

is an average of hourly values for the duration for which the data were collected. The data at Aligarh give an accuracy of one percent while the limitations of time made it difficult to achieve the same accuracy at the other two stations. This, however, does not change the general conclusion.

Since fast neutrons in the atmosphere are presumably created by nuclear disintegrations caused by the interaction of cosmic radiation and atomic nuclei, it was thought worthwhile to study the latitude variation of cosmic-ray particles which produce disintegrations in nuclei of air atoms. These measurements indicate a very large latitude effect amounting to about twenty-five percent between Aligarh ( $18^{\circ}12'N$ ) and the geomagnetic equator. The value of the neutron intensity at Madras should be slightly less than that at Nagpur, keeping in view the fact that the general latitude curve for radiation passing through 12 cm of lead is fairly flat from the equator to around  $10^{\circ}N$ . On the other hand, the change is very rapid in the intermediate latitudes of  $15^{\circ}$  to  $30^{\circ}$ . The time of observation at these two stations at our disposal made it impossible to increase the accuracy of measurements. Such a large latitude effect would mean that cosmic-ray particles responsible for the production of up to 10 Mev neutrons in the atmosphere are highly field-sensitive. This effect is of the same order of magnitude as that on large cosmic-ray bursts shown by Jesse and Gill.<sup>2</sup> Perhaps the burst-producing radiation is the same which generates fast cosmic-ray neutrons in the atmosphere. These observations suggest that more extensive measurements of this nature covering larger range of latitudes should be taken.

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<sup>1</sup> L. F. Curtiss and P. S. Gill (to be published).

<sup>2</sup> W. P. Jesse and P. S. Gill, Phys. Rev. 55, 414 (1939).

### Rotational Structure of the $\nu_3$ Raman Band of Methane

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ACCORDING to Teller's<sup>1</sup> theory of the Coriolis interaction in tetrahedral molecules the  $\nu_3$  Raman band of methane consists of fifteen sub-branches; only three of these are active in infrared absorption. In the early work of Dickinson, Dillon, and Rasetti<sup>2</sup> fourteen Raman lines were observed, corresponding to an unresolved  $Q$  branch and higher members of the intense  $S^+$  and  $O^-$  branches. In the present investigation a multiple reflection Raman tube<sup>3</sup> and a quartz spectrograph with a dispersion of 27  $\text{cm}^{-1}/\text{mm}$  at 2537A were used to obtain greater detail of the band. Sixty-eight lines were resolved, and evidence was found for all but one ( $O^+$ ) of the fifteen sub-branches. The results of an analysis of these Raman data, combined with the infrared measurements of Nielsen and Nielsen,<sup>4</sup> are reported here.

A preliminary study showed that forty-two of the Raman lines were unblended and could be measured with sufficient accuracy for use in the analysis. By means of combination sum relations the following constants were derived:

$$\left. \begin{aligned} \nu_0 &= 3018.7 \text{ cm}^{-1} \\ B_0 - B_1 &= 0.050 \text{ cm}^{-1} \end{aligned} \right\} \text{from } S^0 \text{ and } O^0 \text{ lines,}$$

$$\left. \begin{aligned} \nu_0 &= 3018.1 \text{ cm}^{-1} \\ B_0 - B_1 &= 0.035 \text{ cm}^{-1} \end{aligned} \right\} \text{from infrared } R^- \text{ and } P^+ \text{ lines,}$$

$$\left. \begin{aligned} \nu_0 + 3B_1\zeta_1 &= 3019.6 \text{ cm}^{-1} \\ B_0 - B_1 &= 0.036 \text{ cm}^{-1} \end{aligned} \right\} \text{from } S^+ \text{ and } O^- \text{ lines.}$$

The value  $B_1\zeta_1 = 0.29$  was determined from the relation

$$S^+(J-1) + O^-(J) - R^-(J) - P^+(J-1) = 12B_1\zeta_1.$$

The two values of  $\nu_0$  indicate a systematic difference between the Raman and infrared frequencies; to obtain consistency the infrared frequencies (reduced to  $\text{cm}^{-1}$  in vacuo) were raised by 0.6  $\text{cm}^{-1}$ . The marked difference between the convergence factors  $B_0 - B_1$  for branches involving  $F_1^0$  states and those involving  $F_1^+$  and  $F_1^-$  states shows a departure from the simple theory. The rotational constants,  $B$  and  $D$ , were therefore determined from combination differences of lines of the same type (e.g.,  $S^+$  and  $P^+$  lines). A least-squares analysis gave the following values:

$$\left. \begin{aligned} B_0 &= 5.253, D_0 = 1.9 \times 10^{-4} \\ B_1 &= 5.200, D_1 = 1.0 \times 10^{-4} \end{aligned} \right\} \text{from } S^0 \text{ and } O^0 \text{ lines,}$$

$$\left. \begin{aligned} B_0 &= 5.232, D_0 = 1.5 \times 10^{-4} \\ B_1 &= 5.202, D_1 = 1.0 \times 10^{-4} \end{aligned} \right\} \text{from } S^+ \text{ and infrared } P^+ \text{ lines,}$$

$$\left. \begin{aligned} B_0 &= 5.233, D_0 = 1.0 \times 10^{-4} \\ B_1 &= 5.197, D_1 = 0.8 \times 10^{-4} \end{aligned} \right\} \text{from } O^- \text{ and infrared } R^- \text{ lines.}$$

The perturbation in the ground state, manifested by the different values of  $B_0$ , is not understandable from the theoretical viewpoint. It is therefore concluded that the tacit assumption of identical upper states in the combination differences is not valid for some of the relations used.

A more acceptable analysis was obtained by assuming that the ground state is unperturbed, and has rotational constants,  $B_0 = 5.253$  and  $D_0 = 1.9 \times 10^{-4}$ , as found from combination differences of  $S^0$  and  $O^0$  lines. The upper rotational states,  $F_1(J)$ , for the various branches were then calculated from the observed frequencies, and these values of  $F_1(J)$  were used to derive constants,  $B_1$  and  $D_1$ , for each branch. The results are given in Table I. This

TABLE I. Rotational constants of the upper state of the  $\nu_3$  band of  $\text{CH}_4$  assuming  $B_0 = 5.253 \text{ cm}^{-1}$  and  $D_0 = 1.9 \times 10^{-4} \text{ cm}^{-1}$ .

Branch	$B_1$ ( $\text{cm}^{-1}$ )	$D_1$ ( $\text{cm}^{-1} \times 10^4$ )
$O^-$ (R. E.)	5.235	3.8
$R^+, P^-$ (R. E.)	5.235	3.1
$R^0, P^0$ (R. E.)	5.217	1.8
$R^-, P^+$ (I. R. and R. E.)	5.217	1.8
$S^+$ (R. E.)	5.206	1.0
$S^0, O^0$ (R. E.)	5.202	1.8

array of rotational constants for the  $\nu=1$  vibrational state gives a consistent analysis of the Raman and infrared bands; the observed frequencies are reproduced with an average discrepancy of about 0.1  $\text{cm}^{-1}$ , and the values of  $B_0 - B_1$  are in agreement with those calculated from combination sums. However, the reason for the multiplicity of  $B_1$  values is not immediately apparent from the theory. A perturbation of  $\nu_3$  due to Coriolis interaction with the  $E$  part of  $2\nu_2$  does not explain the results satisfactorily. It is probable that second-order perturbations due to centrifugal distortion and anharmonicities, such as those considered by Shaffer, Nielsen, and Thomas,<sup>5</sup> are of the same order of magnitude as the perturbation by  $2\nu_2$  and must also be taken into account.

Although the individual lines of the  $Q$  branch were not resolved, the contour at high dispersion is striking: there is a sharp maximum of intensity at  $\Delta\nu = 3021.5 \text{ cm}^{-1}$ , a broad maximum at about  $\Delta\nu = 3017 \text{ cm}^{-1}$ , and a gradual decrease in intensity towards smaller frequency shifts. This intensity distribution is readily explained by the convergence and Coriolis terms in the frequency formulas for the  $Q$  sub-branches. The  $Q^0$  and  $Q^-$  sub-branches are degraded towards lower frequency shifts; the  $Q^+$  sub-branch forms a band head at  $\Delta\nu = 3021.5 \text{ cm}^{-1}$ , on the side of the band origin towards higher frequency shifts. At low dispersion this band head is the most prominent feature of the  $Q$  branch and has been measured by the earlier workers as  $\nu_3$ .

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<sup>1</sup> E. Teller, Hand-und Jahrb. d. Chem. Phys. 9, II, 43 (1934).

<sup>2</sup> Dickinson, Dillon, and Rasetti, Phys. Rev. 34, 582 (1929).

<sup>3</sup> Welsh, Cumming, and Stansbury, J. Opt. Soc. Am. (to be published).

<sup>4</sup> A. H. Nielsen and H. H. Nielsen, Phys. Rev. 48, 864 (1935).

<sup>5</sup> Shaffer, Nielsen, and Thomas, Phys. Rev. 56, 895 (1939).