Mechanisms of the "Forbidden" Submillimeter Spectra Formation in the (0001) State of Arsine

The mechanisms of the intensities of "forbidden" transitions in the excited (0001) state of arsine have been investigated by experimental intensity measurements of hyperfine components of two submillimeter "forbidden" transitions $(J, \tilde{K}) = (5, 3) \leftarrow (5, 1)$ and $(J, \tilde{K}) = (6, 3) \leftarrow (6, 1)$.

Observation of such weak "forbidden" transitions with a good signal-to-noise ratio was achieved through the use of multipass cavity cells (Refs. (*1, 2*)) in a submillimeter RAD spectrometer with frequency-stabilized backward-wave oscillators (as in Ref. (*3*)). Absorption coefficients of hfs components of both allowed $J = 1 \leftarrow 0$ and "forbidden" transitions in the (0001) state of AsH_3 were measured by comparison with known absorption coefficients of N_2O in the (001), (200), and (040) excited vibrational states and $J = 1 \leftarrow 0$ and "forbidden" Q-branch ($\tilde{K} = 6 \leftarrow 9, 4 \leftarrow 7$) transitions of the AsH_3 molecule in the ground (0000) state. Our detailed description of the measurement procedure and test of the accuracy of the measurements are given in Ref. (*4*).

The "forbidden" transitions in the (0001) state of AsH_3 can originate from two mechanisms:

(1) The strong Coriolis resonance between the (0100) and (0001) states leads to the hybridization of the $|JK\sigma\rangle$ states with different values for the K quantum number. As a consequence, in the matrix element of the effective dipole moment operator $\langle \alpha\Gamma|\mathcal{P}|\beta\Gamma'\rangle$ in the vibration–rotation line intensity formula (*1*)[1]

$$S_{\alpha\beta} = \frac{8\pi^3 N\nu}{3hcQ(T)} \exp\left(-\frac{E_\alpha}{kT}\right)\left\{1 - \exp\left(-\frac{hc\nu}{kT}\right)\right\}g_\alpha[\Gamma_\alpha]|\langle \alpha\Gamma_\alpha|\mathcal{P}|_\beta\Gamma_\beta\rangle|^2 \tag{1}$$

there appear nonzero contributions from the permanent dipole moment operator μ_z^0 (Γ's are the symmetries of the states considered; $[\Gamma]$ is the dimension of the representation Γ).

(2) The presence of the $R^{\Omega K(\tilde{K})}$ operators in the effective dipole moment $\mathcal{P}$ (see Ref. (*5*)) results in the appearance of matrix elements with $\Delta K \neq 0$ ($K = |k|$).

To define the roles of each of these two mechanisms we must first determine numerically the $\langle \alpha\Gamma_\alpha|\mathcal{P}|_\beta\Gamma_\beta\rangle$ values from Eq. (1). To find the latter we use

$$\frac{8\pi^2\nu[\Gamma_\alpha]}{3hcQ(T)} \exp\left(-\frac{E_\alpha}{kT}\right)\left\{1 - \exp\left(-\frac{hc\nu}{kT}\right)\right\}g_\alpha|\langle \alpha\Gamma_\alpha|\mathcal{P}|\beta\Gamma_\beta\rangle|^2 = kT(\Delta\gamma/\Delta P)\sum_n k_J(\nu_n), \tag{2}$$

where $(\Delta\gamma/\Delta P)$ is the broadening coefficient, $k_J(\nu_n)$ is the line center absorption coefficient, and the summation is carried out over all the components of a given multiplet. We used broadening coefficients equal to 3.24 (30) MHz/Torr HWHM, measured in Ref. (*7*) for the $J = 1 \leftarrow 0$ transition; estimations based on experimental records of the forbidden lines considered here vary only slightly from line to line. To obtain Eq. (2) the

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[1] The meanings of the values from Eq. (1) and the subsequent relations are not, as a rule, explained. The notations used can be found, e.g., in Refs. (*5, 6*), but the designations for the functions should be noted here. Functions $|\alpha\Gamma\rangle$ in Eq. (1) or $|J\tilde{K}\Gamma\rangle$ in Eq. (5) are the eigenfunctions of the vibration–rotation molecular Hamiltonian. Functions $|JK\Gamma\sigma\rangle$ ($0 \leqslant K \leqslant J$; $\sigma = 1, 2$; $\Gamma = A_1, A_2$ or E is the symmetry of the function) are

$$|JK\Gamma\sigma\rangle = \frac{1}{\sqrt{2(1 + \delta_{K0})}}\{|JK\rangle + (-1)^\sigma|J - K\rangle\}, \tag{*}$$

where $|Jk\rangle(-J \leqslant k \leqslant J)$ are the usual symmetric-top functions. In this case for K in multiples of 3 the symmetry $\Gamma = A_1$ or $\Gamma = A_2$; for K not in multiples of 3 $\Gamma = E$.

following considerations were taken into account: the intensity of an individual multiplet component (e.g., from Table I) can be determined from the relation (Ref. (8))

$$S(\text{cm}^{-2}) = \pi\gamma \cdot k_J (\text{cm}^{-1}) \tag{3}$$

or

$$S = \pi P(\Delta\gamma/\Delta P)k_J = \pi NkT(\Delta\gamma/\Delta P)k_J, \tag{4}$$

where γ is the line half-width and P is the pressure. The total intensity of the vibration–rotation transition is determined, on the one hand, by Eq. (1), and, on the other, it is the sum of intensities of all the individual components Eq. (4). Hence, Eq. (2) is obtained (on the left-hand and right-hand sides of Eq. (2) the common factor πN was omitted).

It should be noted that $(k_J(\nu_n)$ from the right-hand side of Eq. (2) are known and are taken from the next to the last column of Table I. All the values on the left-hand side, with the exception of $|\langle\alpha\Gamma_\alpha|\mathcal{P}|\beta\Gamma_\beta\rangle|$, are also known (the energies E_α, the transitions frequencies ν, and the partition function $Q(T)$ are found from solution of the Schrödinger equation for dyad bands ν_2 and ν_4, see Ref. (10)). Hence, Eq. (2) can be used to determine the values $|\langle\alpha\Gamma_\alpha|\mathcal{P}|\beta\Gamma_\beta\rangle|$ for the two transitions

$$\mathcal{P}_5 = |\langle J = 5 \tilde{K} = 1E|\mathcal{P}|J = 5 \tilde{K} = 3E\rangle|$$

and

$$\mathcal{P}_6 = |\langle J = 6 \tilde{K} = 1E|\mathcal{P}|J = 6 \tilde{K} = 3E\rangle|. \tag{5}$$

TABLE I

Observed and Calculated Values of the Peak Absorption Coefficients $k_J(\nu_n)$ of Submillimeter "Forbidden" Transitions $(\Delta\tilde{K} = 2)$ of AsH_3 in the (0001) State[a]

Transition				Frequency	$k_J(\nu_n)_{obs}$	$k_J(\nu_n)_{calc}$
$J' — J$		$F' — F$		MHz	10^8 cm^{-1}	10^8 cm^{-1}
				$\tilde{K} = 3 — 1$		
		7/2	7/2	323 401.54	3.9(8)	4.3
		13/2	13/2	323 409.79	7.0(10)	7.8
5 — 5		9/2	9/2	323 430.42	4.6(9)	5.1
		11/2	11/2	323 438.66	5.6(10)	6.2
		9/2	9/2	346 601.80	6.8(13)	6.4
		15/2	15/2	346 606.79	11.0(20)	10.4
6 — 6		11/2	11/2	346 622.72	7.7(15)	7.3
		13/2	13/2	346 627.61	9.1(18)	8.6
				$\tilde{K} = 0 — 0$		
		3/2	3/2	230 562.18	530(100)	548
1 — 0		5/2	3/2	230 602.28	800(140)	822
		1/2	3/2	230 633.69	270(50)	274

[a] Measurements were carried out at room temperature and arsine pressure $P = 0.2$–0.6 Torr.

The values $\mathcal{P}_5$ and $\mathcal{P}_6$ obtained from the experimental data by means of the method above are

$$\mathcal{P}_5^{\mathrm{exp}} = 0.0246\mathrm{D} \quad \text{and} \quad \mathcal{P}_6^{\mathrm{exp}} = 0.0324\mathrm{D}. \tag{6}$$

The procedure for determining the $\langle J\tilde{K}\Gamma | \mathcal{P} | J\tilde{K}'\Gamma' \rangle$ matrix elements was tested on the *allowed* $J = 1 \leftarrow 0$, $K = 0$ transition. For the calculations the value of the permanent dipole moment $\mu_z^0 = 0.217\mathrm{D}$ was taken from Ref. (9). The line center absorption coefficients for the hfs components of the $J = 1 \leftarrow 0$, $\tilde{K} = 0$ transition were both measured experimentally and calculated theoretically. The results together with the experimental conditions are presented in Table I, which shows that the calculations are in satisfactory agreement with the experimental values.

To determine which mechanism of the "forbidden" transition formation dominates, the contributions of $\mathcal{P}_5^0$ and $\mathcal{P}_6^0$ to $\mathcal{P}_5$ and $\mathcal{P}_6$ due to the permanent dipole moment μ_z^0 were calculated. The vibration–rotation functions required for calculations were found with the data of Ref. (10), where the dyad treatment of ν_2 and ν_4 bands was used (for details of the model see Ref. (10)). To illustrate the value of hybridization, Table II presents the expansion coefficients of the Hamiltonian eigenfunctions $|J\tilde{K} = 1E\rangle$ and $|J\tilde{K} = 3E\rangle$ from Eq. (5) over the symmetrized vibration–rotation functions ($|v_2 = 1, v_4 = 0, A_1\rangle \otimes |JKE\rangle)_\sigma^E \equiv |v_2 = 1, v_4 = 0, A_1\rangle |JKE\sigma\rangle$ and ($|v_2 = 0, v_4 = 1, E\rangle \otimes |JK\Gamma\rangle)_\sigma^E$. Here $|v_2 = 1, v_4 = 0, A_1\rangle$ is the vibrational function of the (0100) state; $|v_2 = 0, v_4 = 1, E\sigma\rangle$ are two components of the vibrational function for the (0001) state; $|JK\Gamma\sigma\rangle$ are the functions (*). Functions ($|v_2 = 0, v_4 = 1, E\rangle \otimes |JK\Gamma\rangle)_\sigma^E$ are constructed by the conventional rules of tensorial set theory (see, e.g., Ref. (5)).

As a result of the procedures described above the following values were obtained:

TABLE II

The Coefficients $\alpha_{k\Gamma}^{v_1 v_2 J\tilde{K}}$ of Expansions of the $|J\tilde{K} = 3E\rangle$, $|J\tilde{K} = 1E\rangle$ Functions from Eq. (5) in Terms of the Basis Functions ($|v_1 v_2 \Gamma\rangle \otimes |Jk\Gamma\rangle)^E$

v_1	v_2	J	k	Γ	$\tilde{K}$	$\alpha_{k\Gamma}^{v_1 v_2 J\tilde{K}}$	v_1	v_2	J	k	Γ	$\tilde{K}$	$\alpha_{k\Gamma}^{v_1 v_2 J\tilde{K}}$
1	0	5	1	E	1	0.01011	1	0	6	1	E	1	0.01243
					3	0.00438						3	0.01039
			2	E	1	0.12091				2	E	1	0.12646
					3	−0.15236						3	−0.18752
			4	E	1	−0.00035				4	E	1	−0.00079
					3	−0.00018						3	−0.00460
			5	E	1	0.00181				5	E	1	0.00423
					3	0.00494						3	0.02250
0	1	5	0	A_2	1	−0.04445	0	1	6	0	A_1	1	−0.05381
					3	−0.02123						3	−0.03885
			1	E	1	0.97135				1	B	1	0.95268
					3	−0.17975						3	−0.23984
			2	E	1	−0.02218				2	E	1	−0.03492
					3	0.01667						3	0.03456
			3	A_1	1	0.19769				3	A_1	1	0.00462
					3	0.97095						3	0.00213
			3	A_2	1	0.00235				3	A_2	1	0.26725
					3	−0.00035						3	0.93802
			4	E	1	0.01445				4	E	1	0.02574
					3	0.03039						3	0.04378
			5	E	1	0.00033				5	E	1	0.00115
					3	−0.00344						3	−0.03705
										6	A_1	1	0.00473
												3	−0.03885
										6	A_2	1	−0.00005
												3	0.00099

$$\mathcal{P}_5^0 = 0.0475D,$$

$$\mathcal{P}_6^0 = 0.0574D. \tag{7}$$

Comparison shows that the differences between Eq. (6) and Eq. (7) are significantly larger than the experimental errors. As a consequence, the appearance of the "forbidden" transitions cannot be accounted for by the presence of resonance interactions only. Additional parameters from the operator $\mathcal{P}$ are needed, and as a consequence, one can try to determine the most important of these "forbidden" parameters.

For subsequent analysis, we used the results (Ref. (5)) of the theory of irreducible tensorial sets. As the analysis shows, the most important contribution to the matrix elements $\mathcal{P}_5$ and $\mathcal{P}_6$ should arise from the operators $R_1^{22(2,1E)}$ and $R_2^{22(2,1E)}$, the explicit form of which is given in Ref. (5). The corresponding parameter $Y^{22(2,1E)}$ was determined from the values $(\mathcal{P}_5^{exp} - \mathcal{P}_5^0)$ and $(\mathcal{P}_6^{exp} - \mathcal{P}_6^0)$ as

$$iY^{22(2,1E)} = -0.0050D$$

from the first expression, and

$$iY^{22(2,1E)} = -0.0042D$$

from the second.

It can be seen that both numbers are of a reasonable order of magnitude and satisfactorily agree with each other. Some discrepancy between the values of $iY^{22(2,1E)}$ above can be attributed both to the experimental errors in determination of the coefficients and to the approximate character of the calculations of the $(\mathcal{P}^{exp} - \mathcal{P}^0)$ values, in which only the main contributions (depending on the $iY^{22(2,1E)}$ parameters) were taken into account. Results of calculations of the coefficients $k_J(\nu_n)$ with the values of $iY^{22(2,1E)} = -0.0046D$ and μ_z^0 from Ref. (9) are presented in Table I. Sufficiently good agreement between experimental and calculated values supports the accuracy of our value for $Y^{22(2,1E)}$.

The result obtained is the first estimate of one of the parameters of the reduced dipole moment of AsH$_3$ that is responsible for "forbidden" transitions in the excited (0001) vibrational state. It can be used for estimating intensities of not only submillimeter transitions but also of microwave and infrared lines. Moreover, if the dependence of the obtained $Y^{22(2,1E)}$ parameter on the parameters of the vibration–rotation Hamiltonian and the parameters of the dipole moment $P = \sum_\alpha k_{z\alpha}(\mu_\alpha^0 + \sum_\lambda \mu_\alpha^\lambda q_\lambda + \cdots)$ are determined in explicit form, then one can attempt to estimate the parameters μ_α^λ. This will enable one to estimate the parameters $Y^{\Omega K(K',n\Gamma)}$ responsible for the corresponding "forbidden" or allowed transitions in the other vibrational states or bands of AsH$_3$ and species isotopic to it.

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