MEASUREMENTS ON SPECTRA OF GASES OF PLANETARY INTEREST*

II. H_2, CO_2, NH_3, AND CH_4

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ABSTRACT

An empirical curve of growth on the $S(1)$ line of the 1–0 hydrogen quadrupole band was obtained. With this curve the laboratory and planetary hydrogen quadrupole spectra can be corrected for saturation. Self-broadening and nitrogen-broadening together with intensity measurements were made on the 121–000 CO_2 band. The region of the ammonia band around 6450 Å was observed, and nitrogen-broadening coefficients for eighteen selected lines were obtained. The self- and hydrogen-broadening coefficients for several low J-lines of the $2\nu_3$ methane band at 1.67 μ were measured.

INTRODUCTION

Since the construction of the 44-meter multiple reflection absorption tube and the publication by Rank, Fink, Foltz, and Wiggins (1964) of a paper on planetary gases, we have made additional measurements on a number of features of gases of astrophysical interest. Some of these have already been relayed by private communication to the persons most directly interested in these measurements. We now wish to publish these data, which we have accumulated over the past year or so, in order to make them generally available. We present data on the hydrogen quadrupole spectrum, the 121–000 band of CO_2 at 2.1 μ, the NH_3 band at 6450 Å, and the CH_4 band at 1.67 μ.

We have obtained a curve of growth for the $S(1)1$–0 line of the hydrogen quadrupole spectrum. The curve shows that saturation was much larger than expected. We can now correct for saturation and obtain a more meaningful abundance estimate of planetary hydrogen. We have also completed an analysis of our measured and pressure-corrected quadrupole frequencies to obtain precise molecular constants. Relative intensity measurements in the 1–0 band have been compared with theoretical calculations by James and Coolidge (1938) and more recent proposed corrections by James and Klemperer (1964). Since this work is of less astrophysical interest, it has been submitted by Fink, Wiggins, and Rank (1965) for publication elsewhere.

Considerable astrophysical work has been done on the group of CO_2 bands located at 2 μ by Kuiper (1963) and Sinton (1963). These bands are quite sensitive to pressure broadening, and Howard, Burch, and Williams (1955) have shown that the total band absorption is dependent essentially on the product of the CO_2 concentration and the effective pressure. It is therefore of particular interest to know both the self-broadening and foreign gas-broadening parameters for the lines of these bands. It is also of interest to compare the recent photographic measurements of Rank *et al.* (1964) on the Venus band $5\nu_3$ located at 8700 Å with the present results obtained with a PbS detector.

On several spectrograms of Jupiter obtained in the past few years it has been noticed by Giver (1964) and Spinrad and Trafton (1963) that the lines in the ammonia band at 6450 Å were broader than the resolving power would dictate for an infinitely narrow spectrum line. It is reasonable to assume that these lines are broadened by the gas pressure in the Jovian atmosphere where they are formed. For this reason we have obtained laboratory data on the pressure broadening of the 6450 Å NH_3 band. The band revealed a very complex degree of fine structure which probably accounts for the large widths of these ammonia lines on Jovian spectra.

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On the same plates that show the ammonia lines, weak methane lines are found at 6190 Å. Spinrad and Trafton (1963) have shown that these lines are much narrower than the ammonia lines and, on the Jovian plates, show a half-width essentially the same as the instrument width. They have already used these lines to estimate an upper limit of about 1.4 atmospheres for the average pressure in the atmosphere of Jupiter. Very few laboratory data exist on the broadening of methane. We therefore decided to make some pressure-broadening measurements on methane. For experimental reasons we have chosen the $2\nu_3$ band at 1.67 μ. Presumably in a non-polar molecule like methane the broadening should be essentially the same for all of its bands.

HYDROGEN

It has been shown in our previous communication that the equivalent width even for lines as sharp as the hydrogen quadrupole lines is independent of the resolving power over a wide range. We therefore believed that the measurements we made were on the linear part of the curve of growth. At the request of Spinrad and Giver we have examined the problem of saturation more closely and found that saturation was much larger than we expected.

TABLE 1

EQUIVALENT WIDTHS IN $CM^{-1} \times 10^{-3}$ OF THE $S(1)$ LINE OF THE 1–0 H_2 QUADRUPOLE BAND FOR DIFFERENT RESOLVING POWERS AND PATH LENGTHS AT A DENSITY OF 1.20 AMAGATS

No. of Passes.....	2	4	8	12	20	32
Km-amagats.....	0.106	0.212	0.423	0.635	1.058	1.694
Resolving Power						
95000.....	8.28	16.0	23.8	31.9	39.4	52.0
70000.....	8.12	15.4	24.5	31.6	42.3	53.1
60000.....	8.21	15.3	24.8	32.2	44.7	52.5
44000.....	9.19	15.7	20.9	32.0	45.0	51.9

The measurements to obtain the curve of growth are listed in Table 1 and were taken on the $S(1)$ line of the 1–0 band since this line could be obtained over a large range of absorption. They were obtained by keeping the hydrogen gas density in our 44-meter White cell at 1.20 amagats and changing the number of passes from 2 to 32. For each path length several different slit openings were used thus giving the range of resolving powers indicated in the table. The independence of the equivalent width with the resolving power is again borne out, and the values for the same absorbing path were averaged. The logarithm of these average values was now plotted against the logarithm of the product ρl, and from the linear portion of that curve the line strength S_0 was obtained. The resultant S_0 was the same as that obtained by plotting the integrated absorption on a simplified curve of growth as described by Fink, Wiggins, and Rank (1965).

The composite curve of growth shown in Figure 1 was constructed by plotting the measured equivalent width against the value of $S_0\rho l$ on log paper. The solid black points are the values for the $S(1)$ line listed in Table 1. The curved line is the theoretical curve of growth as given by Kaplan and Eggers (1956) which was fitted to the experimental points. The linear and square root asymptotes are also indicated. The circles represent other lines in the 1–0 and 2–0 band that were corrected by the method described in our paper and then plotted on Figure 1. Their proximity to the $S(1)$ curve of growth shows that these lines were correctly adjusted for saturation.

In Table 2 we give the experimental line strengths of the $S(1)$ line in the 1–0, 2–0, and

3–0 bands. The lines of the 1–0 and 2–0 band were measured with a PbS detector. The 3–0 line was photographed as previously described. All lines were corrected by means of our curve of growth. The line strength of the $S(1)$ line of the 4–0 band, which is much too weak to be observable in the laboratory, was calculated by a procedure described by Foltz and Rank (1963). They used the quadrupole moment given by Kolos and Roothan (1960) together with the line-strength expression by James and Coolidge (1938) but imposed the additional restriction that the quadrupole expansion used must be such as to give a ratio of 1–0/2–0 = 5.8 (our preliminary intensity ratio) while the ratio of the 1–0/3–0 bands was varied from 70 to 93. This procedure was necessary because the intensity of the overtone bands depends strongly on the higher-order terms in the quadrupole expansion which are very poorly known. Until a better expression for the quadrupole moment becomes available, this method, although somewhat uncertain, is the best that can be done.

We can now use our curve of growth together with our line strengths to form an esti-

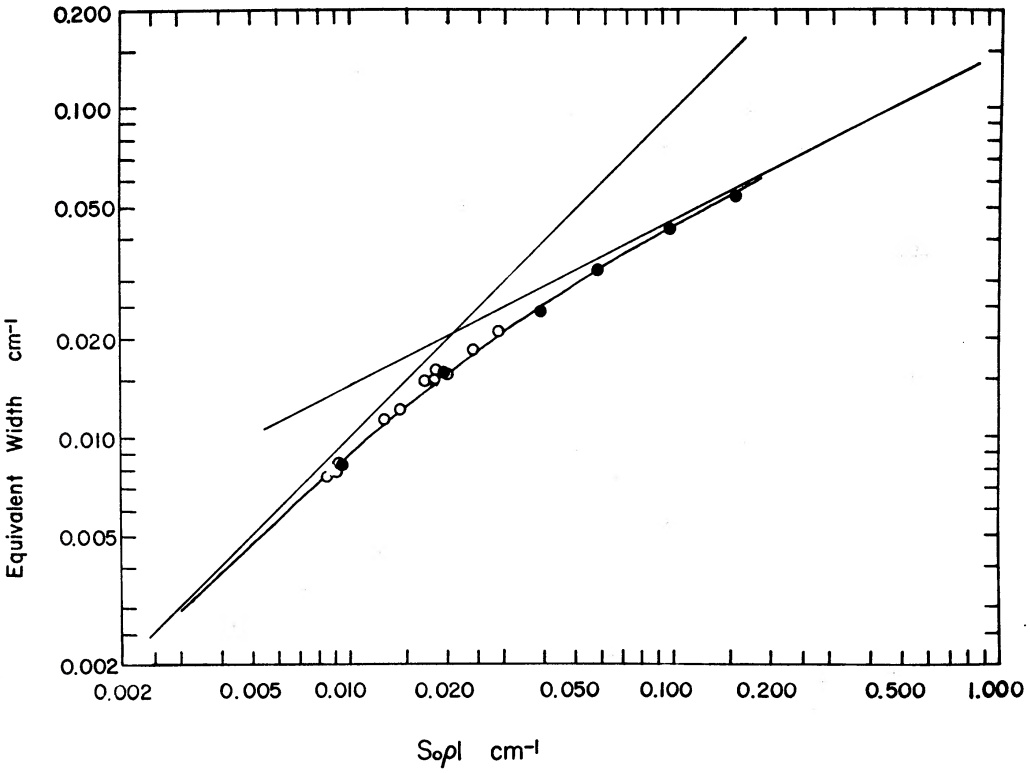

FIG. 1.—Composite curve of growth for the $S(1)$ 1–0 hydrogen quadrupole line

TABLE 2

LINE STRENGTHS IN CM^{-1}/KM-AMAGAT FOR THE $S(1)$ LINE OF THE HYDROGEN QUADRUPOLE SPECTRUM

Band	1–0	2–0	3–0	4–0
Line strength	0.0900	0.0140	0.0013	0.00009*
Ratio	1	1/6.4	1/69	1/1000*

* Calculated.

mate of the molecular hydrogen abundance on Jupiter. Our calculations are summarized in Table 3. From the equivalent widths given for these lines in the paper of Spinrad and Trafton (1963) and our curve of growth, the product $S_0\rho l$ was obtained. This was then combined with our laboratory strengths S_0 which were corrected to 150° K to obtain the abundance shown in the last column. As can be seen, there is a considerable scatter which is enhanced by the necessary correction for saturation. The average value of the total amount of H_2 observed is about 250 km-amagats. It appears now that the abundance of molecular hydrogen is considerably larger than was obtained in the earlier estimates of Zabriskie (1962) and Spinrad and Trafton (1963).

THE 121 BAND OF CARBON DIOXIDE

We have measured both the self-broadening and the nitrogen-broadening of the 121–000 band of CO_2 at 2.1 μ. In addition we have measured the integrated intensities for both the self-broadened and nitrogen-broadened lines of this band. The measurements were taken on the echelle spectrograph described by Rank, Eastman, Birtley, Skorinko,

TABLE 3

ABUNDANCE DETERMINATION OF MOLECULAR HYDROGEN ON JUPITER BY MEANS OF THE $S(1)$ QUADRUPOLE LINE

	Equivalent Width		$S_0\rho l$ (cm^{-1})	S_0 Laboratory at 150° K (cm^{-1}/km-amagat)	Abundance (km-amagat)
	mÅ	cm^{-1}			
3–0 band:					
Zabriskie (1962)	80	0.121	0.66	0.0014	471
Spinrad and Trafton (1963):					
C.M.	40	.060	.175	.0014	125
Equator	28	.042	.092	.0014	66
4–0 band:					
Spinrad and Trafton (1963)	8	0.020	0.0275	0.000097	284

and Wiggins (1960) using a PbS detector. With the entrance slit set at 0.2 mm a resolving power of about 130000 was obtained in the twelfth order of our 73.25 lines/mm Bausch and Lomb double-passed grating. The absorption cells ranged from 5.2 to 92 cm in length and the CO_2 pressures for the self-broadening case from 11 cm Hg to 70 cm Hg. The nitrogen-broadening experiments were carried out at a total pressure of about 1 atm with the CO_2 pressure a few centimeters of mercury.

a) Integrated Intensity

Intensity measurements on individual lines suffer from the drawback that a considerable portion of the absorption may be lost in determining the base line in the noise of the background. In addition the integrated absorption will be measured as too small unless the frequency scan is sufficiently great to include the extensive wings of the lines. In this experiment we have tried to correct the measured integrated intensities

$$S = \frac{1}{\rho l} \int \ln \frac{I_0}{I} \, d\nu$$

as follows. If the length of the base line of the trace is expressed in units of the half-intensity width and a Lorentz shape is assumed for the line, the amount of absorption missed can then be calculated. In the case of our CO_2 measurements the base line had a

length of from 3–10 half-widths, giving calculated correction factors, respectively, of 1.67 and 1.14.

The measured integrated intensity for each of our lines was now multiplied by its corresponding correction factor as determined by the length of its base line. The results are listed in the second column of Table 4. The numbers listed represent averages of self-broadened and nitrogen-broadened lines. The nitrogen-broadened measurements gave somewhat lower results possibly due to a small error in measuring the amount of

TABLE 4

INTEGRATED INTENSITY AND PRESSURE-BROADENING COEFFICIENTS AT 300° K OF THE 121 BAND OF CO_2

Line	Integrated Intensity (cm^{-1}/cm-amagat)	N_2 Broadened (cm^{-1}/amagat N_2)	Self-broadened (cm^{-1}/amagat CO_2)
$R(0)$	0.0026		
$R(2)$	.0083	0.170	
$R(4)$	.0157	.177	0.226
$R(6)$	.0236	.....	.227
$R(8)$	.0240	.170	.213
$R(12)$	.0303	.163	.216
$R(18)$	.0336	.161	.....
$R(20)$	.....	.....	.185
$R(26)$	.0284	.157	.....
$R(28)$	.....	.....	.174
$R(32)$	.0182	.163	.....
$R(34)$	.0133	.....	.175
$R(38)$	.0074	.160	.....
$R(40)$	.....	.....	.176
$R(44)$	.0041	.168	.....
$R(46)$	.0030	.....	.165
$P(4)$	.0120	.175	.219
$P(6)$	.0162	.183	.210
$P(8)$	.0262	.162	.207
$P(12)$	.0289	.167	.209
$P(16)$	.0317	.163	.208
$P(20)$	.0306	.160	.208
$P(28)$	.0221	.157	.188
$P(34)$	.0126	.151	.163
$P(38)$	.0083	.148	.168
$P(42)$	.0044	.153	.160
Total $J=0$ to $J=50$ (from Fig. 2).....	0.905	Mean..0.165	0.195

absorbent CO_2. The average or effective correction factor for the whole band was about 1.30. This factor, we feel, may be somewhat too large especially if the CO_2 lines do not have a Lorentz profile in the wings. The integrated intensities that we list are therefore possibly overcorrected and slightly too large.

The integrated intensities of Table 4 are plotted versus J in Figure 2. As can be seen, this band shows the R-branch and the P-branch to have approximately equal intensities. This is in contrast to the situation in the $5\nu_3$ band of CO_2 where Rank *et al.* (1960) have definitely established that the R-branch is stronger than the P-branch. Addition of all the lines from $J = 0$ to $J = 50$ taken from the smooth curve drawn in Figure 2 gives a value of 0.905 cm^{-1}/cm-amagat. If we wish to compare these results with measurements

of the total band absorption, we have to add 1 per cent for the isotope band ^{13}C and 4 per cent (using a Boltzmann distribution) for the hot band 131–010. We then obtain 0.950 cm^{-1}/cm-amagat. This value agrees quite well with the 1.00 cm^{-1}/cm-atm obtained by Weber, Holm, and Penner (1952) from measurements of the total absorption.

b) Half-Intensity Widths

The half-intensity widths that were measured from the records were first corrected for the instrument width and the Doppler width by the method described by Pigott and Rank (1957). The corrections ranged from about 20 per cent at the lowest pressures to about 2–3 per cent at atmospheric pressure. In addition the half-intensity widths measured are slightly too small due to the absorption that is lost at the base of the line as discussed above. This correction varied from about 1.11 to 1.01.

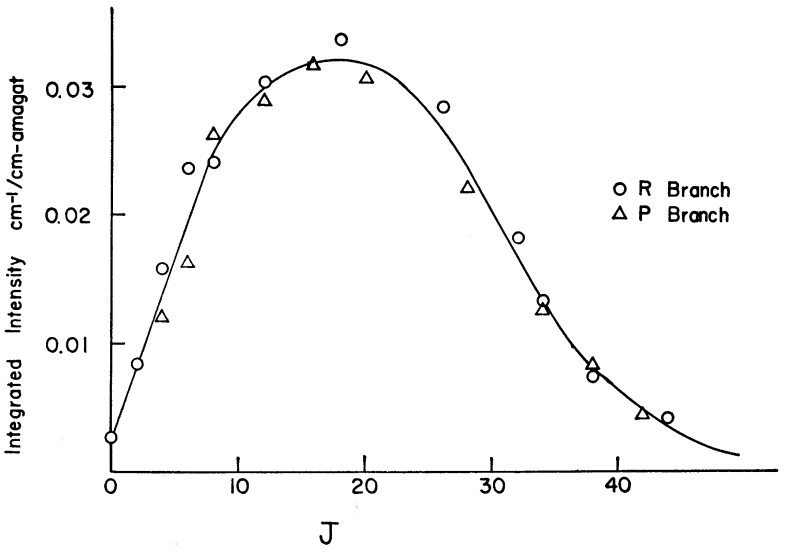

FIG. 2.—Integrated intensity of the 121–000 CO_2 band

The corrected half-widths now are the pure Lorentz components of the measured line widths. From these the pressure-broadening coefficients in cm^{-1}/amagat were found. It was noted that for pressures above a half-atmosphere the pressure-broadening coefficient obtained from lines uncorrected for Doppler and instrument width differed very little from the one using the corrected values.

The results are listed in Table 4 and are plotted versus J, the rotational ground state quantum number, in Figure 3. No difference between the P- and the R-branches can be noticed. A slight J-dependence for both N_2- and self-broadened lines is apparent. Self-broadening is seen to be slightly larger than N_2-broadening. It is, however, quite clear that self-broadening is not as much as 2.2 times more effective than N_2-broadening, as was assumed in the calculations of the total pressure on Mars by Kaplan, Münch, and Spinrad (1964).

Because of the possibility of planetary argon as a pressure-broadening agent, argon-broadening was measured for four lines from $P(8)$ to $P(20)$. With 2.3 cm CO_2 and 66.3 cm Ar, the half-widths averaged 0.162 cm^{-1}. This indicates that argon-broadening is not significantly different from self- or nitrogen-broadening.

The mean value for the nitrogen-broadened lines is 0.165 cm^{-1}/amagat, while for the self-broadened lines it is 0.195 cm^{-1}/amagat both at 300° K. Quite significantly the above result agrees very well with our measurements on nitrogen-broadening made by Rank *et*

al. (1964) on a different band of CO_2, $5\nu_3$, using photographic techniques. The result obtained there was that within the limit of experimental accuracy the broadening of the rotational lines was independent of J, while the mean increase in half intensity width was found to be 0.172 cm^{-1}/amagat of nitrogen at 300° K.

THE AMMONIA BAND AT 6450 Å

We have scanned the region around 6450 Å with a 300 lines/mm 5 × 10-inch Bausch and Lomb grating mounted in our 10-meter Czerny-Turner spectrometer. The grating was used in the ninth order and, with 0.1-mm entrance and exit slits, gave a resolving power of about 240000. Detection was by means of a 1P21 photomultiplier cooled to dry-ice temperature. Wavelength calibration and a dispersion-curve were obtained from five neon emission lines in overlapping orders. Two photoelectric recordings were taken

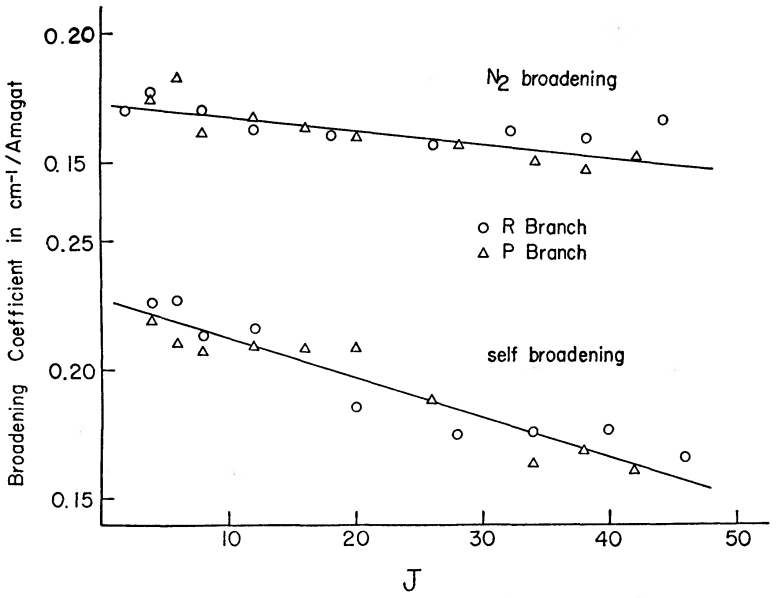

FIG. 3.—Self- and nitrogen-broadening coefficients of the 121–000 band of CO_2

with 11.3 cm ammonia and four passes of our 44-meter White tube. We then added 108 cm of hydrogen to the ammonia and took two more photoelectric tracings with four and eight passes of the tube. The region scanned contained a large number of ammonia lines with no discernible band structure. The "band" at 6450 Å consists of a complicated combination and overtone structure which has not yet been analyzed so that no J numbers could be assigned. Most lines showed a very complex fine structure under the high resolution that was employed.

We have measured the half-intensity widths of eighteen lines from 6443 to 6491 Å. These lines were selected by Giver (1964) and Spinrad and Trafton (1963) because most of them are relatively unblended with solar Fraunhofer lines and terrestrial water-vapor lines in the spectrograms of Jupiter. The measured half-widths were corrected for instrument broadening after the manner of Pigott and Rank (1957) with the instrument width taken as 0.065 cm^{-1}. From the corrected widths the pressure-broadening coefficients were found. They are listed in Table 5. To provide an idea of the strength of these lines we also list crude measurements of the equivalent width. Separation of blends with neighboring lines was sometimes quite difficult, and the measurements often include poorly resolved fine structure close to the lines.

The measured broadening coefficients vary considerably due to the complex structure

of the lines. The broadening coefficients for several lines which are considerably larger than the average are not realistic but are caused by the blending of the fine structure in the pressure-broadened case. Since only a few lines resemble a Lorentz profile the listed pressure-broadening coefficients should not be associated with a single line. The cleanest-looking line except for some small structure at its base appears to be the one at 6457.13 Å. The average pressure-broadening coefficient is 0.175 cm^{-1}/amagat.

THE $2\nu_3$ BAND OF METHANE

In the case of carbon dioxide we found in this investigation that the pressure-broadening coefficients for the $5\nu_3$ band and the 121 band were the same within experimental error. Broadening coefficients for methane are of considerable astrophysical interest; yet,

TABLE 5

EQUIVALENT WIDTHS AND PRESSURE-BROADENING COEFFICIENTS OF 18 LINES IN THE 6450 Å AMMONIA BAND

Wavelength (Å)	Equivalent Width ($\times 10^{-3}$ cm^{-1}/m-amagat)	Pressure-broadening Coefficient at 300° K (cm^{-1}/amagat of N_2)
6443.79	2.8	0.262
6444.57	3.8	.178
6445.53	5.2	.136
6446.49	5.6	.164
6447.30	4.0	.322
6449.30	1.4	.302
6451.14	3.6	.140
6452.15	1.5	.164
6452.64	4.1	.154
6457.13	4.5	.178
6459.09	1.8	.213
6460.49	1.9	.158
6465.35	3.6	.176
6469.64	1.8	.126
6479.25	2.5	.066
6488.31	2.9	.144
6489.91	3.3	.156
6490.46	1.7	.114
		Mean..0.175

to our knowledge, no direct measurements of methane-broadening exist in the literature. Since it was comparatively easy to work on the $2\nu_3$ band of methane at 1.67 μ, we decided to make measurements on this band. It seems very unlikely that the broadening coefficients for the other bands should be very much different.

The measurements of self- and hydrogen-broadening were restricted to lines of low J, since Rank, Eastman, Skorinko, and Wiggins (1960) have shown that the higher J lines of this band show considerable Coriolis splitting. The 5-meter spectrograph described by Rank, Eastman, Birtley, Skorinko, and Wiggins (1960) was double-passed in the fourteenth and fifteenth order with a resulting resolution of about 140000. A 1-meter absorption tube contained methane at low pressure and hydrogen at approximately atmospheric pressure for measurement of hydrogen-broadening. For self-broadening 5- and 10-cm cells were used at about atmospheric methane pressure. The lines were corrected for instrument and Doppler width after the manner of Pigott and Rank (1957). The lines $R(3)$, $R(4)$, and $P(3)$ were additionally corrected for the unresolved line splitting shown by Rank, Eastman, Skorinko, and Wiggins (1960) to exist in these lines. The results are

listed in Table 6. Integrated intensity measurements in $R(0)$ and $P(2)$ of the same band have been reported by Fink, Wiggins, and Rank (1965) in conjunction with the abundance determination of methane in the Earth's atmosphere. The broadening coefficient obtained in this paper for the $2\nu_3$ band is considerably larger than the 0.08 cm^{-1}/atm assumed by Spinrad and Trafton (1963).

TABLE 6

HYDROGEN- AND SELF-BROADENING COEFFICIENTS OF SOME LOW J LINES IN THE $2\nu_3$ BAND OF METHANE

Line	Hydrogen-broadening Coefficient (cm^{-1}/amagat)	Self-broadening Coefficient (cm^{-1}/amagat)
$R(0)$	0.146	0.171
$R(1)$	.153	.181
$R(2)$	.144	.172
$P(2)$	.156	.172
$R(3)$	.142	.....
$R(4)$	.150	.....
$P(3)$	.150	.....
Mean	0.149	0.174

We are indebted to T. A. Davis, R. V. Wick, and C. P. Scoboria for preliminary work on CO_2, NH_3, and CH_4. This preliminary work has been the subject of Master's theses by the above-mentioned persons. We have been assisted in part of this work by L. P. Giver, particularly the work on NH_3.

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