

# <sup>1</sup>Infrared Absorption Spectrum of Methane From 2470 to 3200 cm<sup>-1</sup>

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(January 11, 1960)

The absorption spectrum of methane has been measured from 2470 to 3200 cm<sup>-1</sup> with a high-resolution infrared spectrometer. Pressures from 0.01 to 4.5 cm of the gas were used in order to observe both intense and weak lines. A total of 2,460 lines were measured in the entire region. The  $\nu_3$  band at 3018 cm<sup>-1</sup> was measured at very slow scanning rates and the lines of the *P* and *R* branches were resolved into several components. The observed spectrum is shown in five figures.

## 1. Introduction

A number of researches have been made on the infrared spectrum of methane since the first interpretation of the observed spectrum was made by Dennison in 1925 [1].<sup>2</sup> It is now well established that the tetrahedral model is in accord with all the measurements of the infrared and the Raman spectrum. There are four fundamental vibrations which occur at about 2914, 1534, 3018, and 1306 cm<sup>-1</sup> which are designated as  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$ , respectively. For a rigid molecule of this symmetry only the  $\nu_3$  and  $\nu_4$  vibrations are active in the infrared, but on account of interactions  $\nu_2$  becomes active in the infrared spectrum. This band has been measured by Burgess, Bell, and Nielsen [2]. More recently it has been shown by Allen and Plyler [3] that the  $\nu_3$  vibration at 3018 cm<sup>-1</sup> which is triply degenerate has a weak component with a  $Q(F^+)$  branch at 3022 cm<sup>-1</sup>. The  $Q(F^-)$  branch is also probably active, but it has not been observed and may be strongly overlapped by the strong  $Q(F^0)$  branch.

When the  $\nu_3$  band of methane is measured with low resolution the lines of the *P* and *R* branches are observed as single. With better resolution lines having large *J*'s begin to split up into several components. This splitting was found by Nielsen [4] to be rather large in  $\nu_4$ , and Childs and Jahn [5] explained the splitting as produced by the Coriolis interaction between  $\nu_2$  and  $\nu_4$ . The rotational structure of  $\nu_3$  also shows splittings in the *P* and *R* branches, but the separation between the components is much less than in  $\nu_4$ . With a resolution of 0.05 cm<sup>-1</sup> the lines of the *P* branch with  $J \geq 2$  and the lines of the *R* branch with  $J \geq 3$  have all been split into components (see ref. 3), the lines from *P* 9 to *P* 15 each showing four components. The present investigation was undertaken to ascertain if, with higher resolution, the rotational lines

of the *P* and *R* branches of  $\nu_3$  could be split into a greater number of components and to search for other bands which may appear in the region 2470 to 3200 cm<sup>-1</sup>.

## 2. Experimental Method

There was available in the Radiometry Section of the Bureau an infrared spectrometer which has a resolution between 0.02 and 0.03 cm<sup>-1</sup>. The instrument is equipped with a 10,000 line/inch grating which has a ruled surface of 4 $\frac{3}{4}$  x 8 in. The grating is double-passed and the energy is detected by a cooled PbS cell. A full description of the instrument is given in a previous paper [6]. The spectra were measured by using the fringes of a Fabry-Perot interferometer to interpolate between standard lines. As this method of measurement has been previously described [7] the details will not be repeated.

The methane gas was obtained from the Matheson Company and the purity was given as 99 percent. No further purification of the gas was made. In the measurement of the spectra the gas pressure for different spectral regions was varied from 0.1 mm to 4.5 cm. The absorption cell had a path of 6 m which made it possible to use very low pressures in the regions of strong absorption. The spectrum was observed at various scanning speeds. In the regions where it was desired to bring out as much structure as possible, the spectrum was scanned at the rate of one wavenumber in 10 min, but in scanning the entire region from 2470 to 3200 cm<sup>-1</sup> one wavenumber was recorded per minute. Even at this faster rate 12 hr were necessary and 32 ft of recorder paper were required for scanning the entire region. For the measuring charts a slower speed was used and 60 hr were required to cover the region included in figures 1, 2, and 3.

## 3. Experimental Results

Photographs of the recorder traces of the observed spectrum are shown in figures 1, 2, and 3. Figure 1

<sup>1</sup> This work was supported by the Geophysics Research Directorate, Air Force.  
<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

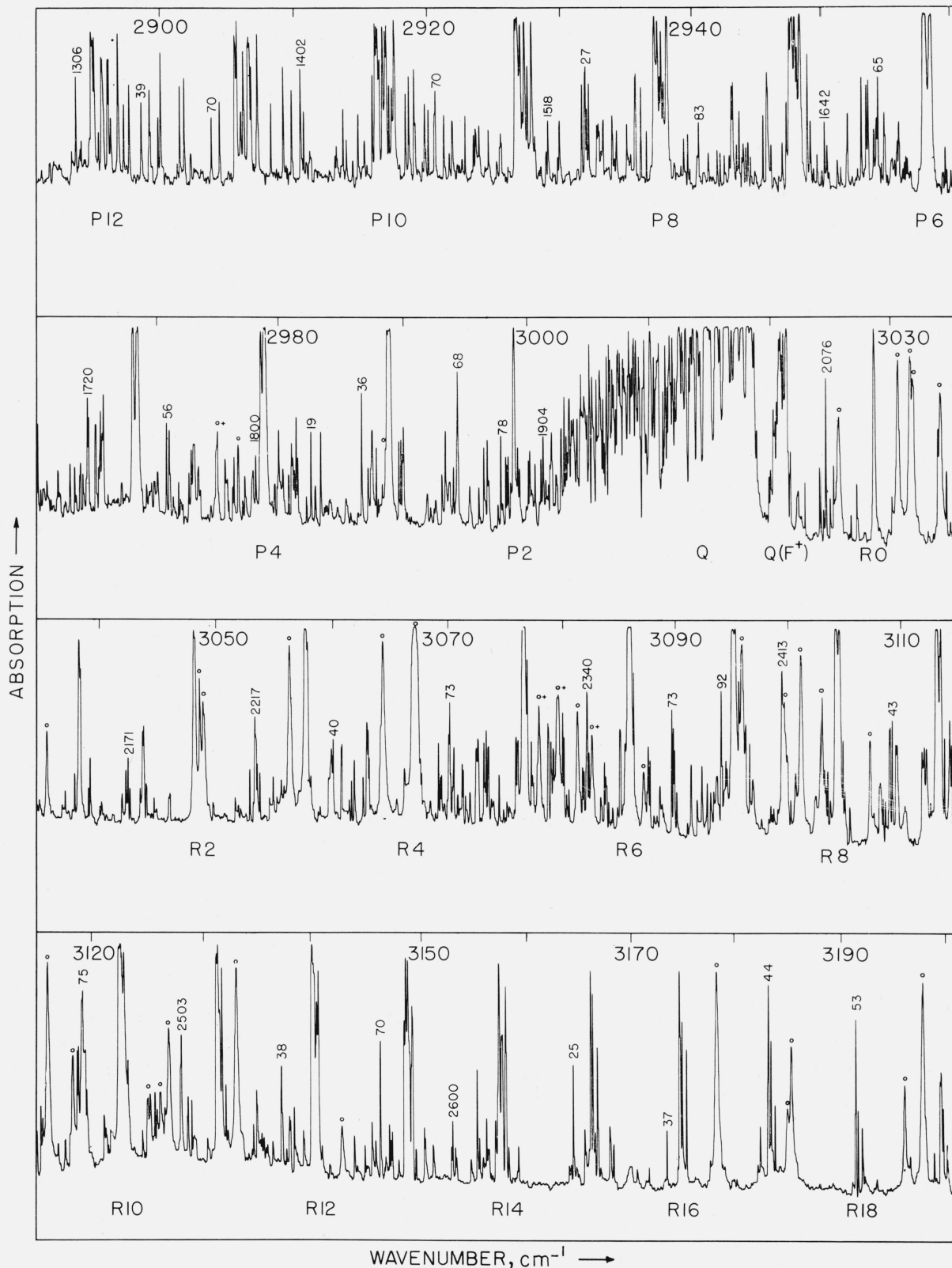


FIGURE 1. The infrared absorption of methane from 2890 to 3200  $\text{cm}^{-1}$  as observed with a 10,000 lines/in grating used double pass.

The gas pressure was 2 cm in a 6-m cell. The numbers on the lines correspond with those given in table 1.

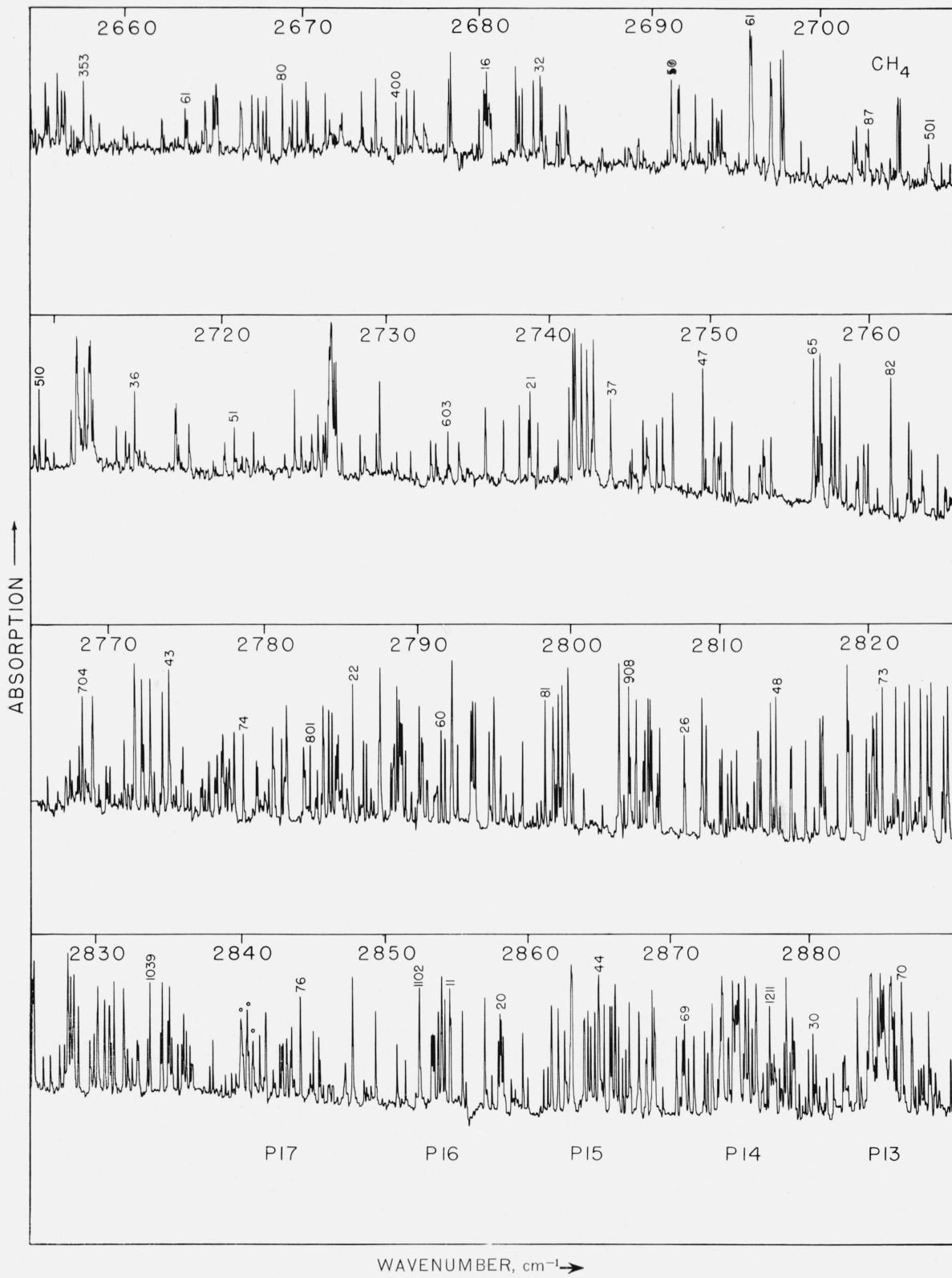


FIGURE 2. The observed spectrum of methane from 2655 to 2890  $\text{cm}^{-1}$ .

The conditions of measurement were the same as for figure 1.

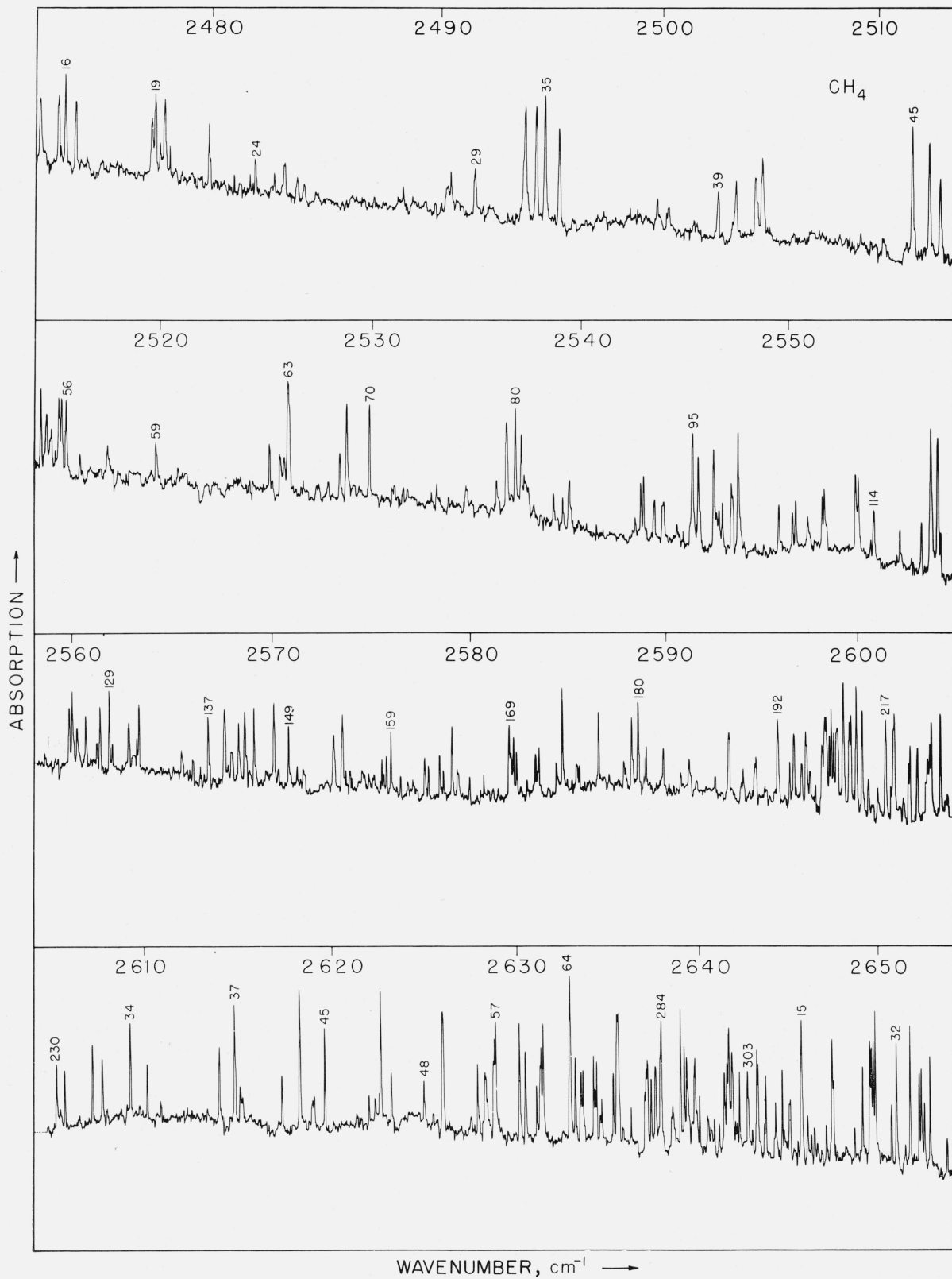


FIGURE 3. The observed spectrum of methane from 2470 to 2655  $\text{cm}^{-1}$ .

The pressure of the gas was 4.5 cm. The other conditions of measurement were the same as for the spectra in figures 1 and 2.



covers the region from 2890 to 3200  $\text{cm}^{-1}$  and includes the intense component of  $\nu_3$  from  $R$  18 to  $P$  12. The pressure of the gas in the cell was 2 cm for the spectrum in figures 1 and 2 and 4.5 cm for the results shown in figure 3. These pressures were selected in order to make it possible to observe the lines between the  $P$  and  $R$  branches of the main band.

About 2,650 lines were measured in the region from 2470 to 3200  $\text{cm}^{-1}$  and serial numbers were placed on the figures which correspond with the line numbers given in table 1. This makes it possible to ascertain the wavenumber of any line in the observed spectrum.

The amount of gas was too large and the scanning speed was too rapid to properly measure the components of the lines in the  $P$ ,  $Q$ , and  $R$  branches of the most intense component of  $\nu_3$ . In figure 4 is shown the spectrum of the  $Q$  branch and the  $P$  branch of this component as observed with 0.1 mm of pressure of methane.

The  $Q(P^\circ)$  branch has very intense lines and the spectrum can be better represented by using less gas and scanning at a slower speed. The  $Q$  branch of this band, shown at the bottom strip of figure 5, was observed with a pressure between 0.1 and 0.01 mm and the scanning speed is one-third of that used in figure 4.

TABLE 1. *Vibration-rotation wavenumbers of methane from 2,450 to 3,200  $\text{cm}^{-1}$*

| Line No. | $\text{cm}^{-1}$ | Line No. | $\text{cm}^{-1}$ | Line No. | $\text{cm}^{-1}$ | Line No. | $\text{cm}^{-1}$ | Line No. | $\text{cm}^{-1}$ | Line No. | $\text{cm}^{-1}$ |
|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|
| 1        | 2450.87          | 60       | 2525.17          | 120      | 2557.55          | 181      | 2589.01          | 242      | 2618.90          | 300      | 2642.13          |
| 2        | 2451.10          | 61       | 2525.68          | 121      | 2559.83          | 182      | 2589.87          | 243      | 2618.94          | 301      | 2642.24          |
| 3        | 2452.32          | 62       | 2525.85          | 122      | 2560.00          | 184      | 2591.21          | 244      | 2619.03          | 302      | 2642.55          |
| 4        | 2452.87          | 63       | 2526.05          | 123      | 2560.20          | 185      | 2591.56          | 245      | 2619.59          | 303      | 2642.70          |
| 5        | 2459.59          | 64       | 2526.10          | 124      | 2560.57          | 186      | 2593.26          | 245a     | 2622.50          | 304      | 2642.98          |
| 6        | 2459.80          | 65       | 2527.38          | 125      | 2560.64          | 187      | 2593.91          | 246      | 2622.61          | 305      | 2643.22          |
| 7        | 2463.38          | 66       | 2527.46          | 126      | 2561.11          | 188      | 2593.99          | 247      | 2623.19          | 306      | 2643.29          |
| 8        | 2464.70          | 67       | 2527.94          | 127      | 2561.19          | 189      | 2594.60          | 248      | 2624.93          | 307      | 2643.64          |
| 9        | 2464.93          | 68       | 2528.46          | 128      | 2561.35          | 190      | 2594.65          | 249      | 2625.95          | 308      | 2643.72          |
| 10       | 2465.74          | 69       | 2528.81          | 129      | 2561.82          | 191      | 2595.18          | 250      | 2625.98          | 309      | 2643.82          |
| 11       | 2466.58          | 70       | 2529.88          | 130      | 2561.96          | 192      | 2595.79          | 251      | 2627.86          | 310      | 2644.18          |
| 12       | 2467.16          | 71       | 2530.96          | 131      | 2562.78          | 193      | 2596.43          | 252      | 2627.96          | 311      | 2644.24          |
| 13       | 2471.03          | 72       | 2531.08          | 132      | 2562.98          | 194      | 2596.66          | 253      | 2628.26          | 312      | 2644.65          |
| 14       | 2472.50          | 73       | 2531.46          | 133      | 2563.19          | 195      | 2597.09          | 254      | 2628.32          | 313      | 2645.04          |
| 15       | 2473.31          | 74       | 2533.09          | 134      | 2563.31          | 196      | 2597.28          | 255      | 2628.70          | 314      | 2645.09          |
| 16       | 2473.61          | 75       | 2534.53          | 135      | 2565.44          | 197      | 2597.34          | 256      | 2628.76          | 315      | 2645.73          |
| 17       | 2474.05          | 76       | 2535.99          | 136      | 2566.04          | 198      | 2597.52          | 257      | 2628.86          | 316      | 2646.04          |
| 18       | 2477.35          | 77       | 2536.45          | 137      | 2566.82          | 199      | 2598.13          | 258      | 2630.17          | 317      | 2646.24          |
| 19       | 2477.51          | 78       | 2536.49          | 138      | 2567.65          | 200      | 2598.27          | 259      | 2630.48          | 318      | 2646.40          |
| 20       | 2477.72          | 79       | 2536.68          | 139      | 2567.81          | 201      | 2598.36          | 260      | 2631.08          | 319      | 2646.58          |
| 21       | 2477.91          | 80       | 2536.88          | 140      | 2567.95          | 202      | 2598.53          | 261      | 2631.27          | 320      | 2646.84          |
| 22       | 2478.12          | 81       | 2537.01          | 141      | 2568.02          | 203      | 2598.65          | 262      | 2631.34          | 321      | 2647.08          |
| 23       | 2479.86          | 82       | 2537.17          | 142      | 2568.30          | 204      | 2598.76          | 263      | 2631.47          | 322      | 2647.31          |
| 24       | 2481.86          | 83       | 2537.33          | 143      | 2568.61          | 205      | 2598.88          | 264      | 2632.93          | 323      | 2647.42          |
| 25       | 2483.16          | 84       | 2537.39          | 144      | 2568.72          | 206      | 2598.92          | 265      | 2633.21          | 324      | 2647.50          |
| 26       | 2483.70          | 85       | 2538.72          | 145      | 2569.10          | 207      | 2598.97          | 266      | 2633.44          | 325      | 2648.66          |
| 27       | 2490.32          | 86       | 2539.17          | 146      | 2569.64          | 208      | 2599.27          | 267      | 2633.52          | 326      | 2649.14          |
| 28       | 2490.50          | 87       | 2539.48          | 147      | 2570.10          | 209      | 2599.52          | 268      | 2633.62          | 327      | 2649.52          |
| 29       | 2491.62          | 88       | 2542.94          | 148      | 2570.31          | 210      | 2599.57          | 269      | 2634.21          | 328      | 2649.61          |
| 30       | 2493.09          | 89       | 2543.08          | 149      | 2570.83          | 211      | 2599.64          | 270      | 2634.30          | 329      | 2649.71          |
| 31       | 2493.70          | 90       | 2543.55          | 150      | 2573.06          | 212      | 2599.79          | 271      | 2634.39          | 330      | 2649.83          |
| 32       | 2493.82          | 91       | 2543.92          | 151      | 2573.46          | 213      | 2599.93          | 272      | 2634.58          | 331      | 2650.74          |
| 33       | 2493.90          | 92       | 2544.00          | 152      | 2573.53          | 214      | 2600.27          | 273      | 2634.66          | 332      | 2651.02          |
| 34       | 2494.38          | 93       | 2545.28          | 153      | 2573.73          | 215      | 2600.58          | 274      | 2635.29          | 333      | 2651.50          |
| 35       | 2494.77          | 94       | 2545.35          | 154      | 2573.92          | 216      | 2601.06          | 275      | 2635.50          | 334      | 2651.81          |
| 36       | 2495.40          | 95       | 2545.39          | 155      | 2575.12          | 217      | 2601.49          | 276      | 2635.56          | 335      | 2652.29          |
| 37       | 2499.81          | 96       | 2545.68          | 156      | 2575.50          | 218      | 2601.86          | 277      | 2636.31          | 336      | 2652.42          |
| 38       | 2500.30          | 97       | 2546.42          | 157      | 2575.60          | 219      | 2601.92          | 278      | 2636.99          | 337      | 2652.59          |
| 39       | 2502.58          | 98       | 2546.54          | 158      | 2575.73          | 220      | 2602.66          | 279      | 2637.07          | 338      | 2652.92          |
| 40       | 2503.40          | 99       | 2546.66          | 159      | 2575.98          | 222      | 2602.76          | 280      | 2637.14          | 339      | 2653.85          |
| 41       | 2504.30          | 100      | 2546.84          | 160      | 2576.46          | 223      | 2603.02          | 281      | 2637.33          | 340      | 2654.58          |
| 42       | 2504.38          | 101      | 2547.12          | 161      | 2576.82          | 224      | 2603.13          | 282      | 2637.58          | 341      | 2654.72          |
| 43       | 2504.58          | 102      | 2547.27          | 162      | 2577.11          | 225      | 2603.57          | 283      | 2637.85          | 342      | 2654.98          |
| 44       | 2504.63          | 103      | 2547.36          | 163      | 2577.70          | 226      | 2603.66          | 284      | 2637.90          | 343      | 2655.54          |
| 45       | 2511.55          | 104      | 2547.62          | 164      | 2577.89          | 227      | 2603.77          | 285      | 2638.45          | 344      | 2655.68          |
| 46       | 2512.33          | 105      | 2549.59          | 166      | 2578.48          | 228      | 2603.86          | 286      | 2638.52          | 345      | 2655.85          |
| 47       | 2512.84          | 106      | 2550.26          | 167      | 2578.67          | 229      | 2604.32          | 287      | 2638.97          | 346      | 2655.96          |
| 47a      | 2512.92          | 107      | 2550.42          | 168      | 2579.09          | 230      | 2605.34          | 288      | 2639.18          | 347      | 2656.14          |
| 48       | 2514.50          | 108      | 2551.03          | 169      | 2582.01          | 230a     | 2605.52          | 289      | 2639.30          | 348      | 2656.21          |
| 49       | 2514.67          | 109      | 2551.74          | 170      | 2582.08          | 231      | 2605.75          | 290      | 2639.37          | 349      | 2656.36          |
| 50       | 2514.75          | 110      | 2551.84          | 171      | 2582.22          | 232      | 2607.25          | 290a     | 2639.60          | 350      | 2656.44          |
| 51       | 2514.90          | 111      | 2553.38          | 172      | 2582.39          | 233      | 2607.75          | 291      | 2639.71          | 351      | 2656.62          |
| 52       | 2514.96          | 112      | 2553.50          | 173      | 2583.35          | 234      | 2609.25          | 292      | 2639.76          | 352      | 2656.65          |
| 53       | 2515.14          | 113      | 2553.58          | 174      | 2583.52          | 235      | 2610.16          | 293      | 2639.83          | 353      | 2657.71          |
| 54       | 2515.31          | 114      | 2554.28          | 175      | 2584.42          | 236      | 2614.16          | 294      | 2640.00          | 354      | 2658.11          |
| 55       | 2515.45          | 115      | 2555.54          | 176      | 2584.73          | 237      | 2614.77          | 295      | 2641.41          | 355      | 2658.58          |
| 56       | 2515.66          | 116      | 2555.64          | 177      | 2586.59          | 238      | 2615.06          | 296      | 2641.54          | 356      | 2659.90          |
| 57       | 2516.28          | 117      | 2556.60          | 178      | 2588.30          | 239      | 2615.18          | 297      | 2641.66          | 357      | 2662.06          |
| 58       | 2517.58          | 118      | 2557.08          | 179      | 2588.40          | 240      | 2617.29          | 298      | 2641.85          | 358      | 2662.10          |
| 59       | 2519.84          | 119      | 2557.42          | 180      | 2588.64          | 241      | 2618.27          | 299      | 2642.03          | 359      | 2663.01          |

TABLE 1. *Vibration-rotation wavenumbers of methane from 2,450 to 3,200 cm<sup>-1</sup>—Continued*

| Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> |
|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|
| 360      | 2663.28          | 450      | 2691.20          | 530      | 2712.94          | 619      | 2738.14          | 702      | 2767.96          | 784      | 2780.26          |
| 361      | 2663.38          | 451      | 2691.39          | 531      | 2713.05          | 620      | 2738.68          | 703      | 2768.06          | 785      | 2780.53          |
| 362      | 2663.48          | 452      | 2691.59          | 532      | 2713.66          | 621      | 2738.79          | 704      | 2768.27          | 786      | 2780.60          |
| 364      | 2664.51          | 453      | 2691.66          | 533      | 2714.22          | 622      | 2739.26          | 705      | 2768.45          | 787      | 2780.64          |
| 366      | 2664.77          | 453a     | 2692.31          | 534      | 2714.35          | 623      | 2740.24          | 705a     | 2768.52          | 788      | 2780.73          |
| 367      | 2664.96          | 454      | 2692.64          | 535      | 2714.43          | 624      | 2740.36          | 706      | 2768.59          | 789      | 2780.90          |
| 368      | 2665.07          | 455      | 2693.40          | 536      | 2714.76          | 625      | 2740.48          | 707      | 2768.64          | 790      | 2781.08          |
| 369      | 2665.16          | 456      | 2693.62          | 537      | 2715.06          | 626      | 2741.19          | 708      | 2768.91          | 791      | 2781.21          |
| 370      | 2665.27          | 457      | 2693.88          | 538      | 2716.84          | 627      | 2741.44          | 709      | 2768.94          | 792      | 2781.26          |
| 371      | 2666.28          | 458      | 2693.99          | 539      | 2717.07          | 628      | 2741.58          | 710      | 2769.05          | 793      | 2781.40          |
| 372      | 2666.47          | 459      | 2694.17          | 540      | 2717.21          | 629      | 2741.96          | 711      | 2769.21          | 794      | 2781.48          |
| 373      | 2666.53          | 460      | 2694.37          | 541      | 2717.29          | 630      | 2742.28          | 712      | 2769.32          | 795      | 2781.93          |
| 374      | 2667.13          | 461      | 2695.82          | 542      | 2717.42          | 631      | 2742.35          | 713      | 2769.43          | 796      | 2782.37          |
| 375      | 2667.46          | 462      | 2695.85          | 543      | 2717.95          | 632      | 2742.55          | 714      | 2769.52          | 797      | 2782.51          |
| 376      | 2667.74          | 463      | 2695.89          | 544      | 2718.05          | 633      | 2742.60          | 715      | 2769.67          | 798      | 2782.61          |
| 377      | 2667.94          | 464      | 2695.95          | 545      | 2718.13          | 634      | 2742.73          | 716      | 2769.73          | 799      | 2782.71          |
| 378      | 2668.10          | 465      | 2696.01          | 546      | 2718.20          | 636      | 2743.68          | 717      | 2769.78          | 800      | 2782.77          |
| 379      | 2668.24          | 466      | 2696.24          | 547      | 2719.46          | 637      | 2743.78          | 718      | 2769.88          | 801      | 2782.93          |
| 380      | 2668.85          | 467      | 2696.55          | 548      | 2719.62          | 638      | 2744.94          | 719      | 2770.04          | 802      | 2783.22          |
| 383      | 2669.25          | 468      | 2696.64          | 549      | 2720.10          | 639      | 2745.08          | 720      | 2770.20          | 803      | 2783.28          |
| 384      | 2669.41          | 469      | 2696.95          | 550      | 2720.15          | 640      | 2745.72          | 721      | 2770.32          | 804      | 2783.34          |
| 385      | 2669.70          | 470      | 2697.00          | 551      | 2720.78          | 641      | 2745.84          | 722      | 2770.45          | 805      | 2783.42          |
| 386      | 2669.92          | 471      | 2697.06          | 552      | 2720.90          | 642      | 2745.93          | 723      | 2770.62          | 806      | 2783.68          |
| 387      | 2670.20          | 472      | 2697.12          | 553      | 2721.13          | 643      | 2746.04          | 724      | 2770.76          | 807      | 2783.78          |
| 388      | 2670.32          | 473      | 2697.49          | 554      | 2721.23          | 644      | 2746.57          | 725      | 2770.82          | 808      | 2783.83          |
| 390      | 2670.54          | 474      | 2697.66          | 555      | 2721.38          | 645      | 2746.95          | 726      | 2770.94          | 809      | 2784.08          |
| 391      | 2671.28          | 475      | 2697.81          | 556      | 2721.49          | 646      | 2747.61          | 727      | 2771.05          | 810      | 2784.15          |
| 392      | 2671.53          | 476      | 2698.83          | 557      | 2721.78          | 647      | 2749.49          | 728      | 2771.18          | 811      | 2784.36          |
| 394      | 2672.12          | 477      | 2699.19          | 558      | 2721.90          | 648      | 2749.66          | 729      | 2771.27          | 812      | 2784.58          |
| 395      | 2672.22          | 478      | 2699.26          | 559      | 2721.94          | 649      | 2750.16          | 730      | 2771.43          | 813      | 2784.67          |
| 398      | 2673.35          | 478a     | 2700.37          | 560      | 2722.10          | 650      | 2750.20          | 731      | 2771.60          | 814      | 2784.76          |
| 399      | 2674.15          | 479      | 2701.51          | 561      | 2722.20          | 651      | 2750.45          | 732      | 2771.67          | 815      | 2784.90          |
| 400      | 2675.28          | 480      | 2701.61          | 562      | 2722.42          | 652      | 2750.62          | 733      | 2772.09          | 816      | 2785.01          |
| 401      | 2675.64          | 481      | 2701.90          | 563      | 2723.79          | 653      | 2750.88          | 734      | 2772.21          | 817      | 2785.10          |
| 402      | 2675.91          | 482      | 2702.03          | 564      | 2723.90          | 654      | 2751.31          | 735      | 2772.56          | 818      | 2785.20          |
| 403      | 2676.27          | 483      | 2702.10          | 565      | 2724.26          | 655      | 2752.40          | 736      | 2772.63          | 819      | 2785.26          |
| 404      | 2676.34          | 484      | 2702.40          | 566      | 2724.35          | 656      | 2752.60          | 737      | 2772.73          | 820      | 2785.32          |
| 405      | 2676.92          | 485      | 2702.66          | 567      | 2724.40          | 657      | 2752.99          | 738      | 2772.92          | 821      | 2785.68          |
| 406      | 2677.01          | 486      | 2702.72          | 568      | 2724.79          | 658      | 2753.07          | 739      | 2773.26          | 822      | 2785.72          |
| 407      | 2677.64          | 487      | 2702.81          | 569      | 2725.04          | 659      | 2753.24          | 740      | 2773.43          | 823      | 2786.10          |
| 408      | 2678.30          | 488      | 2703.31          | 570      | 2725.29          | 660      | 2753.33          | 741      | 2773.71          | 824      | 2786.26          |
| 409      | 2678.34          | 489      | 2703.59          | 571      | 2725.40          | 663      | 2753.75          | 742      | 2773.77          | 825      | 2786.42          |
| 410      | 2678.48          | 490      | 2704.11          | 572      | 2725.48          | 664      | 2756.37          | 743      | 2773.84          | 826      | 2786.63          |
| 411      | 2678.70          | 491      | 2704.32          | 573      | 2725.81          | 665      | 2756.46          | 744      | 2773.96          | 827      | 2786.82          |
| 412      | 2679.20          | 492      | 2704.56          | 574      | 2726.12          | 666      | 2756.61          | 745      | 2774.14          | 828      | 2786.88          |
| 413      | 2680.00          | 493      | 2704.61          | 575      | 2726.27          | 667      | 2756.71          | 746      | 2774.32          | 829      | 2787.07          |
| 414      | 2680.37          | 494      | 2704.73          | 576      | 2726.43          | 668      | 2756.88          | 747      | 2774.65          | 830      | 2787.21          |
| 415      | 2680.46          | 495      | 2704.82          | 577      | 2726.50          | 669      | 2756.98          | 748      | 2774.73          | 831      | 2787.28          |
| 416      | 2680.55          | 496      | 2705.13          | 578      | 2726.63          | 670      | 2757.14          | 749      | 2774.94          | 832      | 2787.44          |
| 417      | 2680.64          | 499      | 2706.17          | 580      | 2726.68          | 671      | 2757.46          | 750      | 2775.05          | 833      | 2787.51          |
| 418      | 2680.68          | 500      | 2706.34          | 581      | 2726.79          | 672      | 2757.58          | 751      | 2775.30          | 834      | 2787.84          |
| 419      | 2680.80          | 501      | 2706.40          | 582      | 2726.91          | 673      | 2757.82          | 752      | 2775.52          | 835      | 2788.19          |
| 420      | 2681.37          | 502      | 2707.50          | 583      | 2727.25          | 674      | 2758.13          | 753      | 2775.93          | 836      | 2788.32          |
| 421      | 2681.56          | 503      | 2707.76          | 584      | 2728.37          | 675      | 2758.54          | 754      | 2776.02          | 837      | 2788.39          |
| 422      | 2682.23          | 504      | 2707.15          | 585      | 2728.63          | 676      | 2759.10          | 755      | 2776.18          | 838      | 2788.43          |
| 423      | 2682.35          | 505      | 2707.28          | 586      | 2728.69          | 677      | 2759.18          | 756      | 2776.38          | 839      | 2788.60          |
| 424      | 2682.42          | 506      | 2707.64          | 587      | 2729.34          | 678      | 2759.27          | 757      | 2776.44          | 840      | 2788.72          |
| 425      | 2682.61          | 507      | 2708.52          | 588      | 2729.56          | 679      | 2759.63          | 758      | 2776.78          | 841      | 2788.76          |
| 426      | 2682.72          | 508      | 2708.73          | 589      | 2730.10          | 680      | 2759.70          | 759      | 2776.92          | 842      | 2788.84          |
| 427      | 2682.86          | 509      | 2708.82          | 590      | 2730.29          | 681      | 2759.92          | 760      | 2777.10          | 843      | 2788.94          |
| 429      | 2683.25          | 510      | 2709.05          | 591      | 2730.61          | 682      | 2761.35          | 761      | 2777.18          | 844      | 2789.15          |
| 430      | 2683.45          | 511      | 2709.41          | 592      | 2730.70          | 683      | 2762.34          | 762      | 2777.28          | 845      | 2789.55          |
| 431      | 2683.52          | 512      | 2709.51          | 593      | 2713.46          | 684      | 2762.47          | 763      | 2777.31          | 846      | 2789.66          |
| 432      | 2683.64          | 513      | 2709.91          | 594      | 2731.80          | 685      | 2762.65          | 764      | 2777.39          | 847      | 2789.77          |
| 433      | 2683.75          | 514      | 2710.08          | 597      | 2732.68          | 686      | 2763.33          | 765      | 2777.51          | 848      | 2789.93          |
| 434      | 2683.95          | 515      | 2710.96          | 598      | 2733.00          | 687      | 2763.40          | 766      | 2777.55          | 849      | 2790.06          |
| 435      | 2684.58          | 516      | 2711.27          | 599      | 2733.13          | 688      | 2764.30          | 767      | 2777.69          | 850      | 2790.23          |
| 436      | 2684.64          | 517      | 2711.32          | 601      | 2733.56          | 689      | 2764.74          | 768      | 2777.74          | 851      | 2790.30          |
| 437      | 2684.74          | 518      | 2711.41          | 602      | 2733.68          | 690      | 2764.83          | 769      | 2777.84          | 852      | 2790.42          |
| 438      | 2685.12          | 519      | 2711.46          | 603      | 2733.74          | 691      | 2765.06          | 770      | 2777.95          | 853      | 2790.56          |
| 439      | 2685.25          | 520      | 2711.49          | 604      | 2733.83          | 692      | 2765.20          | 771      | 2778.04          | 854      | 2790.60          |
| 441      | 2687.18          | 521      | 2711.58          | 605      | 2733.88          | 693      | 2765.72          | 774      | 2778.64          | 856      | 2791.03          |
| 442      | 2688.52          | 522      | 2711.71          | 606      | 2733.94          | 694      | 2766.02          | 776      | 2779.48          | 857      | 2791.10          |
| 443      | 2688.72          | 523      | 2711.76          | 607      | 2734.44          | 695      | 2766.68          | 777      | 2779.57          | 858      | 2791.17          |
| 444      | 2689.17          | 524      | 2711.95          | 610      | 2734.90          | 696      | 2767.18          | 778      | 2779.72          | 859      | 2791.24          |
| 445      | 2689.25          | 525      | 2712.05          | 611      | 2735.00          | 697      | 2767.23          | 779      | 2779.76          | 860      | 2791.47          |
| 446      | 2689.33          | 526      | 2712.11          | 613      | 2735.44          | 698      | 2767.48          | 780      | 2779.87          | 861      | 2791.75          |
| 447      | 2689.53          | 527      | 2712.14          | 614      | 2736.04          | 699      | 2767.62          | 781      | 2779.98          | 862      | 2792.14          |
| 448      | 2689.60          | 528      | 2712.27          | 617      | 2737.04          | 700      | 2767.70          | 782      | 2780.07          | 863      | 2792.22          |
| 449      | 2690.96          | 529      | 2712.36          | 618      | 2737.16          | 701      | 2767.86          | 783      | 2780.20          | 864      | 2792.24          |

TABLE 1. *Vibration-rotation wavenumbers of methane from 2,450 to 3,200 cm<sup>-1</sup>—Continued*

| Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> |
|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|
| 865      | 2792.58          | 948      | 2813.72          | 1049     | 2836.48          | 1208     | 2876.66          | 1351     | 2901.05          | 1497     | 2925.62          |
| 865a     | 2793.33          | 949      | 2813.99          | 1049b    | 2836.67          | 1210     | 2876.95          | 1352     | 2901.30          | 1511     | 2928.14          |
| 866      | 2793.44          | 951      | 2814.70          | 1049d    | 2837.75          | 1211     | 2877.15          | 1353     | 2901.50          | 1512     | 2928.22          |
| 867      | 2793.55          | 952      | 2814.79          | 1049e    | 2837.97          | 1212     | 2877.29          | 1354     | 2901.85          | 1513     | 2928.42          |
| 868      | 2793.58          | 953      | 2815.00          | 1049h    | 2839.29          | 1213     | 2877.36          | 1355     | 2902.23          | 1514     | 2928.50          |
| 869      | 2793.68          | 954      | 2815.74          | 1051     | 2839.91          | 1214     | 2877.47          | 1356     | 2902.28          | 1515     | 2928.59          |
| 870      | 2793.74          | 955      | 2816.32          | 1052     | 2839.96          | 1215     | 2877.53          | 1357     | 2902.34          | 1516     | 2928.98          |
| 871      | 2794.64          | 957      | 2816.70          | 1053     | 2840.00          | 1216     | 2877.62          | 1358     | 2902.53          | 1517     | 2929.01          |
| 872      | 2794.76          | 958      | 2816.84          | 1054     | 2840.10          | 1217     | 2877.84          | 1368     | 2903.60          | 1518     | 2929.14          |
| 872a     | 2794.94          | 959      | 2816.90          | 1055     | 2840.33          | 1218     | 2877.97          | 1370     | 2903.83          | 1520     | 2929.53          |
| 873      | 2794.97          | 960      | 2817.06          | 1056     | 2840.36          | 1219     | 2878.02          | 1373     | 2904.48          | 1522     | 2929.74          |
| 875      | 2795.41          | 962      | 2817.88          | 1057     | 2840.46          | 1220     | 2878.16          | 1374     | 2905.07          | 1523     | 2929.89          |
| 876      | 2795.69          | 963      | 2818.55          | 1059     | 2840.71          | 1221     | 2878.33          | 1391     | 2907.56          | 1524     | 2930.01          |
| 877      | 2795.75          | 964      | 2818.63          | 1060     | 2840.75          | 1222     | 2878.58          | 1392     | 2907.92          | 1525     | 2931.41          |
| 878      | 2795.93          | 965      | 2818.86          | 1063     | 2841.21          | 1223     | 2878.62          | 1393     | 2908.29          | 1526     | 2931.72          |
| 879      | 2796.06          | 966      | 2819.82          | 1064     | 2841.61          | 1224     | 2878.81          | 1394     | 2908.52          | 1527     | 2931.96          |
| 880      | 2796.20          | 967      | 2820.03          | 1066     | 2842.14          | 1225     | 2878.84          | 1395     | 2908.72          | 1528     | 2932.08          |
| 880b     | 2796.62          | 968      | 2820.20          | 1068     | 2842.59          | 1226     | 2878.93          | 1396     | 2908.88          | 1529     | 2932.22          |
| 880c     | 2796.83          | 969      | 2820.26          | 1069     | 2842.72          | 1227     | 2879.26          | 1397     | 2909.23          | 1530     | 2932.87          |
| 880e     | 2797.10          | 970      | 2820.33          | 1070     | 2842.80          | 1228     | 2879.38          | 1399     | 2909.54          | 1531     | 2932.96          |
| 880f     | 2797.32          | 971      | 2820.51          | 1071     | 2843.06          | 1229     | 2879.93          | 1401     | 2909.85          | 1532     | 2932.99          |
| 880g     | 2797.52          | 973      | 2820.90          | 1072     | 2843.30          | 1230     | 2880.27          | 1402     | 2910.52          | 1533     | 2933.04          |
| 880h     | 2797.77          | 977      | 2821.59          | 1073     | 2843.33          | 1231     | 2880.39          | 1403     | 2910.62          | 1534     | 2933.13          |
| 880i     | 2797.84          | 978      | 2821.81          | 1074     | 2843.41          | 1232     | 2880.49          | 1404     | 2910.78          | 1535     | 2933.18          |
| 880j     | 2798.06          | 979      | 2821.94          | 1076     | 2844.01          | 1233     | 2880.70          | 1405     | 2910.95          | 1537     | 2933.33          |
| 881      | 2798.31          | 983      | 2822.37          | 1077     | 2844.49          | 1234     | 2880.86          | 1406     | 2911.15          | 1539     | 2933.59          |
| 882      | 2798.49          | 984      | 2822.47          | 1078     | 2844.56          | 1235     | 2881.07          | 1407     | 2911.24          | 1540     | 2933.70          |
| 883      | 2798.62          | 985      | 2822.72          | 1079     | 2844.67          | 1236     | 2881.22          | 1410     | 2911.59          | 1541     | 2934.01          |
| 884      | 2798.81          | 987      | 2823.05          | 1081     | 2844.91          | 1237     | 2881.26          | 1420     | 2912.70          | 1542     | 2934.08          |
| 885      | 2798.87          | 990      | 2823.34          | 1082     | 2845.30          | 1238     | 2881.73          | 1423     | 2913.08          | 1543     | 2934.17          |
| 886      | 2799.03          | 991      | 2823.46          | 1083     | 2845.40          | 1241     | 2882.39          | 1424     | 2913.15          | 1544     | 2934.20          |
| 887      | 2799.18          | 993      | 2823.89          | 1093     | 2847.14          | 1242     | 2882.47          | 1425     | 2913.27          | 1545     | 2934.33          |
| 888      | 2799.32          | 994      | 2824.00          | 1094     | 2847.68          | 1243     | 2882.52          | 1426     | 2913.32          | 1546     | 2934.38          |
| 889      | 2799.42          | 995      | 2824.14          | 1095     | 2848.48          | 1244     | 2882.69          | 1427     | 2913.58          | 1548     | 2934.94          |
| 892      | 2799.81          | 996      | 2824.86          | 1096     | 2849.29          | 1245     | 2882.78          | 1428     | 2913.76          | 1549     | 2935.13          |
| 893      | 2799.87          | 997      | 2824.99          | 1097     | 2850.79          | 1247     | 2882.97          | 1429     | 2913.81          | 1550     | 2935.25          |
| 894      | 2799.94          | 998      | 2825.19          | 1098     | 2851.38          | 1249     | 2883.42          | 1431     | 2914.02          | 1551     | 2935.37          |
| 896      | 2800.15          | 999      | 2825.28          | 1114     | 2855.61          | 1250     | 2883.68          | 1432     | 2914.47          | 1552     | 2935.44          |
| 898      | 2800.34          | 1001     | 2825.48          | 1115     | 2856.94          | 1251     | 2884.13          | 1433     | 2914.89          | 1554     | 2935.76          |
| 899      | 2800.84          | 1002     | 2825.60          | 1116     | 2857.10          | 1252     | 2884.28          | 1434     | 2915.24          | 1555     | 2935.81          |
| 900      | 2801.30          | 1003     | 2825.66          | 1117     | 2857.44          | 1271     | 2886.74          | 1435     | 2915.30          | 1556     | 2936.20          |
| 902      | 2802.10          | 1004     | 2825.74          | 1119     | 2857.90          | 1272     | 2887.30          | 1436     | 2915.39          | 1557     | 2936.63          |
| 904      | 2803.10          | 1005     | 2825.78          | 1120     | 2858.00          | 1273     | 2887.37          | 1437     | 2915.56          | 1572     | 2938.77          |
| 905      | 2803.21          | 1006     | 2826.35          | 1121     | 2858.11          | 1274     | 2887.57          | 1452     | 2917.68          | 1573     | 2938.82          |
| 907      | 2803.55          | 1007     | 2826.86          | 1122     | 2858.24          | 1275     | 2887.80          | 1453     | 2917.83          | 1574     | 2938.93          |
| 908      | 2803.84          | 1008     | 2827.49          | 1124     | 2858.78          | 1276     | 2887.95          | 1455     | 2918.03          | 1576     | 2939.27          |
| 909      | 2803.94          | 1009     | 2827.83          | 1126     | 2859.60          | 1277     | 2888.01          | 1456     | 2918.46          | 1578     | 2939.49          |
| 911      | 2804.19          | 1010     | 2828.06          | 1127     | 2859.96          | 1278     | 2888.18          | 1457     | 2918.71          | 1579     | 2939.61          |
| 912      | 2804.25          | 1010a    | 2828.11          | 1128     | 2861.09          | 1279     | 2888.31          | 1459     | 2919.09          | 1580     | 2939.80          |
| 913      | 2804.30          | 1011     | 2828.25          | 1129     | 2861.37          | 1280     | 2888.52          | 1460     | 2919.19          | 1581     | 2939.98          |
| 914      | 2804.46          | 1012     | 2828.40          | 1130     | 2861.61          | 1281     | 2888.66          | 1463     | 2919.70          | 1582     | 2940.50          |
| 915      | 2804.55          | 1013     | 2828.48          | 1131     | 2861.65          | 1281a    | 2888.70          | 1464     | 2919.88          | 1583     | 2940.64          |
| 917      | 2804.76          | 1014     | 2828.77          | 1148     | 2865.90          | 1283     | 2888.92          | 1465     | 2919.97          | 1584     | 2940.98          |
| 918      | 2804.86          | 1015     | 2829.56          | 1149     | 2866.11          | 1284     | 2889.03          | 1466     | 2920.16          | 1585     | 2941.38          |
| 919      | 2805.07          | 1018     | 2829.86          | 1151     | 2866.35          | 1291     | 2890.12          | 1467     | 2920.27          | 1587     | 2941.79          |
| 920      | 2805.23          | 1020     | 2830.07          | 1152     | 2866.65          | 1293     | 2890.63          | 1469     | 2920.58          | 1588     | 2942.08          |
| 921      | 2805.35          | 1021     | 2830.13          | 1153     | 2866.84          | 1296     | 2891.32          | 1470     | 2920.65          | 1589     | 2942.33          |
| 923      | 2805.66          | 1022     | 2830.58          | 1155     | 2867.09          | 1300     | 2891.90          | 1471     | 2921.30          | 1590     | 2942.65          |
| 924      | 2805.75          | 1023     | 2830.89          | 1156     | 2867.74          | 1304     | 2892.57          | 1472     | 2921.70          | 1591     | 2942.76          |
| 925      | 2805.90          | 1024     | 2830.94          | 1158     | 2868.21          | 1305     | 2893.51          | 1473     | 2921.91          | 1593     | 2943.03          |
| 926      | 2807.54          | 1025     | 2831.05          | 1159     | 2868.27          | 1306     | 2893.82          | 1474     | 2921.95          | 1594     | 2943.12          |
| 927      | 2807.61          | 1026     | 2831.25          | 1160     | 2868.69          | 1308     | 2894.07          | 1475     | 2922.10          | 1595     | 2943.19          |
| 928      | 2808.62          | 1027     | 2831.90          | 1161     | 2868.82          | 1309     | 2894.14          | 1476     | 2922.29          | 1596     | 2943.21          |
| 929      | 2808.73          | 1028     | 2831.95          | 1162     | 2868.94          | 1310     | 2894.22          | 1477     | 2922.44          | 1597     | 2943.30          |
| 930      | 2808.79          | 1029     | 2832.00          | 1164     | 2869.44          | 1312     | 2894.36          | 1478     | 2922.63          | 1599     | 2943.59          |
| 931      | 2809.02          | 1030     | 2832.16          | 1165     | 2870.35          | 1313     | 2894.42          | 1479     | 2922.88          | 1600     | 2943.66          |
| 933      | 2809.93          | 1032     | 2832.49          | 1166     | 2870.40          | 1314     | 2894.53          | 1480     | 2923.37          | 1601     | 2943.78          |
| 934      | 2810.07          | 1034     | 2832.86          | 1168     | 2870.87          | 1335     | 2897.35          | 1481     | 2923.42          | 1602     | 2943.99          |
| 935      | 2810.34          | 1035     | 2832.96          | 1169     | 2870.99          | 1336     | 2897.57          | 1482     | 2923.55          | 1693     | 2944.09          |
| 936      | 2810.48          | 1037     | 2833.56          | 1171     | 2871.30          | 1338     | 2897.75          | 1483     | 2923.65          | 1604     | 2944.12          |
| 937      | 2810.71          | 1039     | 2833.73          | 1173     | 2871.68          | 1339     | 2898.65          | 1484     | 2923.71          | 1605     | 2944.29          |
| 938      | 2811.05          | 1040     | 2834.45          | 1174     | 2872.32          | 1340     | 2899.23          | 1485     | 2923.77          | 1606     | 2944.46          |
| 939      | 2811.20          | 1041     | 2834.57          | 1175     | 2872.44          | 1341     | 2899.28          | 1486     | 2923.83          | 1607     | 2944.50          |
| 940      | 2811.75          | 1042     | 2834.94          | 1176     | 2872.67          | 1342     | 2899.36          | 1487     | 2923.91          | 1608     | 2944.69          |
| 942      | 2811.24          | 1043     | 2835.04          | 1178     | 2872.96          | 1343     | 2899.48          | 1488     | 2924.00          | 1609     | 2944.75          |
| 943      | 2812.48          | 1044     | 2835.23          | 1179     | 2873.01          | 1345     | 2899.88          | 1490     | 2924.62          | 1610     | 2945.01          |
| 944      | 2812.54          | 1045     | 2835.63          | 1180     | 2873.39          | 1346     | 2900.08          | 1491     | 2924.77          | 1611     | 2945.20          |
| 945      | 2812.69          | 1046     | 2835.90          | 1181     | 2873.53          | 1347     | 2900.28          | 1493     | 2925.27          | 1612     | 2945.40          |
| 946      | 2813.35          | 1047     | 2836.01          | 1206     | 2876.53          | 1348     | 2900.43          | 1495     | 2925.49          | 1613     | 2945.51          |
| 947      | 2813.55          | 1048     | 2836.22          | 1207     | 2876.62          | 1350     | 2900.67          | 1496     | 2925.56          | 1614     | 2945.62          |

TABLE 1. *Vibration-rotation wavenumbers of methane from 2,450 to 3,200 cm<sup>-1</sup>—Continued*

| Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> |
|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|
| 1615     | 2945.92          | 1703     | 2962.51          | 1790     | 2976.56          | 1887     | 2999.12          | 2139     | 3034.24          | 2250     | 3063.20          |
| 1616     | 2945.95          | 1704     | 2962.64          | 1791     | 2976.66          | 1888     | 2999.20          | 2140     | 3034.32          | 2251     | 3064.19          |
| 1617     | 2946.05          | 1705     | 2962.70          | 1792     | 2976.79          | 1889     | 2999.32          | 2141     | 3034.48          | 2252     | 3064.40          |
| 1518     | 2946.25          | 1706     | 2962.87          | 1794     | 2977.16          | 1890     | 2999.46          | 2142     | 3034.68          | 2253     | 3064.50          |
| 1619     | 2946.48          | 1707     | 2963.00          | 1795     | 2977.34          | 1891     | 2999.68          | 2143     | 3034.78          | 2254     | 3065.58          |
| 1620     | 2946.65          | 1708     | 2963.10          | 1797     | 2977.87          | 1892     | 2999.81          | 2144     | 3034.81          | 2255     | 3066.28          |
| 1621     | 2947.09          | 1709     | 2963.15          | 1800     | 2978.21          | 1893     | 3000.00          | 2145     | 3035.14          | 2256a    | 3067.00          |
| 1633     | 2948.56          | 1710     | 2963.42          | 1801     | 2979.38          | 1895     | 3000.17          | 2146     | 3035.61          | 2257     | 3067.64          |
| 1634     | 2948.73          | 1711     | 2963.48          | 1802     | 2979.51          | 1896     | 3000.31          | 2147     | 3035.77          | 2258     | 3067.76          |
| 1635     | 2949.10          | 1712     | 2963.65          | 1803     | 2979.74          | 1897     | 3000.44          | 2152     | 3037.26          | 2259     | 3068.04          |
| 1636     | 2949.24          | 1713     | 2963.86          | 1804     | 2979.77          | 2021     | 3019.00          | 2153     | 3037.33          | 2260     | 3068.15          |
| 1637     | 2949.32          | 1714     | 2964.95          | 1805     | 2979.95          | 2022     | 3019.10          | 2155     | 3037.57          | 2261     | 3068.31          |
| 1638     | 2949.53          | 1715     | 2964.26          | 1806     | 2980.03          | 2023     | 3019.18          | 2157     | 3037.93          | 2262     | 3068.52          |
| 1639     | 2949.81          | 1716     | 2964.31          | 1807     | 2980.07          | 2024     | 3019.31          | 2158     | 3038.13          | 2262a    | 3068.59          |
| 1640     | 2949.89          | 1717     | 2965.51          | 1808     | 2980.19          | 2025     | 3019.47          | 2162     | 3038.69          | 2263     | 3068.98          |
| 1641     | 2950.13          | 1718     | 2964.60          | 1809     | 2980.39          | 2026     | 3019.58          | 2165     | 3039.27          | 2264     | 3069.16          |
| 1642     | 2950.33          | 1719     | 2964.78          | 1810     | 2980.59          | 2027     | 3019.62          | 2166     | 3039.42          | 2265     | 3069.24          |
| 1643     | 2950.52          | 1720     | 2964.86          | 1811     | 2980.73          | 2028     | 3019.67          | 2167     | 3042.06          | 2266     | 3069.42          |
| 1644     | 2950.65          | 1721     | 2964.94          | 1812     | 2980.84          | 2029     | 3019.81          | 2170     | 3042.41          | 2267     | 3069.54          |
| 1645     | 2950.85          | 1722     | 2965.09          | 1813     | 2981.08          | 2030     | 3019.88          | 2171     | 3042.57          | 2268     | 3069.63          |
| 1646     | 2951.30          | 1723     | 2965.28          | 1814     | 2981.17          | 2031     | 3020.02          | 2172     | 3042.73          | 2269     | 3069.72          |
| 1647     | 2951.38          | 1724     | 2965.45          | 1815     | 2981.31          | 2032     | 3020.15          | 2173     | 3043.59          | 2270     | 3069.79          |
| 1648     | 2951.56          | 1725     | 2965.51          | 1816     | 2981.46          | 2033     | 3020.22          | 2174     | 3043.74          | 2271     | 3070.01          |
| 1649     | 2952.04          | 1726     | 2965.59          | 1817     | 2981.59          | 2034     | 3020.38          | 2175     | 3043.79          | 2272     | 3070.13          |
| 1650     | 2952.11          | 1727     | 2965.74          | 1818     | 2982.26          | 2035     | 3020.46          | 2176     | 3043.90          | 2273     | 3070.22          |
| 1651     | 2952.40          | 1727a    | 2965.83          | 1819     | 2982.64          | 2036     | 3020.55          | 2177     | 3043.97          | 2274     | 3070.32          |
| 1652     | 2952.46          | 1728     | 2965.86          | 1820     | 2982.98          | 2037     | 3020.67          | 2178     | 3044.11          | 2275     | 3070.48          |
| 1653     | 2952.65          | 1729     | 2965.96          | 1821     | 2983.38          | 2038     | 3020.78          | 2179     | 3044.17          | 2276     | 3070.58          |
| 1654     | 2952.77          | 1730     | 2966.00          | 1822     | 2983.45          | 2039     | 3020.85          | 2180     | 3044.56          | 2277     | 3070.61          |
| 1655     | 2952.87          | 1731     | 2966.10          | 1823     | 2983.61          | 2040     | 3020.93          | 2181     | 3044.78          | 2278     | 3070.93          |
| 1656     | 2953.08          | 1732     | 2966.46          | 1824     | 2983.69          | 2041     | 3021.06          | 2182     | 3044.95          | 2279     | 3071.10          |
| 1657     | 2953.18          | 1733     | 2966.56          | 1825     | 2983.81          | 2042     | 3021.17          | 2183     | 3045.98          | 2281     | 3071.31          |
| 1658     | 2953.40          | 1734     | 2966.62          | 1827     | 2984.08          | 2043     | 3021.30          | 2184     | 3046.04          | 2282     | 3071.41          |
| 1659     | 2953.53          | 1735     | 2966.78          | 1828     | 2984.16          | 2044     | 3021.38          | 2185     | 3046.10          | 2283     | 3071.62          |
| 1660     | 2953.67          | 1736     | 2966.86          | 1831     | 2985.36          | 2045     | 3021.46          | 2186     | 3047.91          | 2284     | 3071.72          |
| 1661     | 2953.71          | 1737     | 2967.03          | 1832     | 2985.42          | 2046     | 3021.49          | 2190     | 3048.58          | 2285     | 3072.00          |
| 1663     | 2954.15          | 1738     | 2967.10          | 1836     | 2986.70          | 2047     | 3021.63          | 2191     | 3048.65          | 2286     | 3072.06          |
| 1664     | 2954.34          | 1739     | 2967.23          | 1837     | 2987.22          | 2048     | 3021.78          | 2192     | 3048.77          | 2287     | 3072.53          |
| 1665     | 2954.44          | 1740     | 2967.50          | 1838     | 2987.43          | 2049     | 3021.82          | 2193     | 3048.94          | 2288     | 3072.57          |
| 1666     | 2954.54          | 1741     | 2967.70          | 1839     | 2987.53          | 2051     | 3022.31          | 2194     | 3049.01          | 2289     | 3072.66          |
| 1667     | 2954.60          | 1742     | 2967.85          | 1840     | 2987.70          | 2052     | 3022.37          | 2196     | 3049.80          | 2290     | 3072.71          |
| 1668     | 2954.70          | 1744     | 2969.10          | 1841     | 2987.88          | 2053     | 3022.43          | 2198     | 3050.17          | 2291     | 3073.10          |
| 1669     | 2954.76          | 1745     | 2969.28          | 1842     | 2988.03          | 2056     | 3022.69          | 2199     | 3050.29          | 2292     | 3073.21          |
| 1670     | 2954.91          | 1746     | 2969.46          | 1843     | 2988.13          | 2057     | 3022.82          | 2204     | 3051.71          | 2293     | 3073.30          |
| 1671     | 2955.00          | 1747     | 2969.64          | 1844     | 2988.18          | 2058     | 3022.93          | 2206     | 3051.92          | 2294     | 3073.42          |
| 1672     | 2955.17          | 1748     | 2969.70          | 1845     | 2988.34          | 2059     | 3023.03          | 2209     | 3052.19          | 2295     | 3073.58          |
| 1673     | 2955.42          | 1749     | 2969.78          | 1846     | 2989.69          | 2060     | 3023.12          | 2211     | 3052.64          | 2296     | 3073.63          |
| 1674     | 2955.47          | 1750     | 2969.89          | 1847     | 2989.88          | 2073     | 3024.28          | 2213     | 3052.93          | 2298     | 3073.85          |
| 1675     | 2955.54          | 1751     | 2970.07          | 1848     | 2989.98          | 2074     | 3024.42          | 2216     | 3053.28          | 2299     | 3073.99          |
| 1676     | 2955.69          | 1752     | 2970.12          | 1849     | 2990.08          | 2075     | 3024.56          | 2217     | 3053.39          | 2300     | 3074.06          |
| 1677     | 2955.76          | 1753     | 2970.24          | 1850     | 2990.22          | 2076     | 3024.72          | 2218     | 3053.46          | 2301     | 3074.55          |
| 1678     | 2955.93          | 1754     | 2970.32          | 1851     | 2990.36          | 2077     | 3025.07          | 2219     | 3053.49          | 2302     | 3074.90          |
| 1679     | 2955.98          | 1755     | 2970.38          | 1852     | 2990.70          | 2080     | 3025.35          | 2220     | 3053.60          | 2303     | 3075.07          |
| 1680     | 2956.08          | 1756     | 2971.06          | 1853     | 2991.92          | 2081     | 3025.46          | 2221     | 3053.83          | 2304     | 3075.22          |
| 1680a    | 2956.13          | 1757     | 2971.27          | 1854     | 2991.99          | 2082     | 3025.57          | 2223     | 3054.64          | 2305     | 3075.41          |
| 1680b    | 2956.30          | 1758     | 2971.34          | 1855     | 2992.27          | 2083     | 3025.68          | 2225     | 3054.97          | 2306     | 3075.99          |
| 1680c    | 2956.39          | 1759     | 2971.59          | 1856     | 2992.53          | 2084     | 3025.73          | 2226     | 3055.06          | 2307     | 3076.13          |
| 1680d    | 2956.52          | 1761     | 2972.02          | 1857     | 2992.67          | 2085     | 3025.77          | 2227     | 3055.33          | 2308     | 3076.17          |
| 1680e    | 2956.63          | 1762     | 2972.15          | 1859     | 2993.19          | 2086     | 3025.82          | 2228     | 3055.65          | 2309     | 3076.36          |
| 1680f    | 2956.74          | 1763     | 2972.36          | 1860     | 2993.47          | 2087     | 3025.87          | 2229     | 3055.89          | 2313     | 3077.16          |
| 1681     | 2959.50          | 1767     | 2972.83          | 1861     | 2993.53          | 2088     | 3025.96          | 2231     | 3056.34          | 2314     | 3077.36          |
| 1682     | 2959.60          | 1768     | 2973.01          | 1862     | 2993.63          | 2089     | 3026.07          | 2231a    | 3056.53          | 2315     | 3077.44          |
| 1683     | 2959.73          | 1769     | 2973.18          | 1863     | 2993.73          | 2092     | 3026.35          | 2232     | 3057.90          | 2316     | 3077.53          |
| 1684     | 2959.85          | 1770     | 2973.23          | 1864     | 2993.84          | 2097     | 3026.79          | 2233     | 3058.18          | 2318     | 3077.87          |
| 1686     | 2960.20          | 1771     | 2973.56          | 1866     | 2994.14          | 2098     | 3026.94          | 2234     | 3058.80          | 2319     | 3077.95          |
| 1687     | 2960.38          | 1772     | 2973.62          | 1867     | 2994.29          | 2102     | 3027.30          | 2235     | 3058.95          | 2320     | 3078.02          |
| 1688     | 2960.66          | 1773     | 2973.77          | 1868     | 2994.46          | 2107     | 3027.88          | 2236     | 3059.47          | 2321     | 3078.12          |
| 1689     | 2960.77          | 1774     | 2974.57          | 1871     | 2995.46          | 2111     | 3028.82          | 2237     | 3059.73          | 2322     | 3078.77          |
| 1690     | 2960.86          | 1775     | 2974.83          | 1873     | 2996.16          | 2114     | 3029.17          | 2238     | 3059.89          | 2323     | 3078.82          |
| 1691     | 2960.94          | 1777     | 2975.01          | 1874     | 2996.60          | 2122     | 3030.21          | 2239     | 3059.94          | 2324     | 3079.04          |
| 1692     | 2961.14          | 1778     | 2975.09          | 1875     | 2996.88          | 2125     | 3030.68          | 2240     | 3060.10          | 2325     | 3079.13          |
| 1693     | 2961.32          | 1779     | 2975.13          | 1876     | 2996.99          | 2126     | 3030.73          | 2241     | 3060.79          | 2326     | 3079.27          |
| 1694     | 2961.43          | 1781     | 2975.68          | 1877     | 2997.71          | 2127     | 3030.85          | 2242     | 3060.84          | 2327     | 3079.44          |
| 1695     | 2961.65          | 1782     | 2975.74          | 1878     | 2997.96          | 2131     | 3031.71          | 2243     | 3061.42          | 2328     | 3079.58          |
| 1697     | 2961.85          | 1783     | 2975.78          | 1879     | 2998.10          | 2132     | 3031.77          | 2244     | 3061.49          | 2329     | 3079.66          |
| 1698     | 2961.99          | 1784     | 2975.86          | 1880     | 2998.27          | 2133     | 3031.91          | 2245     | 3061.69          | 2329a    | 3079.72          |
| 1699     | 2962.13          | 1785     | 2975.93          | 1881     | 2998.36          | 2134     | 3032.04          | 2246     | 3061.91          | 2330     | 3080.05          |
| 1700     | 2962.19          | 1786     | 2976.03          | 1882     | 2998.45          | 2135     | 3032.14          | 2247     | 3062.68          | 2331     | 3080.18          |
| 1701     | 2962.31          | 1788     | 2976.33          | 1883     | 2998.58          | 2137     | 3033.98          | 2248     | 3063.00          | 2332     | 3080.42          |
| 1702     | 2962.43          | 1789     | 2976.45          | 1884     | 2998.78          | 2138     | 3034.06          | 2249     | 3063.10          | 2333     | 3080.62          |



TABLE I. *Vibration-rotation wavenumbers of methane from 2,450 to 3,200 cm<sup>-1</sup>*—Continued

| Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> | Line No. | cm <sup>-1</sup> |
|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|
| 2334     | 3081.10          | 2380     | 3091.29          | 2425     | 3103.40          | 2473     | 3118.64          | 2533     | 3135.93          | 2605     | 3155.42          |
| 2336     | 3081.35          | 2381     | 3091.46          | 2426     | 3103.59          | 2474     | 3118.94          | 2534     | 3136.41          | 2606     | 3155.63          |
| 2338     | 3081.82          | 2382     | 3092.00          | 2427     | 3103.77          | 2475     | 3119.01          | 2535     | 3136.61          | 2607     | 3155.99          |
| 2339     | 3081.92          | 2383     | 3092.40          | 2428     | 3104.90          | 2476     | 3119.16          | 2536     | 3136.88          | 2608     | 3156.16          |
| 2340     | 3082.17          | 2384     | 3092.70          | 2429     | 3105.08          | 2477     | 3119.41          | 2538     | 3137.26          | 2609     | 3156.32          |
| 2341     | 3082.22          | 2385     | 3092.84          | 2430     | 3105.52          | 2478     | 3119.51          | 2539     | 3137.34          | 2610     | 3156.47          |
| 2342     | 3082.35          | 2386     | 3092.89          | 2432     | 3107.33          | 2479     | 3120.95          | 2540     | 3137.70          | 2611     | 3156.54          |
| 2343     | 3082.52          | 2387     | 3093.21          | 2433     | 3107.65          | 2480     | 3121.10          | 2541     | 3137.82          | 2612     | 3156.72          |
| 2344     | 3082.62          | 2388     | 3093.29          | 2434     | 3107.74          | 2481     | 3121.18          | 2542     | 3137.97          | 2613     | 3156.88          |
| 2345     | 3082.71          | 2389     | 3093.47          | 2435     | 3107.90          | 2482     | 3121.33          | 2543     | 3138.08          | 2614     | 3157.15          |
| 2346     | 3082.82          | 2390     | 3093.68          | 2436     | 3108.17          | 2484     | 3123.11          | 2544     | 3138.44          | 2615     | 3157.40          |
| 2347     | 3083.41          | 2391     | 3093.76          | 2437     | 3108.24          | 2485     | 3123.66          | 2545     | 3138.52          | 2620     | 3158.14          |
| 2348     | 3083.50          | 2392     | 3094.14          | 2438     | 3108.34          | 2486     | 3124.42          | 2546     | 3138.72          | 2621     | 3158.38          |
| 2349     | 3083.74          | 2393     | 3094.24          | 2439     | 3108.52          | 2487     | 3124.66          | 2547     | 3138.89          | 2622     | 3159.26          |
| 2350     | 3083.87          | 2394     | 3094.38          | 2440     | 3108.72          | 2488     | 3124.88          | 2549     | 3139.26          | 2623     | 3164.04          |
| 2351     | 3083.96          | 2395     | 3094.46          | 2441     | 3109.10          | 2489     | 3124.94          | 2550     | 3139.36          | 2624     | 3164.20          |
| 2353     | 3084.15          | 2396     | 3094.53          | 2442     | 3109.14          | 2490     | 3125.12          | 2557     | 3140.98          | 2625     | 3164.41          |
| 2354     | 3084.35          | 2397     | 3094.64          | 2443     | 3109.33          | 2493     | 3125.56          | 2558     | 3141.71          | 2628     | 3164.96          |
| 2355     | 3084.48          | 2399     | 3095.79          | 2444     | 3109.67          | 2494     | 3125.68          | 2559     | 3142.66          | 2629     | 3165.48          |
| 2355a    | 3084.81          | 2400     | 3095.95          | 2445     | 3109.79          | 2495     | 3125.72          | 2560     | 3142.77          | 2630     | 3165.61          |
| 2355b    | 3084.82          | 2401     | 3096.29          | 2446     | 3109.90          | 2496     | 3126.01          | 2561     | 3142.88          | 2635     | 3167.90          |
| 2355c    | 3084.92          | 2402     | 3096.66          | 2447     | 3110.33          | 2497     | 3126.44          | 2562     | 3143.98          | 2636     | 3168.25          |
| 2355d    | 3084.99          | 2403     | 3096.92          | 2448     | 3110.48          | 2498     | 3126.81          | 2563     | 3144.23          | 2637     | 3173.34          |
| 2356     | 3085.11          | 2404     | 3097.04          | 2449     | 3110.65          | 2499     | 3126.89          | 2564     | 3144.97          | 2638     | 3174.55          |
| 2357     | 3085.15          | 2405     | 3098.30          | 2451     | 3111.32          | 2501     | 3127.75          | 2567     | 3145.62          | 2642     | 3181.97          |
| 2358     | 3085.57          | 2406     | 3098.36          | 2452     | 3111.74          | 2502     | 3127.91          | 2568     | 3145.70          | 2643     | 3182.20          |
| 2360     | 3087.19          | 2407     | 3098.52          | 2453     | 3111.91          | 2503     | 3127.97          | 2569     | 3145.95          | 2650     | 3184.83          |
| 2361     | 3087.27          | 2408     | 3098.66          | 2454     | 3112.03          | 2504     | 3128.53          | 2570     | 3146.41          | 2651     | 3185.24          |
| 2362     | 3087.34          | 2409     | 3098.80          | 2455     | 3112.13          | 2505     | 3128.59          | 2571     | 3146.78          | 2652     | 3191.29          |
| 2363     | 3087.44          | 2410     | 3098.88          | 2456     | 3112.20          | 2506     | 3128.92          | 2572     | 3146.89          | 2653     | 3191.36          |
| 2364     | 3087.55          | 2410a    | 3099.14          | 2457     | 3112.39          | 2507     | 3129.05          | 2575     | 3147.25          | 2654     | 3191.70          |
| 2365     | 3087.66          | 2411     | 3099.28          | 2458     | 3112.77          | 2508     | 3129.18          | 2576     | 3147.40          | 2655     | 3192.00          |
| 2365a    | 3087.71          | 2412     | 3099.34          | 2459     | 3114.50          | 2513     | 3130.34          | 2577     | 3147.53          | 2656     | 3196.09          |
| 2366     | 3087.82          | 2413     | 3099.50          | 2461     | 3114.50          | 2519     | 3132.09          | 2581     | 3148.14          | 2657     | 3197.84          |
| 2367     | 3088.14          | 2414     | 3099.69          | 2462     | 3114.71          | 2520     | 3132.25          | 2594     | 3149.77          | 2658     | 3199.57          |
| 2368     | 3088.40          | 2415     | 3099.81          | 2463     | 3114.86          | 2523     | 3133.06          | 2595     | 3150.54          | 2659     | 3199.67          |
| 2369     | 3088.68          | 2416     | 3099.98          | 2464     | 3114.93          | 2524     | 3134.52          | 2596     | 3150.63          | 2660     | 3199.69          |
| 2369a    | 3088.77          | 2417     | 3100.05          | 2465     | 3115.27          | 2525     | 3134.64          | 2597     | 3150.76          | 2661     | 3200.26          |
| 2370     | 3088.86          | 2418     | 3100.35          | 2466     | 3115.42          | 2526     | 3134.95          | 2598     | 3151.34          |          |                  |
| 2371     | 3088.90          | 2419     | 3100.65          | 2467     | 3115.88          | 2527     | 3135.04          | 2599     | 3153.05          |          |                  |
| 2372     | 3089.04          | 2420     | 3100.72          | 2468     | 3117.42          | 2528     | 3135.09          | 2600     | 3153.19          |          |                  |
| 2373     | 3089.75          | 2421     | 3101.17          | 2469     | 3117.90          | 2529     | 3135.28          | 2601     | 3153.44          |          |                  |
| 2374     | 3089.90          | 2422     | 3102.51          | 2470     | 3118.12          | 2530     | 3135.42          | 2602     | 3153.66          |          |                  |
| 2375     | 3090.01          | 2423     | 3103.06          | 2471     | 3118.27          | 2531     | 3135.58          | 2603     | 3154.78          |          |                  |
| 2376     | 3090.19          | 2424     | 3103.30          | 2472     | 3118.55          | 2532     | 3135.78          | 2604     | 3154.88          |          |                  |

The two upper strips of figure 5 represent the  $R(F^-)$  branch of the  $\nu_3$  band as observed with 0.2-mm pressure. The regions between the successive  $R$  lines were not recorded as at this low pressure very few lines were observed. Some lines of the atmospheric water band,  $2\nu_2$ , overlap this region and they are marked by small circles. The atmospheric water vapor lines are much broader than the methane lines on account of pressure broadening and they can be identified easily.

In table 2 the wavenumbers of the lines of the  $P$ ,  $Q$ , and  $R$  branches are listed. This table applies to the experimental results shown in figures 4 and 5. The lines in the  $P$  and  $R$  branches are grouped under the  $J$  values so they can be related to the observed spectrum.

#### 4. Discussion of Results

The spectrum of methane recorded in figures 1, 2, and 3 shows many lines which may be associated with several bands. The most prominent band is the allowed component of  $\nu_3$  which has  $P(F^+)$ ,  $Q(F^0)$ , and  $R(F^-)$  branches. The  $P$ ,  $Q$ , and  $R$  branches of this band have been split into several components for

each  $J$  as is shown by the experimental results in figures 4 and 5. Other normally forbidden transitions with components comprising the  $P(F^0)$ ,  $P(F^-)$ ,  $Q(F^-)$ ,  $R(F^0)$ , and  $R(F^+)$  branches occur in the same region as the strong component of  $\nu_3$ , but with much less intensity. The  $Q(F^+)$  branch is the prominent feature near  $3021.18\text{ cm}^{-1}$ . Other lines in this region may arise from isotopic molecules and from hot bands. Boyd and Thompson [8] showed the presence of a hot band in this region by measuring the absorption spectrum at elevated temperatures. There appears to be some experimental evidence for a weak  $Q$  branch at  $3070\text{ cm}^{-1}$ . The Raman spectra shows an intense line in this region and it has been classified as  $2\nu_2$ . If the forbidden components of this band become active by interactions, there would be a total of two  $Q$  branches. A double type  $Q$  branch is observed in the region from  $2820$  to  $2835\text{ cm}^{-1}$  which is one component of  $\nu_2 + \nu_4$ . If all transitions are active there is a possibility for six components of this band. The  $\nu_1$  band, which arises from the totally symmetric vibration at  $2914.4\text{ cm}^{-1}$ , is the most intense in the Raman spectrum, but there is no evidence of a  $Q$  branch in this region of the observed spectrum. That is, at a pressure of  $2\text{ cm}$  for a cell length of  $6\text{ m}$  this band is not observed.

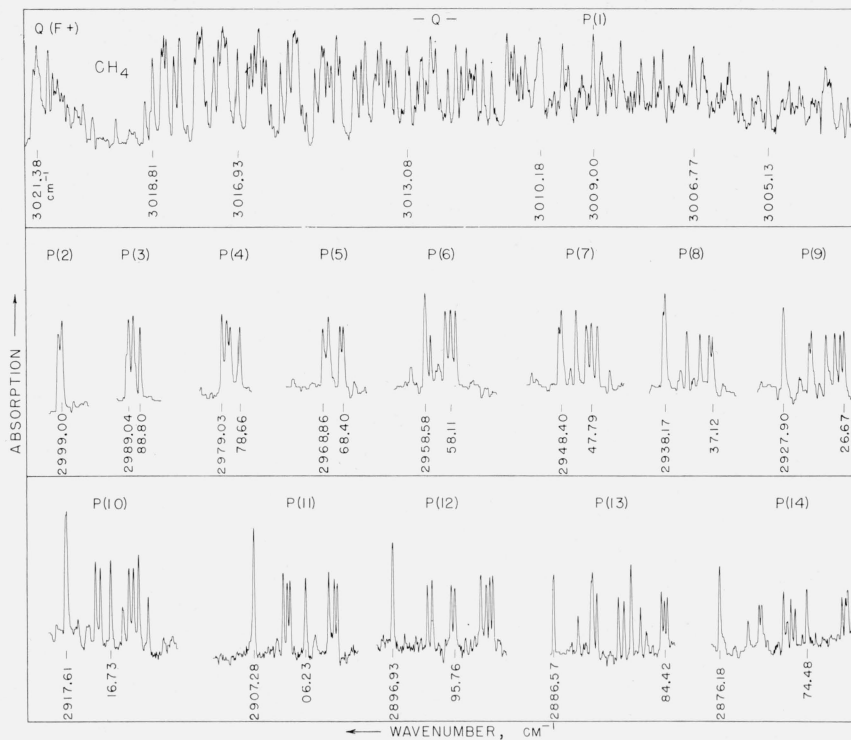


FIGURE 4. The  $Q(F^+)$  and  $Q(F^0)$  branches and the  $P(F^+)$  branch of  $\nu_3$  of methane as measured with slow scanning speeds and a pressure 0.1 mm in a 6-m cell.

The regions between consecutive  $J$ 's were omitted.

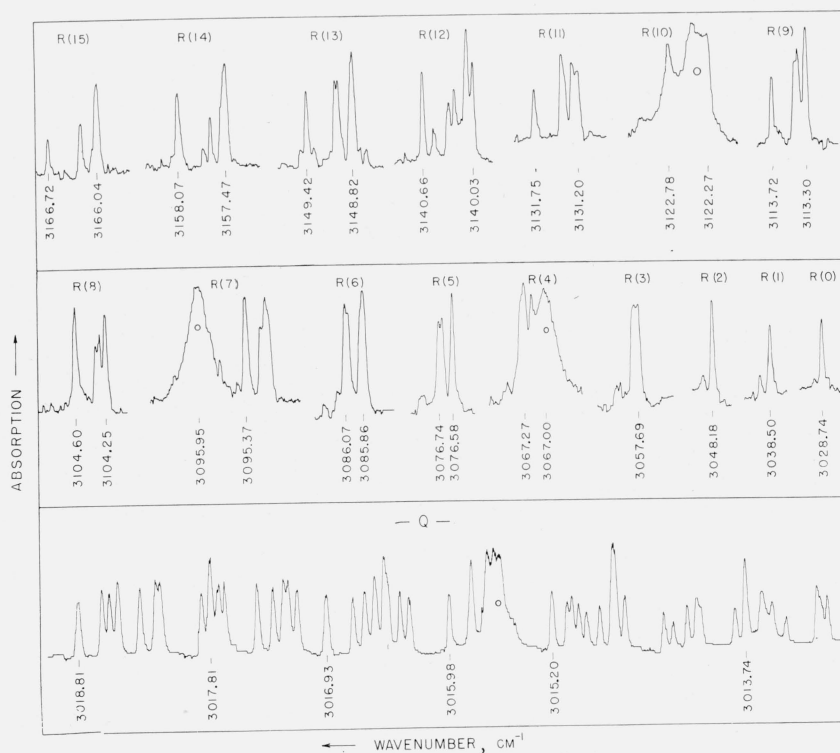


FIGURE 5. The  $R(F^-)$  branch of methane as measured with a pressure 0.2 mm and the  $Q(F^0)$  branch as measured with a pressure  $< 0.1$  mm.

TABLE 2. *Vibration-rotation wavenumbers for the  $\nu_3$  fundamental band of methane at 3018.9  $\text{cm}^{-1}$  at low pressures*

| <i>P</i> | $\text{cm}^{-1}$   | Line No.   | <i>R</i> | $\text{cm}^{-1}$   | Line No.   | <i>Q</i> | $\text{cm}^{-1}$ | Line No. |
|----------|--|--|----------|--|--|----------|------------------|----------|
|          |  |  | 0-----   | 3028.744   | 2110   |          | 3018.815         | 2020     |
| 1-----   | 3009.000   | 1975   | 1-----   | 3038.498   | 2160   |          | 3018.649         | 2019n    |
|          |  |  |          |  |  |          | 3018.602         | 2019m    |
|          |  |  |          |  |  |          | 3018.533         | 2019l    |
|          |  |  |          |  |  |          | 3018.349         | 2019k    |
| 2-----   | 2999.057<br>2999.000   | 1886<br>1885   | 2-----   | 3048.180   | 2188   |          | 3018.230         | 2019j    |
|          |  |  |          |  |  |          | 3018.210         | 2019i    |
|          |  |  |          |  |  |          | 3017.874         | 2019h    |
| 3-----   | 2989.045<br>2988.945<br>2978.800   | 1845d<br>1845c<br>1845b  | 3-----   | 3057.692<br>3057.739   | 2231b <sub>1</sub><br>2231b <sub>2</sub>                   |          | 3017.820         | 2019g    |
|          |  |  |          |  |  |          | 3017.748         | 2019f    |
|          |  |  |          |  |  |          | 3017.708         | 2019e    |
|          |  |  |          |  |  |          | 3017.453         | 2019d    |
| 4-----   | 2979.033<br>2978.937<br>2978.872<br>2988.656   | 1800d<br>1800c<br>1800b<br>1800a                                     | 4-----   | 3067.167<br>3067.266   | 2256a<br>2256b   |          | 3017.325         | 2019c    |
|          |  |  |          |  |  |          | 3017.245         | 2019b    |
|          |  |  |          |  |  |          | 3017.167         | 2019a    |
|          |  |  |          |  |  |          | 3016.930         | 2019     |
|          |  |  |          |  |  |          | 3016.730         | 2018f    |
| 5-----   | 2968.861<br>2968.748<br>2968.456<br>2968.404   | 1743d<br>1743c<br>1743b<br>1743a                                     | 5-----   | 3076.576<br>3076.696<br>3076.738                                     | 2310<br>2310a<br>2311                                      |          | 3016.640         | 2018e    |
|          |  |  |          |  |  |          | 3016.573         | 2018d    |
|          |  |  |          |  |  |          | 3016.480         | 2018c    |
|          |  |  |          |  |  |          | 3016.384         | 2018b    |
|          |  |  |          |  |  |          | 3016.304         | 2018a    |
| 6-----   | 2958.636<br>2958.508<br>2958.430<br>2958.210<br>2958.109<br>2958.009                                     | 1680p<br>1680o<br>1680n<br>1680m<br>1680l<br>1680k                   | 6-----   | 3085.862<br>3086.046<br>3086.070                                     | 2358a<br>2358b <sub>1</sub><br>2358b <sub>2</sub>          |          | 3015.978         | 2018     |
|          |  |  |          |  |  |          | 3015.790         | 2017b    |
|          |  |  |          |  |  |          | 3015.660         | 2017a    |
|          |  |  |          |  |  |          | 3015.549         | 2017     |
|          |  |  |          |  |  |          | 3015.208         | 2016f    |
| 7-----   | 2948.465<br>2948.405<br>2948.230<br>2948.120<br>2948.081<br>2947.888<br>2947.792<br>2947.660<br>2947.415 | 1632<br>1631<br>1629<br>1628<br>1627<br>1625<br>1624<br>1623<br>1622 | 7-----   | 3095.110<br>3095.174<br>3095.368<br>3095.680                         | 2397a<br>2397b<br>2397c<br>2398                            |          |                  |          |
| 8-----   | 2938.222<br>2938.168<br>2937.928<br>2937.900<br>2937.736<br>2937.620<br>2937.456<br>2937.260<br>2937.208 | 1569<br>1568<br>1566<br>1565<br>1564<br>1563<br>1562<br>1560<br>1559 | 8-----   | 3104.248<br>3104.309<br>3104.374<br>3104.598                         | 2427a<br>2427b<br>2427c<br>2427d                           |          |                  |          |
| 9-----   | 2927.932<br>2927.903<br>2927.378<br>2927.342<br>2927.025<br>2926.837<br>2926.750<br>2926.670             | 1510<br>1509<br>1506<br>1505<br>1503<br>1501<br>1500<br>1499         | 9-----   | 3113.300<br>3113.403<br>3113.423<br>3113.720                         | 2458a<br>2458b<br>2458b <sub>1</sub><br>2458c <sub>2</sub> |          |                  |          |
| 10-----  | 2917.610<br>2917.032<br>2916.938<br>2916.730<br>2916.480<br>2916.373<br>2916.293<br>2916.173<br>2915.983 | 1451<br>1447<br>1446<br>1445<br>1444<br>1443<br>1442<br>1441<br>1440 | 10-----  | 3122.272<br>3122.382<br>3122.435<br>3122.775                         | 2482a<br>2482b<br>2482c<br>2483                            |          |                  |          |
| 11-----  | 2907.285<br>2906.688<br>2906.592<br>2906.560<br>2906.232<br>2906.062<br>2905.770<br>2905.647<br>2905.507 | 1390<br>1385<br>1384<br>1383<br>1381<br>1380<br>1377<br>1376<br>1375 | 11-----  | 3131.197<br>3131.259<br>3131.382<br>3131.749                         | 2515<br>2515a<br>2516<br>2518                              |          |                  |          |
| 12-----  | 2896.932<br>2896.253<br>2896.157<br>2895.765<br>2895.705<br>2895.187<br>2895.078<br>2895.000<br>2894.960 | 1333<br>1330<br>1329<br>1325<br>1324<br>1320<br>1319<br>1318<br>1317 | 12-----  | 3140.028<br>3140.107<br>3140.235<br>3140.320<br>3140.515<br>3140.660 | 2551<br>2552<br>2553<br>2554<br>2555<br>2556               |          |                  |          |

TABLE 2. *Vibration-rotation wavenumbers for the  $\nu_3$  fundamental band of methane at 3018.9  $\text{cm}^{-1}$  at low pressures—Continued*

| <i>P</i> | $\text{cm}^{-1}$ | Line No. | <i>R</i> | $\text{cm}^{-1}$ | Line No. | <i>Q</i> | $\text{cm}^{-1}$ | Line No. |      |
|----------|------------------|----------|----------|------------------|----------|----------|------------------|----------|------|
| 13-----  | 2886.570         | 1270     | 13-----  | 3148.815         | 2587     |          |                  |          |      |
|          | 2886.070         | 1268     |          | 3149.010         | 2588a    |          |                  |          |      |
|          | 2885.813         | 1266     |          | 3149.050         | 2588b    |          |                  |          |      |
|          | 2885.718         | 1265     |          | 3149.095         | 2589     |          |                  |          |      |
|          | 2885.310         | 1262     |          | 3149.345         | 2591     |          |                  |          |      |
|          | 2885.190         | 1261     |          | 3149.423         | 2592     |          |                  |          |      |
|          | 2885.050         | 1260     |          | 3149.480         | 2593     |          |                  |          |      |
|          | 2884.867         | 1258     |          |                  |          |          |                  |          |      |
|          | 2884.720         | 1257     |          |                  |          |          |                  |          |      |
|          | 2884.620         | 1256     |          |                  |          |          |                  |          |      |
|          | 2884.463         | 1255     |          |                  |          |          |                  |          |      |
|          | 2884.413         | 1254     |          |                  |          |          |                  |          |      |
|          | 2884.348         | 1253     |          |                  |          |          |                  |          |      |
| 14-----  | 2876.182         | 1205     | 14-----  | 3157.470         | 2616     |          |                  |          |      |
|          | 2875.622         | 1202     |          | 3157.660         | 2617     |          |                  |          |      |
|          | 2875.402         | 1200     |          | 3157.730         | 2618     |          |                  |          |      |
|          | 2875.368         | 1199     |          | 3158.070         | 2619     |          |                  |          |      |
|          | 2874.937         | 1195     |          |                  |          |          |                  |          |      |
|          | 2874.873         | 1194     |          |                  |          |          |                  |          |      |
|          | 2874.783         | 1193     |          |                  |          |          |                  |          |      |
|          | 2874.693         | 1192     |          |                  |          |          |                  |          |      |
|          | 2874.558         | 1190     |          |                  |          |          |                  |          |      |
|          | 2874.477         | 1189     |          |                  |          |          |                  |          |      |
|          | 2873.790         | 1185     |          |                  |          |          |                  |          |      |
|          | 2873.723         | 1184     |          |                  |          |          |                  |          |      |
|          | 2873.695         | 1183     |          |                  |          |          |                  |          |      |
|          | 2873.603         | 1182     |          |                  |          |          |                  |          |      |
| 15-----  | 2865.770         | 1147     | 15-----  | 3166.040         | 2631     |          |                  |          |      |
|          | 2865.340         | 1146     |          | 3166.270         | 2632     |          |                  |          |      |
|          | 2864.952         | 1144     |          | 3166.490         | 2633     |          |                  |          |      |
|          | 2864.683         | 1143     |          | 3166.720         | 2634     |          |                  |          |      |
|          | 2864.403         | 1142     |          |                  |          |          |                  |          |      |
|          | 2864.213         | 1141     |          |                  |          |          |                  |          |      |
|          | 2863.960         | 1140     |          |                  |          |          |                  |          |      |
|          | 2863.890         | 1139     |          |                  |          |          |                  |          |      |
|          | 2863.110         | 1138     |          |                  |          |          |                  |          |      |
|          | 2863.040         | 1137     |          |                  |          |          |                  |          |      |
|          | 2863.005         | 1136     |          |                  |          |          |                  |          |      |
|          | 2862.930         | 1135     |          |                  |          |          |                  |          |      |
| 16-----  | 2854.577         | 1112     | 16-----  | 3174.80          | 2639     |          |                  |          |      |
|          | 2854.507         | 1111     |          | 3175.22          | 2640     |          |                  |          |      |
|          | 2854.137         | 1110     |          | 3178.08          | 2641     |          |                  |          |      |
|          | 2853.912         | 1109     |          |                  |          |          |                  |          |      |
|          | 2853.863         | 1108     |          |                  |          |          |                  |          |      |
|          | 2853.663         | 1107     |          |                  |          |          |                  |          |      |
|          | 2853.420         | 1106     |          |                  |          |          |                  |          |      |
|          | 2853.310         | 1105     |          |                  |          |          |                  |          |      |
|          | 2853.217         | 1104     |          |                  |          |          |                  |          |      |
|          | 2852.377         | 1102     |          |                  |          |          |                  |          |      |
|          | 2852.310         | 1101     |          |                  |          |          |                  |          |      |
|          |                  |          |          | 17-----          | 3183.01  |          |                  |          | 2644 |
|          |                  |          |          |                  | 3183.14  |          |                  |          | 2645 |
|          |                  | 3183.23  | 2646     |                  |          |          |                  |          |      |
|          |                  | 3183.37  | 2647     |                  |          |          |                  |          |      |
|          |                  | 3183.46  | 2648     |                  |          |          |                  |          |      |
|          |                  |          | 3183.66  | 2649             |          |          |                  |          |      |

In figure 3 there is a concentration of lines near  $2600 \text{ cm}^{-1}$  which is a *Q* branch of  $2\nu_4$ . Since  $\nu_4$  is triply degenerate  $2\nu_4$  could, with Coriolis interactions, consist of six separate subbands and may account for the large number of lines observed in the region from  $2470$  to  $2650 \text{ cm}^{-1}$ .

Many features of the spectrum have been explained on the basis of the theoretical work of Jahn [9]. His calculations of the Coriolis interactions carried to a second order approximation have explained the splitting of the lines of the *P*, *Q*, and *R* branches into components. However his results are not adequate to give a quantitative agreement with the experimental results given in this paper. In order to properly account for the observed spectrum still higher order corrections must be included. A theoretical treatment of the spectrum of  $\text{CH}_4$ , which has recently been carried out by Professor Karl Hecht of the University of Michigan, should make possible a better detailed analysis than is known at present. He has obtained excellent agree-

ment with the experimental results for the  $\nu_3$  band for values of  $J \leq 8$ , and a good agreement for values of  $J > 8$ . His results will appear in a separate publication.

### 5. References

- [1] D. M. Dennison, *Astrophys. J.* **62**, 84 (1925).
- [2] J. S. Burgess, E. E. Bell, and H. H. Nielsen, *J. Opt. Soc. Am.* **43**, 1058 (1953).
- [3] H. C. Allen, Jr., and Earle K. Plyler, *J. Chem. Phys.* **26**, 972 (1957).
- [4] A. H. Nielsen and H. H. Nielsen, *Phys. Rev.* **48**, 864 (1935).
- [5] W. H. T. Childs and H. A. Jahn, *Proc. Roy. Soc. [A]* **169**, 451 (1939).
- [6] Earle K. Plyler and L. R. Blaine, *J. Research NBS* **62**, (1959) RP2922
- [7] Earle K. Plyler, L. R. Blaine, and Eugene D. Tidwell, *J. Research NBS* **55**, 279 (1955) RP2630.
- [8] D.R.J. Boyd and H.W. Thompson, *Proc. Roy. Soc. [A]* **213**, 42 (1952).
- [9] H. A. Jahn, *Proc. Roy. Soc. [A]* **171**, 450 (1939).

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(Paper 64A3-44)