NO. 125 NASA ATLAS OF INFRARED SOLAR SPECTRUM, REPORT III

by GERARD P. KUIPER

November 16, 1968

ABSTRACT

The region of the solar spectrum containing the \( v_3 \) band of methane, \( \lambda 3.12-3.46 \mu \), is shown as it appears essentially freed from telluric water vapor. Records taken with both the B- and the 4-meter spectrometer are included. The 4-meter results are somewhat degraded by a modulation due to filter interference and are regarded provisional. The Coriolis fine structure for some of the rotational lines is resolved. The remarkable paucity of solar absorption lines in this region is noted. In addition to the solar spectrum itself, the available observations from the NASA CV 990 illustrate one further aspect: the telluric absorptions other than by \( \text{H}_2\text{O} \) are standing out much more clearly. For, while the \( \text{H}_2\text{O} \) abundance is cut by 100–1000 \( \times \) over a mountain observatory, other telluric absorptions (\( \text{CO}_2, \text{CO}, \text{N}_2\text{O}, \text{CH}_4 \)) are cut by only 4 \( \times \), while \( \text{O}_3 \) is hardly cut at all. Thus, other minor atmospheric constituents might be still found spectroscopically, as \( \text{CH}_4, \text{CO}, \text{and N}_2\text{O} \) were discovered in the recent past. This report considers the region of the \( v_3 \) band of \( \text{CH}_4 \) around 3.3 \( \mu \), from records that are regarded quite provisional.

The upper two strips of Fig. 1 show one of the four traces of the 3.12–3.46 \( \mu \) region taken with the B-spectrometer and a PbSe cell, dry-ice cooled. Two small dips due to guiding errors have been reconstructed in accordance with the other traces. The rotational lines of the \( P \) and \( R \) branches have been numbered. The \( Q \) branch is just beginning to show structure. The resolution is 7–8 \( \AA \) or about 4500, or 0.7 \( \text{cm}^{-1} \). The strength of the \( v_3 \) band may cause surprise with only 3-mm atm. of \( \text{CH}_4 \) at \( p < 200 \text{ mb} \) in the beam.

The lower two strips of Fig. 1 show two separate runs with the 4-meter spectrometer of the region of the \( Q \) branch, and well as \( P(1) \), and \( R(0) \) and \( R(1) \). The other members of the \( R \) branch, up to \( R(15) \), are seen in Fig. 2. Unfortunately, an instrumental interference effect put a rough sine wave on the continuum and the flight schedule did not allow tracing and eliminating the source. (This region will soon be re-observed from the NASA Lear Jet.) From the appearance of \( R(4) \), \( R(5) \), \( R(6) \), \( R(7) \), \( R(10) \), \( R(12) \),
the resolution of the 4-meter records is found to be
1.0–1.2 A or \( R \approx 30,000 \) (or 0.1 cm\(^{-1}\)), close to the
theoretical limit of the optics used. The times and
other flight data are found in Table 1. Above the
spectral traces in Figs. 1 and 2 water-vapor lines are
indicated by dots, and methane absorptions by
lines.

The atlas, *The Solar Spectrum from 2.8–23.7
Microns* (Migeotte et al., 1956) and its companion
Catalogue (Ibid. 1957) previously provided coverage
of this spectral interval, based on observations
from the 3500-meter high Jungfraujoch Interna-
tional Scientific Station in Switzerland. The wave-
length system and identifications there adopted have
been used here also, with additional consultation of
the *Atlas of Nitrous Oxide, Methane, and Ozone
Infrared Absorption Bands* (Migeotte et al., 1957).

The spectral resolution of the Migeotte Solar Atlas
in the 3.5 \( \mu \) region is 0.27 cm\(^{-1}\) (op. cit., Table II),
intermediate between our two resolutions. Fig. 3
reproduces the 5 sections of the Migeotte Atlas that
correspond to the 4-meter records of Figs. 1 and 2.
The Addendum shows laboratory spectra of methane
in the \( \nu_3 \) band region taken with the 4-meter spec-
trometer, matching Figs. 1 and 2. (The resolution
of 0.1 cm\(^{-1}\) is sufficiently higher than that of the
Liège records that a matching laboratory run was
needed.)

Attention is called to the Coriolis multiplicity of
the rotational “lines.” The \( Q \) branch in Fig. 1 and
the Addendum has great complexity which, how-
ever, is minor compared to that shown by truly high-
resolution records (Plyler *et al.*, 1960, p. 202, and
especially Hecht, 1960, p. 399). Since each “line”
of the \( Q \) branch has numerous Coriolis components
and since several of the features shown in Fig. 1 and
the Addendum are blends caused by 2–4 overlapping
multiple “lines,” no classifications have been entered
for the \( Q \) branch. Reference is made to the interpre-
tations by Hecht (op. cit.).

As stated, the present records are merely provi-
sional; but they suffice to show a paucity of solar
lines on this region.

**Acknowledgments.** I am indebted to NASA Hq.
and NASA-Ames for their support and interest in
the high-altitude program; to Messrs. J. Percy and
B. McClendon for assistance with the electronics
during the flights; to Messrs. A. Thomson, G. Sill,
and D. Olsen for their assistance in the operations;
and to Mrs. A. Agniera for her assistance in the
preparation of the figures. This research was sup-
ported through NASA Grant NsG 161-61 and the
University of Arizona Institutional Grant NGR-
03-002-091.

**REFERENCES**

Hecht, K. T. 1960, “Vibration-Rotation Energies
of Tetrahedral \( XY_4 \) Molecules, Part II. The
Fundamental \( \nu_3 \) of \( CH_4 \),” *Journal of Molecular

Migeotte, M., Neven, L., and Swensson, J. 1965,
*The Solar Spectrum from 2.8 to 23.7 Microns,
Part I, Photometric Atlas* (Institut d’Astrophys-
ique de l’Université de Liège). *Ibid.*, 1957,
*Part II, Measures and Identifications*.

Migeotte, M., Neven, L., Swensson, J., and Vigroux,
E. 1957, *Atlas of Nitrous Oxide, Methane, and
Ozone Infrared Absorption Bands* (Institut d’Astro-
physique de l’Université de Liège).

Plyler, E. K., Tidwell, E. T., and Blaine, L. R. 1960,
“Infrared Absorption Spectrum of Methane from
2470 to 3200 cm\(^{-1}\),” *Journal of Research Na-
tional Bureau of Standards*, Vol. 64A, No. 3,
pp. 201–212.

**TABLE 1**

<table>
<thead>
<tr>
<th>FIG.</th>
<th>SPECTR.</th>
<th>( \lambda ) (Å)</th>
<th>1968 DATE</th>
<th>U.T.</th>
<th>ALT. (FT)</th>
<th>TEMP ( ^\circ )C</th>
<th>CABIN ALT.</th>
<th>CELL ( (-7^\circ)C)</th>
<th>GAIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>B</td>
<td>31190–32950</td>
<td>July 19</td>
<td>20:26</td>
<td>39,000</td>
<td>-53</td>
<td>8500</td>
<td>PbSe</td>
<td>5-5</td>
</tr>
<tr>
<td>1b</td>
<td>B</td>
<td>32950–34678</td>
<td>July 19</td>
<td>20:29</td>
<td>39,000</td>
<td>-53</td>
<td>8500</td>
<td>PbSe</td>
<td>5-5</td>
</tr>
<tr>
<td>1c</td>
<td>4.2 m</td>
<td>32898–33265</td>
<td>Aug 7</td>
<td>19:24</td>
<td>41,000</td>
<td>-57</td>
<td>8900</td>
<td>PbS</td>
<td>6-3</td>
</tr>
<tr>
<td>1d</td>
<td>4.2 m</td>
<td>32898–33265</td>
<td>Aug 7</td>
<td>19:27</td>
<td>41,000</td>
<td>-57</td>
<td>8900</td>
<td>PbS</td>
<td>6-(3, 4)</td>
</tr>
<tr>
<td>2a</td>
<td>4.2 m</td>
<td>31487–31843</td>
<td>Aug 7</td>
<td>19:10</td>
<td>41,000</td>
<td>-57</td>
<td>8900</td>
<td>PbS</td>
<td>6-2</td>
</tr>
<tr>
<td>2b</td>
<td>4.2 m</td>
<td>31843–32190</td>
<td>Aug 7</td>
<td>19:13</td>
<td>41,000</td>
<td>-57</td>
<td>8900</td>
<td>PbS</td>
<td>6-2</td>
</tr>
<tr>
<td>2c</td>
<td>4.2 m</td>
<td>32190–32549</td>
<td>Aug 7</td>
<td>19:17</td>
<td>41,000</td>
<td>-57</td>
<td>8900</td>
<td>PbS</td>
<td>6-(2, 3)</td>
</tr>
<tr>
<td>2d</td>
<td>4.2 m</td>
<td>32549–32898</td>
<td>Aug 7</td>
<td>19:20</td>
<td>41,000</td>
<td>-57</td>
<td>8900</td>
<td>PbS</td>
<td>6-3</td>
</tr>
</tbody>
</table>
Fig. 1 (a) (b) B-Spectrometer record of Solar Spectrum, $\lambda$ 3.12–3.46 $\mu$.
(c) (d) Two runs with 4-meter Spectrometer, $\lambda$ 3.290–3.326 $\mu$ (cf. Table 1).
Fig. 3. Five sections of Minot and Atwater's (1956) matching data records of Fig. 1 (bottom) and Fig. 2 (upper four).
ADDENDUM

Laboratory Spectra of the $\nu_3$ Band of CH$_4$

by LAURENS A. BIJL

Figs. 1A–6A reproduce two sets of laboratory spectra which nearly match, in resolution and in the intensities of the methane and water-vapor absorptions, the solar records shown in Figs. 1 and 2, above. Specifically, Figs. 1A and 2A are the laboratory counterparts of the first two strips of Fig. 1, although they were obtained with the 4-meter spectrometer. A wide slit was used to obtain the desired resolution. Figs. 3A–6A were obtained with the same instrument but normal slit width, approximately corresponding to the conditions used in the solar observations. Table 1 gives the details for all 24 spectral records contained in the six figures.

With ambient air the water-vapor content of the spectrometer would have been 10–15 times the amount desired. Since a 70-cm path outside the spectrometer gave the desired strength of the water-vapor absorptions, the spectrometer itself was flushed with dry nitrogen during the operations. The amount of water vapor in Figs. 1A and 2A is the same as in Figs. 1A, b, c, and 2A, a, b, c; whereas, the amount in Figs. 3A, b, d, 4A, b, d, and 5A, b, d, was made higher than in the corresponding methane spectra, to show the lines more clearly. The water-vapor absorptions have been marked with dots above the spectra as in Figs. 1 and 2. The water-vapor absorptions in Fig. 6A are negligible.

The methane absorptions were obtained with a 10-cm cell placed between the laboratory source and the spectrometer slit. The pressure in the cell was adjusted to values recorded in Table 1 which resulted in total absorptions of the amount required. E.g., Figs. 1 and 2 were obtained with pressures of $p = 9$, 4, and 2 cm corresponding to amounts of methane of 12, 5.3, and 2.6 mm atm, whereas the anticipated amount of the gas in the solar beam is approximately 3 mm atm. The records in Figs. 3A–6A were obtained with $p = 8$ cm corresponding to 10.5 mm atm of methane. In order to facilitate the comparison between the solar and laboratory records, the methane absorptions in Figs. 3A, 4A, and 5A have been marked with short vertical lines, as in the solar spectra.

Comparison with the solar records shows that a reasonably good match in resolution was indeed obtained. The most striking difference is the intensity distribution in the P, Q, and R branches, clearly the result of the higher laboratory temperature (about 295° K vs. 220° K for the stratospheric absorptions). The wavelength scale used was based on An Atlas of Nitrous Oxide, Methane and Ozone Infrared Absorption Bands (Migeotte, et al). The scale differs slightly from the one adopted in the solar records, Figs. 1 and 2.

Mrs. A. Agnieray assisted in the preparation of the figures.

REFERENCES


| TABLE 1 |
| Laboratory Records of $\nu_3$ Band of CH$_4$ |
| 4-M Spectrometer, 4-µm Grating (300 Lines/MM), 2.4-µm Filter, PbS Detector (—78°C) |

<table>
<thead>
<tr>
<th>FIG.</th>
<th>CH$_4$ (p/CM)</th>
<th>GAIN</th>
<th>SLIT (MM)</th>
<th>$\tau$ (SEC.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A a</td>
<td>9 4–5, 4–6, 5–2, 5–3</td>
<td>1.0</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>1A b</td>
<td>4 4–5, 4–6, 5–2, 5–3</td>
<td>1.0</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>1A c</td>
<td>2 4–6, 5–1, 5–2, 5–3</td>
<td>1.0</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>1A d</td>
<td>0 4–5, 4–6, 5–2, 5–3</td>
<td>1.0</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>2A a</td>
<td>9 5–3, 5–4, 5–5, 5–6</td>
<td>1.0</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>2A b</td>
<td>4 5–3, 5–4, 5–5, 5–6</td>
<td>1.0</td>
<td>0.12–0.24</td>
<td></td>
</tr>
<tr>
<td>2A c</td>
<td>2 5–3, 5–4, 5–5, 5–6</td>
<td>1.0</td>
<td>0.12–0.24</td>
<td></td>
</tr>
<tr>
<td>2A d</td>
<td>0 5–3, 5–4, 5–5, 5–6</td>
<td>1.0</td>
<td>0.12–0.24</td>
<td></td>
</tr>
<tr>
<td>3A a</td>
<td>8 6–1, 6–2</td>
<td>0.10</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>3A b</td>
<td>6–1, 6–2</td>
<td>0.10</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>3A c</td>
<td>6–1</td>
<td>0.10–0.15</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>3A d</td>
<td>0 6–2</td>
<td>0.10</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>4A a</td>
<td>8 6–2</td>
<td>0.15</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>4A b</td>
<td>0 6–2</td>
<td>0.10–0.20</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>4A c</td>
<td>8 6–2</td>
<td>0.15</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>4A d</td>
<td>0 6–2</td>
<td>0.20</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>5A a</td>
<td>8 6–2, 6–3</td>
<td>0.15</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>5A b</td>
<td>6–2, 6–3</td>
<td>0.20</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>5A c</td>
<td>6–3</td>
<td>0.15</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>5A d</td>
<td>0 6–3</td>
<td>0.20</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>6A a</td>
<td>8 6–4</td>
<td>0.17</td>
<td>0.36*</td>
<td></td>
</tr>
<tr>
<td>6A b</td>
<td>0 6–4, 6–5</td>
<td>0.17</td>
<td>0.36*</td>
<td></td>
</tr>
<tr>
<td>6A c</td>
<td>8 6–5</td>
<td>0.17–0.30</td>
<td>0.36*</td>
<td></td>
</tr>
<tr>
<td>6A d</td>
<td>0 6–5</td>
<td>0.30</td>
<td>0.36*</td>
<td></td>
</tr>
</tbody>
</table>

*Actually, $\tau = 1.8$ sec. used at one-fifth of normal scan rate, thus corresponding to $\tau = 0.36$ sec. at usual scan rate.

Fig. 1A Laboratory spectrum of methane, matching Fig. 1a and 1b in resolution, 3.119–3.296 µ. Three amounts are used: $a$, 12 mm atm; $b$, 5.3 mm atm; and $c$, 2.0 mm atm. The corresponding water-vapor spectrum is found in $d$. 
Fig. 2A Laboratory spectrum of methane, matching Fig. 1a and 1b in resolution, 3.296–3.469 μ. Three amounts are used: a, 12 mm atm; b, 5.3 mm atm; and c 2.6 mm atm. The corresponding water-vapor spectrum is found in d.
Fig. 4. A laboratory spectrum of methane. 10.3 mm atm, p = 8 cm, 3.21/0-3.290 μ, with water-vapor comparisons added.
Fig. 5A  Laboratory spectrum of methane, 10.5 mm atm, $p = 8$ cm, 3.290–3.363 $\mu$, with water-vapor comparisons added.
Fig. 6A  Laboratory spectrum of methane, 10.5 mm atm, p = 8 cm, 3.363–3.504 μ. No observable water absorptions.