(4K^2-1)}{J(J+1)}\right\} f(I, F, J)$$

$$+ (1/2)\left[C_N + (C_K - C_N)\frac{K^2}{J(J+1)}\right][F(F+1) - I(I+1) - J(J+1)], \quad (1)$$

TABLE I

Direct *l*-Type Doubling Transition Frequencies (MHz) in the $v_4 = 1$ of AsH_3

J	F - F'	OBSERVED
1	5/2 — 5/2	9 772.06
	3/2 — 3/2	---
	1/2 — 1/2	---
	3/2 — 1/2	9 736.20
	3/2 — 5/2	9 752.84
	5/2 — 3/2	9 791.83
	1/2 — 3/2	9 808.03
2	1/2 — 1/2	29 060.50
	7/2 — 7/2	29 060.98
	5/2 — 5/2	29 061.49
	3/2 — 3/2	---
	1/2 — 3/2	29 040.72
	7/2 — 5/2	
	3/2 — 5/2	29 047.24
	5/2 — 3/2	29 075.34
	3/2 — 1/2	29 080.68
	5/2 — 7/2	29 081.74
3	3/2 — 3/2	57 380.61
	5/2 — 5/2	
	7/2 — 7/2	
	9/2 — 9/2	
6	9/2 — 9/2	188 858.44
	15/2 —15/2	
	11/2 —11/2	188 859.35
	13/2 —13/2	
7	13/2 —13/2	244 525.68
	15/2 —15/2	
	11/2 —11/2	244 527.83
	17/2 —17/2	
8	13/2 —13/2	303 312.70
	19/2 —19/2	303 313.52
	15/2 —15/2	303 317.79
	17/2 —17/2	303 318.53

where eqQ is the quadrupole coupling constant, χ_J and χ_K are the coefficients of its rotational dependence, χ_d is the Hougen distortion coefficient, $f(I, F, J)$ is the Casimir function, and C_N and C_K are the two magnetic spin–rotation coupling

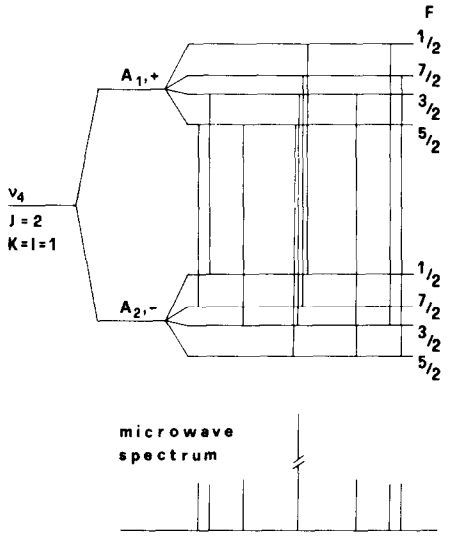

FIG. 1. Direct *l*-type doubling transitions with hyperfine structure (for the sake of simplicity the asymmetry due to ηeqQ is neglected).

constants between the As nucleus and the molecular rotation. The parameter η is a measure of the asymmetry of the electric field gradient produced by the degenerate vibration ν_4, and the $\pm$ refers to the symmetric and antisymmetric component of the *l*-type doublet.

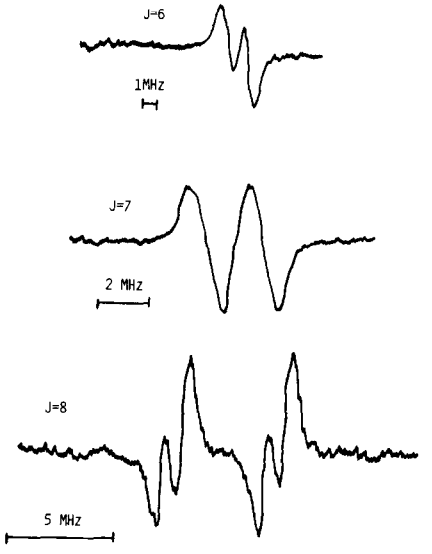

FIG. 2. Recordings of the J = 6, 7, 8 direct *l*-type doubling transitions in the ν_4 = 1 state of AsH_3 showing the ΔF = 0 hyperfine structure components. The derivative line shapes are due to frequency modulation of the source. Sample pressure was between 0.06 and 0.15 Torr; T, 300 K; time constant of detection, 1 sec.

TABLE II

Hyperfine Constants (MHz) of AsH_3 in the $v_4 = 1$ State (standard deviation (MHz) of the fit to the hfs splittings)

ηeqQ	- 1.093(50)
eqQ	- 158.31(17)
c_N	0.1244(93)
c_K	0.1224(64)
χ_J	- 0.476(55)
χ_K	0.580(61)
σ	0.035

Only the $J = 1, 2, 3$ transitions were used for the determination of the hfs and *l*-type doubling constants. In fact, the simple plot of the *l*-type doubling frequencies against $J(J + 1)$ indicates that the $J = 6, 7, 8$ transitions are strongly perturbed by the v_2, v_4 Coriolis interactions while the $J = 1, 2, 3$ still follow an almost linear behavior.

The constants in expression (1) were fitted to the hfs splittings of the $J = 1, 2$ transitions. The pure quadrupole resonances ($v_4 = 1$, $J = 5$, $K = 5$, $l = 1$, $F \leftrightarrow F \pm 1$) measured by Scappini and Oka (*11*) were used together with the present data. The χ_d constant could not be determined because of correlation with most of the parameters in expression (1). The results are shown in Table II. The particularly large values of χ_J and χ_K compared to ground state values (*11*) are expected as a consequence of the mixing between v_2 (J, K) and $v_4(J, K \pm 1, l)$ levels (*11*).

From the "center" line frequencies, that is, the frequencies of the $A_1 \leftrightarrow A_2$, $J = 1, 2, 3$ transitions in the absence of hfs reported in Table III, the *l*-type doubling

TABLE III

Calculated "Center" Line Frequencies (MHz) Corresponding to the Direct *l*-Type Doubling Transitions in the Absence of hfs in the $v_4 = 1$ State of AsH_3 [*l*-type doubling constants (MHz)]

J	CALCULATED
1	9 772.17
2	29 061.08
3	57 380.61

$q_4 = 4907.78$

$q_4' = - 10.918$

$q_4'' = 0.0344$

constant in the $v_4 = 1$ state, and its rotational dependence is determined according to the expression (*5, 12*)

$$\nu = q_4 J(J+1) + q_4' J^2(J+1)^2 + q_4'' J^3(J+1)^3 + \cdots. \quad (2)$$

If only the first two terms are retained the standard deviation of the fit is 2.4 MHz. Thus, the third term is included and the results are given in Table III.

Using expression (2) with the coefficients of Table III, the frequency of the $J = 4$ *l*-type doubling transition is predicted at 94 064 MHz, which is only 10 MHz above the frequency obtained by combination differences of infrared data (*6*). This line was searched for, at Kiel, using the experimental set up described in Section 2 with no success.

The hfs splittings of the $J = 6, 7, 8$ transitions are not accounted for by the constants of Table II, nor are the *l*-type doubling transition frequencies by the constants of Table III, indicating that the v_2, v_4 Coriolis interactions affect not only the *l*-type doubling but also the hfs of the corresponding levels.

By comparison with OCS lines the peak intensities, at 300 K, of the $J = 1, 2, 3$ direct *l*-type doubling transitions of AsH_3 in the $v_4 = 1$ state are estimated to be $\sim 3 \times 10^{-8}$, $\sim 7 \times 10^{-8}$, and $\sim 50 \times 10^{-8}$ cm^{-1}, respectively (in the case of the $J = 1, 2$ transitions the intensity refers to the most intense feature). By comparison with $k = \pm 4 \leftrightarrow \pm 7$, $J = 10$ ground state transition of AsH_3 (*8*), the peak intensity at 300 K of the $J = 7$ *l*-type doubling transition is found at $\sim 30.10^{-8}$ cm^{-1}.

4. CONCLUSIONS

The frequencies of the direct *l*-type doubling transitions measured in the present work, Table I, are very close, within a few MHz, to those calculated by combination differences of rovibrational transitions from the high resolution analysis of the v_4 band (*6*).

The presence of the v_2, v_4 interactions affects the observed spectrum in many respects, as already pointed out. The most interesting feature is the large asymmetry in the hfs of the $J = 6, 7, 8$ *l*-type doubling levels compared to the $J = 1, 2$ levels. Similarly, the *l*-type doubling for the $J = 6, 7, 8$ needs a more extensive treatment than the polynomial approach (*2*) used for $J = 1, 2, 3$. It has already been discussed in the case of PH_3 that different v_2, v_4 Coriolis interactions perturb the *l*-type doubling levels (*13*). For AsH_3 the v_2 and v_4 bands are 34 cm^{-1} closer than in PH_3 and the ζ_{24} Coriolis constant increases to 0.51 from 0.30 in PH_3. It is therefore to be expected that the spectrum in AsH_3 is even more perturbed than in PH_3.

The present microwave work is intended to contribute data with high accuracy to eventually make possible a quantitative analysis of higher-order interactions in the v_2, v_4 states of AsH_3.

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REFERENCES

1. E. A. COHEN AND R. L. POYNTER, *J. Mol. Spectrosc.* **53,** 131–139 (1974).
2. E. A. COHEN, *J. Mol. Spectrosc.* **79,** 496–501 (1980).
3. T. URISU, T. TANAKA, E. HIROTA, AND Y. MORINO, *J. Mol. Spectrosc.* **35,** 345–353 (1970).
4. A. GUARNIERI, F. SCAPPINI, AND G. DI LONARDO, *Chem. Phys. Lett.* **82,** 321–322 (1981).
5. T. OKA, *J. Chem. Phys.* **47,** 5410–5426 (1967).
6. G. DI LONARDO, L. FUSINA, AND J. W. C. JOHNS, *J. Mol. Spectrosc.* **104,** 282 (1984).
7. C. H. TOWNES AND A. L. SCHAWLOW, "Microwave Spectroscopy," Ch. VI, McGraw-Hill, New York, 1955.
8. A. V. BURENIN, V. P. KAZAKOV, A. F. KRUPNOV, A. A. MELNIKOV, AND S. M. SHAPIN, *J. Mol. Spectrosc.* **94,** 253–263 (1982).
9. G. TARRAGO AND S. MAES, *C. R. Acad. Sci. Paris* **266,** 699–702 (1968).
10. E. ARIMONDO, J. G. BAKER, P. GLORIEUX, T. OKA, AND J. SAKAI, *J. Mol. Spectrosc.* **82,** 54–72 (1980).
11. F. SCAPPINI AND T. OKA, *J. Mol. Spectrosc.* **85,** 390–398 (1981); F. SCAPPINI, L. FUSINA, AND G. DI LONARDO, *J. Mol. Spectrosc.* **107,** 419–420 (1984).
12. D. PAPOUŠEK AND M. R. ALIEV, "Molecular Vibrational-Rotational Spectra," Elsevier–Academia, Amsterdam/Prague, 1982.
13. S. P. BELOV, A. F. KRUPNOV, D. PAPOUŠEK, S. URBAN, AND G. CAZZOLI, *J. Mol. Spectrosc.* **98,** 265–268 (1983).