

## INTENSITY MEASUREMENTS IN THE $4.54\mu$ FUNDAMENTAL OF $\text{CH}_3\text{D}$ AT LOW TEMPERATURES\*

SUNIL SARANGI and PRASAD VARANASI

Department of Mechanics, State University of New York, Stony Brook USA

**Abstract**—The integrated intensities of the  $J$ -multiplets  $R(4)$  through  $P(12)$ , including the  $Q$ -branch, of the  $4.54\mu$  fundamental of  $\text{CH}_3\text{D}$  have been measured at  $100^\circ\text{K}$ ,  $150^\circ\text{K}$ ,  $200^\circ\text{K}$ ,  $250^\circ\text{K}$ , and  $298^\circ\text{K}$ . Comparison of the measured line strengths with values calculated using symmetric-top formulae suggests strong intensity anomalies.

### INTRODUCTION

MONODEUTERATED methane ( $\text{CH}_3\text{D}$ ) has been discovered recently in the atmosphere of Jupiter by an identification<sup>(1)</sup> of the lines  $P(2)$  through  $P(12)$  in its vibration-rotation band at  $2200\text{ cm}^{-1}$ . A quantitative interpretation<sup>(2)</sup> of the observed spectrum<sup>(1)</sup> that could lead to an estimate of the abundance of  $\text{CH}_3\text{D}$  and of the  $\text{D}/\text{H}$  ratio in the atmosphere of Jupiter requires intensity data at the relevant planetary temperatures for this band. Therefore, we have measured in our laboratory the intensities of  $J$ -multiplets between  $P(12)$  and  $R(4)$  and of the fully blended  $Q$ -branch, at  $100^\circ\text{K}$ ,  $150^\circ\text{K}$ ,  $200^\circ\text{K}$ ,  $250^\circ\text{K}$  and  $298^\circ\text{K}$ .

### EXPERIMENTAL PROCEDURE

The experimental apparatus is essentially the same as discussed in Ref. (3) for the  $2\nu_3$ -band of methane. The different spectral region considered in the present paper required the use of an infrared glower, 144 l/mm grating and an InSb detector with which we were able to obtain a spectral resolution ranging between  $0.15\text{ cm}^{-1}$  and  $0.2\text{ cm}^{-1}$  and a signal-to-noise ratio of 200:1. The time constant of the lock-in-amplifier was set at 100 msec.

Several mixtures, with the amount of  $\text{CH}_3\text{D}$  in  $\text{H}_2$  ranging from 0.117 to 4 per cent (by volume), were prepared. The gases were allowed to mix for at least a couple of days in lecture bottles before the mixture was introduced into the absorption cells. The sample of  $\text{CH}_3\text{D}$  was supplied by the isotope division of Merck, Sharp and Dohme Canada, Limited, with the following batch analysis: 97.46% of  $\text{CH}_3\text{D}$  and 2.54% of  $\text{CH}_4$  with no detectable trace of  $\text{CH}_2\text{D}_2$  according to mass analysis by the supplier.

With the spectral resolution available to us, it has not been possible to measure the intensities of the individual lines ( $K$ -components) of each  $J$ -multiplet. The procedure we have adapted for deriving multiplet-intensities,  $S_J$  ( $\text{cm}^{-2}\text{ atm}^{-1}$ ), from measured equivalent widths is quite similar to that described in our paper<sup>(3)</sup> on the  $2\nu_3$ -band of methane. Construction of curves-of-growth for blended  $J$ -multiplets required (i) the assumption of theoretical formulae<sup>(4)</sup> for the relative line strengths,  $S_{JK}$  ( $\text{cm}^{-2}\text{ atm}^{-1}$ ), of individual lines of a  $J$ -multiplet, and (ii) the assumption that all of the lines in the band have the same hydrogen-broadened half-width,  $\gamma_{\text{CH}_3\text{D}-\text{H}_2}^0 = (300/T)^{1/2} 0.075\text{ cm}^{-1}\text{ atm}^{-1}$ , as the rotational lines in the  $\nu_3$  band of methane.<sup>(4)</sup> On theoretical

\*Supported by NASA under Grant No. NGR-33-015-139.

grounds,<sup>(6)</sup> it may be argued that the line widths in the bands of CH<sub>3</sub>D and CH<sub>4</sub> would be nearly the same and, thus, due to the lack of data for CH<sub>3</sub>D lines, one may use the data obtained for CH<sub>4</sub> lines, in good approximation. It should be noted, however, that, in the present context, the final results derived for the intensity of the blended multiplet is not strongly dependent upon the choice of value for the line width. Since we are performing measurements in a region of the curve-of-growth that is nearly linear, errors as large as 25 per cent in the assumed line widths could be tolerated.

The theoretical expressions for the relative strengths of the individual lines (*K*-components) in a *J*-multiplet are well known.<sup>(4)</sup> For lines in a parallel ( $\Delta K = 0$ ), fundamental, band of a (prolate) symmetric top molecule such as CH<sub>3</sub>D, we may write

$$S_{JK} \sim T^{-5/2} \nu_{JK} \cdot A_{JK} g_{JK} \exp(-E_{JK}/kT), \quad (1)$$

where

$$A_{JK} = \begin{cases} (J^2 - K^2)/J(2J + 1) & \text{for } \Delta J = -1, \\ K^2/J(J + 1) & \text{for } \Delta J = 0, \\ [(J + 1)^2 - K^2]/(J + 1)(2J + 1) & \text{for } \Delta J = +1, \end{cases}$$

and

$$g_{JK} = \begin{cases} (2 - \delta_{0K})(2J + 1) \frac{(2I + 1)}{3} (4I^2 + 4I + 3) & \text{for } K \text{ divisible by 3 (including zero),*} \\ (2 - \delta_{0K})(2J + 1) \frac{(2I + 1)}{3} (4I^2 + 4I) & \text{for } K \text{ not divisible by 3.} \end{cases}$$

The nuclear spin  $I = \frac{1}{2}$  in the present case.  $\delta_{0K}$  is the Kronecker delta.

The rotational energies in the lower (ground) vibrational level and the line positions were calculated by means of the following expressions:

$$E_{JK} = B''J(J + 1) + (A'' - B'')K^2 + D''_j J^2(J + 1)^2 - D''_{jK} J(J + 1)K^2 - D''_K K^4,$$

and

$$\nu_{JK} = \nu_0 + (B' + B'')m + (B' - B'')m^2 + 2(D'_j + D''_j)m^3 + (D'_j - D''_j)m^4,$$

with  $m = -J, 0$  and  $J + 1$ , respectively, for the *P*-, *Q*- and *R*-branches;  $\nu_0 = 2200 \text{ cm}^{-1}$ ,  $B'' = 3.875 \text{ cm}^{-1}$ ,  $B' = 3.835 \text{ cm}^{-1}$ ,  $D''_j = D'_j = 4 \times 10^{-5} \text{ cm}^{-1}$  and  $D''_K \sim 0$ . The above constants were taken from Refs. (7) and (8).<sup>†</sup>

\*The statistical weight for  $K = 0$  was entered erroneously in Table 3 of Ref. (2). All the entries in column 3 for  $K = 0$  in that tabulation should, therefore, be divided by a factor of two. (F. W. Taylor, private communication).

†There appears to be some confusion among authors<sup>(4,7,8)</sup> in the assignment of a vibrational frequency to this fundamental band. ALLEN and PLYLER<sup>(7)</sup> have stated that they were following HERZBERG<sup>(4)</sup> in assigning the frequency  $\nu_2$  to this band, while we note in HERZBERG<sup>(4)</sup> that it was cited as the  $\nu_1(e)$  fundamental. ANDERSEN<sup>(8)</sup> describes it as the  $\nu_{3a}$  fundamental. However, the identification of the band as a parallel, fundamental band, which is all the information we need in our present study, appears to be unambiguous.

## RESULTS AND DISCUSSION

The results of our measurements are summarized in Table 1. In Table 2, we compare our data with the theoretical intensities of the  $J$ -multiplets, computed according to equation (1) and relative to the measured intensity of the doublet  $P(2)$  at each temperature. The temperature

Table 1. Measured intensities,  $S_j$  ( $\text{cm}^{-2} \text{atm}^{-1}$ ) of several  $J$ -multiplets in the  $P$ - and  $R$ -branches and of the totally blended  $Q$ -branch in the  $4.54\mu$  fundamental of  $\text{CH}_3\text{D}$  at 100°K, 150°K, 200°K, 250°K and 298°K. The quoted error in each value is the standard deviation over the number of measurements shown in parenthesis following the value

Multiplet	$S_j(\text{cm}^{-2} \text{atm}^{-1})$									
	100°K		150°K		200°K		250°K		298°K	
$P(12)$					0.18	(1)	0.226	(1)	0.246 ± 0.016	(2)
$P(11)$			0.148 ± 0.015	(3)	0.271 ± 0.01	(5)	0.317 ± 0.0077	(3)	0.347 ± 0.013	(2)
$P(10)$			0.293 ± 0.026	(9)	0.409 ± 0.013	(7)	0.426 ± 0.012	(3)	0.424 ± 0.008	(3)
$P(9)$	0.241 ± 0.0079	(6)	0.528 ± 0.029	(13)	0.621 ± 0.017	(10)	0.596 ± 0.021	(5)	0.528 ± 0.018	(3)
$P(8)$	0.577 ± 0.030	(11)	0.848 ± 0.062	(10)	0.832 ± 0.023	(8)	0.77 ± 0.052	(7)	0.595 ± 0.0058	(4)
$P(7)$	1.12 ± 0.041	(7)	1.20 ± 0.023	(8)	0.952 ± 0.083	(4)	0.843 ± 0.018	(9)	0.654 ± 0.0093	(7)
$P(6)$	1.83 ± 0.074	(10)	1.54 ± 0.045	(9)	1.14 ± 0.069	(6)	0.830 ± 0.021	(9)	0.632 ± 0.0066	(8)
$P(5)$	2.72 ± 0.14	(8)	1.85 ± 0.062	(8)	1.18 ± 0.057	(7)	0.829 ± 0.032	(11)	0.567 ± 0.0087	(7)
$P(4)$	3.22 ± 0.092	(7)	1.76 ± 0.07	(8)	1.03 ± 0.041	(6)	0.666 ± 0.02	(10)	0.464 ± 0.016	(13)
$P(3)$	2.74 ± 0.11	(8)	1.26 ± 0.049	(10)	0.709 ± 0.036	(7)	0.428 ± 0.017	(15)	0.281 ± 0.0086	(10)
$P(2)$	1.85 ± 0.079	(11)	0.724 ± 0.03	(16)	0.373 ± 0.014	(14)	0.227 ± 0.011	(10)	0.137 ± 0.0026	(8)
$P(1)$	0.635 ± 0.031	(15)	0.228 ± 0.012	(13)	0.122 ± 0.009	(6)				
$Q$	18.5 ± 0.22	(4)	13.1 ± 0.41	(3)	9.29 ± 0.26	(11)	7.63 ± 0.32	(8)	6.33 ± 0.1	(9)
$R(0)$	0.749 ± 0.021	(17)	0.286 ± 0.015	(13)	0.132 ± 0.0069	(6)	0.0758 ± 0.003	(4)	0.0435 ± 0.0076	(3)
$R(1)$	2.51 ± 0.13	(8)	0.946 ± 0.045	(9)	0.484 ± 0.023	(15)	0.281 ± 0.025	(11)	0.175 ± 0.0065	(7)
$R(2)$	4.11 ± 0.099	(6)	1.67 ± 0.048	(10)	0.873 ± 0.039	(10)	0.512 ± 0.015	(13)	0.334 ± 0.0093	(14)
$R(3)$	5.89 ± 0.29	(6)	2.73 ± 0.1	(8)	1.48 ± 0.107	(6)	0.898 ± 0.029	(8)	0.594 ± 0.0081	(7)
$R(4)$	6.06 ± 0.34	(6)	3.29 ± 0.15	(8)	1.93 ± 0.074	(6)	1.22 ± 0.089	(5)	0.832 ± 0.0058	(3)

Table 2. Theoretical intensities and the ratios of experimental to theoretical intensities of  $J$ -multiplets in the  $4.54\mu$  fundamental of  $\text{CH}_3\text{D}$ . The units of  $S_j$  are  $\text{cm}^{-2} \text{atm}^{-1}$

Line	100°K		150°K		200°K		250°K		298°K	
	$S_j(\text{Theo})$	$S_j(\text{Expt})/$ $S_j(\text{Theo})$								
$P(12)$	0.0102		0.0719		0.159	1.14	0.232	0.973	0.252	0.976
$P(11)$	0.0343		0.1539	0.96	0.271	1.00	0.344	0.922	0.342	1.024
$P(10)$	0.1018		0.301	0.976	0.428	0.957	0.478	0.891	0.436	0.972
$P(9)$	0.2647	0.911	0.5315	0.994	0.623	0.997	0.620	0.962	0.522	1.012
$P(8)$	0.6002	0.961	0.856	0.990	0.843	0.987	0.755	1.019	0.594	1.002
$P(7)$	1.18	0.948	1.231	0.975	1.036	0.919	0.846	0.996	0.625	1.046
$P(6)$	1.96	0.932	1.549	0.993	1.139	1.00	0.855	0.971	0.597	1.058
$P(5)$	2.801	0.971	1.765	1.047	1.149	1.030	0.804	1.031	0.536	1.057
$P(4)$	3.242	0.994	1.672	1.055	0.993	1.033	0.656	1.016	0.421	1.102
$P(3)$	2.719	1.008	1.20	1.051	0.654	1.084	0.411	1.04	0.255	1.10
$P(2)$	1.847	1.000	0.724	1.000	0.373	1.000	0.227	1.000	0.137	1.000
$P(1)$	0.667	0.952	0.242	0.941	0.120	1.017	0.0714		0.0426	
$Q$	29.756	0.621	22.26	0.590	18.57	0.500	16.62	0.459	13.95	0.453
$R(0)$	0.751	0.997	0.263	1.090	0.128	1.032	0.0751	1.01	0.0445	0.977
$R(1)$	2.339	1.074	0.853	1.11	0.424	1.14	0.251	1.12	0.150	1.17
$R(2)$	3.878	1.061	1.529	1.093	0.790	1.105	0.480	1.066	0.291	1.15
$R(3)$	5.202	1.13	2.319	1.18	1.272	1.16	0.806	1.11	0.502	1.18
$R(4)$	5.058	1.20	2.647	1.24	1.57	1.23	1.040	1.17	0.669	1.24

dependence of the intensity of  $P(2)$ , as implied in equation (1), is verified in Fig. 1. The measured values for the absolute intensity of  $Q$ -branch are easily seen (Table 1) to vary as  $T^{-1}$ .

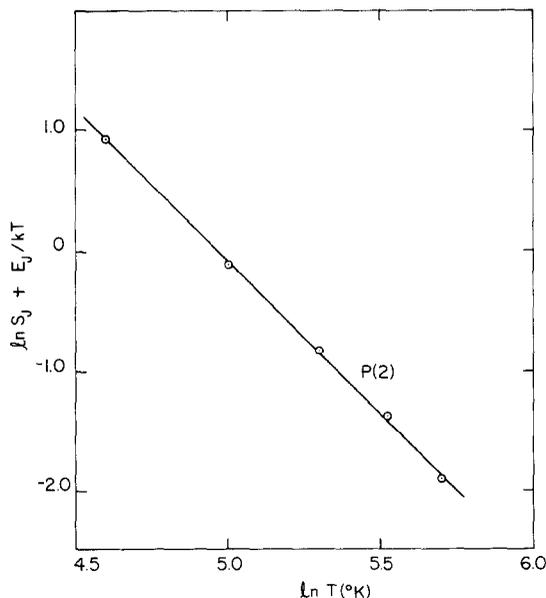


Fig. 1. Temperature dependence of the intensity,  $S_j$  ( $\text{cm}^{-2} \text{atm}^{-1}$ ) of the  $P(2)$  doublet in the  $4.54\mu$  fundamental band of  $\text{CH}_3\text{D}$ . The straight line represents equation (1).

From the ratios  $S_j(\text{Expt})/S_j(\text{Theo})$  presented in Table 2, it is apparent that the  $Q$ - and  $R$ -branches are severely perturbed, while the theoretical relation [equation (1)] for the relative line strengths is fairly well preserved for lines in the  $P$ -branch. The measured intensities of the  $Q$ -branch are significantly lower, at all the temperatures, than the calculated values. On the other hand, the observed intensities in the  $R$ -branch are considerably larger than the theoretical values with the discrepancy increasing progressively with  $J$ . It is our belief that a more thorough investigation that covers all of the lines in the  $R$ -branch of the fundamental and the neighboring band  $2\nu_{4ab}$  at  $2301 \text{ cm}^{-1}$ , which according to ANDERSEN,<sup>(8)</sup> is in Fermi resonance with the  $\nu_{3a}$  fundamental studied here, would reveal the nature of the perturbation that causes the strong intensity anomalies observed by us. Significant "borrowing of intensity" from the  $Q$ -branch by the  $R$ -branch and, perhaps, by  $2\nu_{4ab}$  may be the result of the mixing of the wave functions in the two resonating vibrational levels.

#### REFERENCES

1. R. BEER, C. B. FARMER, R. H. NORTON, J. V. MARTONCHIK and T. G. BARNES, *Science* **175**, 1360 (1972).
2. R. BEER and F. W. TAYLOR, *Astrophys. J.* **179**, 309 (1973).
3. S. SARANGI and P. VARANASI, *JQSRT* **14**, 365 (1974).
4. G. HERZBERG, *Infrared and Raman Spectra*. van Nostrand, Princeton, N.J. (1945).
5. P. VARANASI, S. SARANGI and L. A. PUGH, *Astrophys. J.* **179**, 977 (1973).
6. G. D. T. TEIWANI and P. VARANASI, *J. chem. Phys.* **55**, 1075 (1971).
7. H. C. ALLEN, Jr. and E. K. PLYLER, *J. Res. NBS* **63A**, 145 (1959).
8. F. A. ANDERSEN, *Danske Videnskabernes Selstab Matematisk-Fysiske Meddelelsee* **33**, No. 12 (1963).