Laser Stark Spectroscopy of AsH_3 Using 9.4 and 10.6 μm CO_2 Laser

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Synopsis. Perturbation-allowed transitions of the ν_2 and ν_4 bands of AsH_3 were observed. About 100 Stark components were assigned to six $\Delta(k-l)=0$, six $\Delta(k-l)=\pm3$, and three $\Delta(k-l)=\pm6$ transitions. The Stark patterns and hyperfine splittings were used for confirming the assignment.

Since AsH_3 is a nearly spherical top, the rotational energy levels with various k values for a given J value are very close to one another. This near degeneracy increases the importance of various interactions which are usually insignificant, and it enables observation of the transitions that follow the selection rule, $\Delta(k-l)=\pm3n$ $(n=1,2,\cdots)$. The $\Delta(k-l)=\pm3$ transitions have been observed in the rotational spectrum of AsH_3 in the vibrational ground state.[1-3] In the vibrationally excited states, accidental degeneracies of rotation-vibration levels of the same rovibrational symmetry are also caused by the first-order Coriolis effect and possibly by the near degeneracy of vibrational levels. Transitions with $\Delta(k-l)=\pm3$ in the ν_1 and ν_3 bands of AsH_3 have thus been observed by infrared spectroscopy.[4] Recently, Scappini and Oka[5] observed and assigned the $\Delta(k-l)=\pm3$ transitions in the ν_2 and ν_4 bands by infrared-radiofrequency double resonance. The ν_2 and ν_4 bands are much more complicated than the ν_1 and ν_3 bands by the strong Coriolis interaction between them and are difficult to be assigned definitely. However, they assigned the transitions on the basis of the observed hyperfine patterns.

In the present note, laser Stark spectroscopy was used to observe and assign the $\Delta(k-l)=\pm3n$ transitions in the ν_2 and ν_4 bands. The present assignment has been confirmed by well-resolved Stark splitting patterns. The sensitivity of the spectrometer[6] was such that a number of weak forbidden transitions became detectable.

The Stark spectra were observed up to the field strength of 300 esu (90 kV/cm) with 9.4 and 10.6 μm band CO_2 laser following the $\Delta m_J=0$ and ±1 selection rules. About 1000 Stark components were observed, and about 100 components were assigned to those of 15 transitions. The assigned transitions are listed in Table 1.

The Stark shift for a certain level, J, k, m_J, of AsH_3 is mainly caused by the first-order effect. The first-order Stark shift, $\Delta\nu$, of the J', k', $m_J'\leftarrow J''$, k'', m_J'' transition frequency is given by

$$\Delta\nu = -(\varepsilon/h)[\mu' k' m_J'/J'(J'+1) - \mu'' k'' m_J''/J''(J''+1)], \quad (1)$$

where μ is the electric dipole moment and ε is the applied electric field. The relative signs of k', m_J', k'', and m_J'' are especially important for the assignment of the $\Delta(k-l)\neq0$ transitions. For simple designation of their relative signs, quantum numbers K' for $|k'|$, L for $(k'l)/K'$, and K'' for $(k'k'')/K'$ are used in the present note. Assignments of the transitions were confirmed by the following two criteria: First, all the observed patterns of the Stark components, $\Delta m_J=0$ or $\Delta m_J=\pm1$, must be explained consistently. Second, if a splitting is observed, it must agree with that estimated. The hyperfine splittings were calculated by using a formula for the strong-field case[7] with reported eQq values.[5,8]

It was thus possible to confirm the assignment of the $\Delta(k-l)=\pm3$ transitions by taking into account the relative signs of the quantum numbers mentioned above as in the rotational $\Delta k=\pm3$ transitions.[1] All the components, for which the splittings were estimated to exceed their Doppler widths, were actually resolved with splittings consistent with the estimations. Two of the three observed $\Delta(k-l)=\pm6$ transitions, which involve the $|k-l|=3$ levels, need further consideration in regard to the A_1-A_2 splitting of the levels. However, it was possible to explain their Stark patterns approximately by assuming the A_1-A_2 splitting to be zero (*i.e.*, by simply applying Eq. 1). This assumption is valid for the case in which the magnitude of the Stark shift of the levels is considerably larger than that of the A_1-A_2 splitting.

The difference between the Stark shift of the $\Delta(k-l)=\pm6$ transition and that of the normal $\Delta(k-l)=0$ transition is given by Eq. 1 with the relative signs of k', k'', l', and l'' chosen adequately. This equation shows that the magnitude of the Stark shift of the former transition is larger than that of the latter; this facilitates observation of perturbation-allowed transitions by laser Stark spectroscopy.

The Stark shifts of the observed transitions, given in Table 1, were calculated by diagonalization of a matrix, in which Coriolis interaction between ν_2 and ν_4 was taken into account, by use of the molecular constants determined by Olson *et al.*[4] for the ground state and by Sarka *et al.*[9] for the ν_2 and ν_4 states. However, the results were essentially equal to those calculated by the first-order equation (1). The dipole moments for the ν_2 and ν_4 states were assumed to be equal to that for the ground state, $\mu=0.22$ D.[1] Errors in the calculated shifts are mainly caused by the uncertainty in these values. The total uncertainty of the Stark shift is estimated to be less than 10% of the shift itself. As for the zero-field transition frequencies of the two $\Delta(k-l)=\pm6$ transitions mentioned above, neglect of the A_1-A_2 splitting is not adequate, because the magnitude of the splitting can be larger than the uncertainty in the Stark shift. Since the magnitude of the A_1-A_2 splitting is not exactly known, only approximate first-order values derived from the assumption that there is no A_1-A_2 splitting are listed

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Table 1. Assigned transitions for the ν_2 and ν_4 bands of AsH_3

Transition[a]						Laser line[b]	Stark component[c]		Stark field	Calculated shift	Zero-field transition
J'	K'	L	J''	K''	$\Delta(k-l)$		$M \leftarrow M''$		esu	cm^{-1}	cm^{-1}
2	1	0	1	1	0	10P (44)	0	1	192.4	−0.106	920.935(11)[e]
5	4	0	4	4	0	10P (22)	3	4	200.7[d]	0.089	942.295(9)
6	5	0	5	5	0	10P (14)	4	5	47.5[d]	−0.019	949.498(2)
5	3	1	6	2	0	10R (4)	5	4	146.9	−0.049	964.818(5)
5	4	−1	5	5	0	10R (44)	5	5	110.6[d]	0.037	989.610(4)
9	9	1	9	8	0	9P (44)	9	9	241.8	−0.026	1023.216(3)
6	1	0	5	−2	±3	10P (18)	6	5	43.0	0.023	945.957(2)
8	6	1	9	2	±3	10P (18)	8	8	275.2[d]	−0.150	946.131(15)
8	0	0	7	3	±3	10P (4)	7	7	249.0	−0.104	957.904(10)
6	5	1	5	1	±3	9P (10)	6	5	126.9[d]	0.078	1055.548(8)
7	3	1	6	5	±3	9R (8)	6	6	230.6[d]	−0.105	1070.567(10)
8	6	1	7	2	±3	9R (12)	8	7	131.6[d]	0.062	1073.217(6)
7	5	1	8	−2	±6	10P (10)	7	8	197.9	−0.186	953.066(19)
4	2	−1	5	−3	±6	10P (4)	4	5	108.9		(957.91)[f]
3	2	−1	4	−3	±6	10R (4)	3	4	59.8		(964.70)

a) Transitions with $L=0$ and $L=\pm1$ correspond to the ν_2 (A_1) and ν_4 (E) bands, respectively. b) 10: 10.6 μm CO_2 laser, 9: 9.4 μm CO_2 laser. c) A typical $M' \leftarrow M''$ component is listed for each transition. d) Hyperfine splitting is resolved. The listed field values correspond to the centers of the doublets. e) Number in parentheses represents estimated uncertainty in units of 10^{-3} cm^{-1}. f) Estimated from the assumption that there is no A_1-A_2 splitting.

in Table 1.

The obtained zero-field transition frequencies were analyzed in combination with the reported infrared frequencies.[9] The results of a least-squares analysis were essentially the same as that obtained by the infrared data alone. A further analysis of the strong Coriolis interaction between ν_2 and ν_4 and a larger number of accurate spectroscopic data are needed for a more precise determination of the molecular constants. We note that there is no overlapping between the transitions assigned by Scappini and Oka[5] and those assigned in the present study. This is probably because of the difference in the characteristic ranges of applicability of these techniques; radiofrequency-infrared double resonance is more suitable for observing transitions that are relatively close to the laser frequencies, whereas laser Stark patterns can be resolved and assigned more easily for transitions that are separated farther from the laser lines. In this context, laser Stark spectroscopy provides data complementary to RF-IR double resonance spectroscopy.

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