

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

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### ABSTRACT

The region of the solar spectrum containing the  $\nu_3$  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  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{N}_2\text{O}$  were discovered in the recent past. This report considers the region of the  $\nu_3$  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 recon-

structed 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  $\text{\AA}$  or about 4500, or 0.7  $\text{cm}^{-1}$ . The strength of the  $\nu_3$  band may cause surprise with only 3-mm atm. of  $\text{CH}_4$  at  $p < 200$  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 Å or  $R \approx 30,000$  (or  $0.1 \text{ cm}^{-1}$ ), 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 Jungfrauoch International Scientific Station in Switzerland. The wavelength 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  $3.3 \mu$  region is  $0.27 \text{ cm}^{-1}$  (*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 spectrometer, matching Figs. 1 and 2. (The resolution of  $0.1 \text{ cm}^{-1}$  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, however, 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 interpretations by Hecht (*op. cit.*).

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

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## REFERENCES

- Hecht, K. T. 1960, "Vibration-Rotation Energies of Tetrahedral  $\text{XY}_4$  Molecules, Part II. The Fundamental  $\nu_3$  of  $\text{CH}_4$ ," *Journal of Molecular Spectroscopy*, Vol. 5, pp. 390–404.
- Migeotte, M., Neven, L., and Swensson, J. 1965, *The Solar Spectrum from 2.8 to 23.7 Microns, Part I, Photometric Atlas* (Institut d'Astrophysique 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'Astrophysique 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  $\text{cm}^{-1}$ ," *Journal of Research National Bureau of Standards*, Vol. 64A, No. 3, pp. 201–212.

TABLE 1

SOLAR SPECTRUM RECORDS, NASA 990 JET  
 $4 \mu$  GRATING (300 LINES/MM),  $2.4 \mu$  FILTER, SLIT 0.23 MM,  $\tau = 0.24$  SEC.

FIG.	SPECTR.	$\lambda$ (Å)	1968 DATE	U.T.	ALT. (FT)	TEMP °C	CABIN ALT.	CELL (–78°C)	GAIN
1a	B	31190–32950	July 19	20:26	39,000	–53	8500	PbSe	5–5
1b	B	32950–34678	July 19	20:29	39,000	–53	8500	PbSe	5–5
1c	4.2 m	32898–33265	Aug 7	19:24	41,000	–57	8900	PbS	6–3
1d	4.2 m	32898–33265	Aug 7	19:27	41,000	–57	8900	PbS	6–(3, 4)
2a	4.2 m	31487–31843	Aug 7	19:10	41,000	–57	8900	PbS	6–2
2b	4.2 m	31843–32190	Aug 7	19:13	41,000	–57	8900	PbS	6–2
2c	4.2 m	32190–32549	Aug 7	19:17	41,000	–57	8900	PbS	6–(2, 3)
2d	4.2 m	32549–32898	Aug 7	19:20	41,000	–57	8900	PbS	6–3

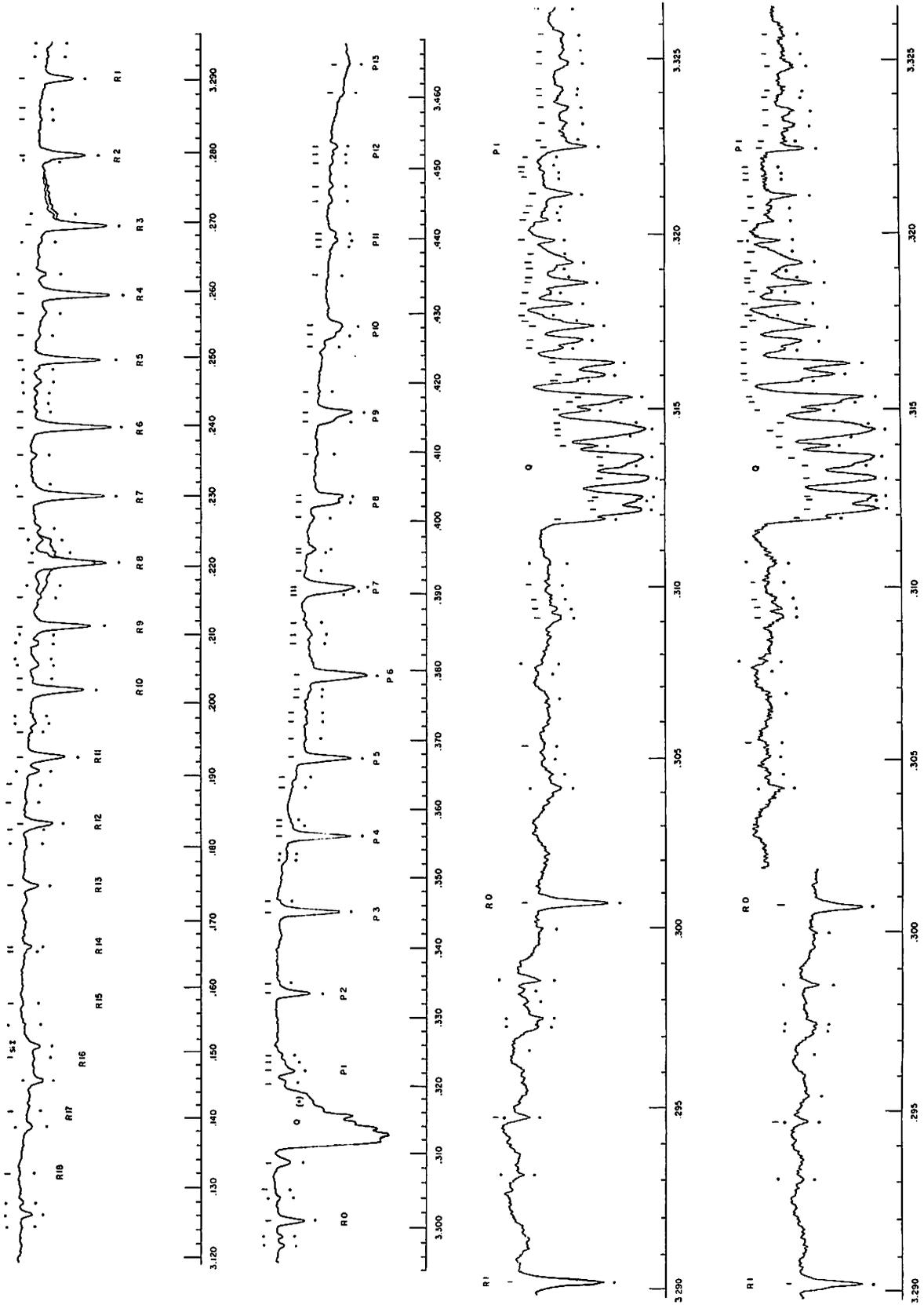


Fig. 1 (a) (b) B-Spectrometer record of Solar Spectrum,  $\lambda$  3.12-3.46  $\mu$ .  
 (c) (d) Two runs with 4-meter Spectrometer,  $\lambda$  3.290-3.326  $\mu$  (cf. Table 1).

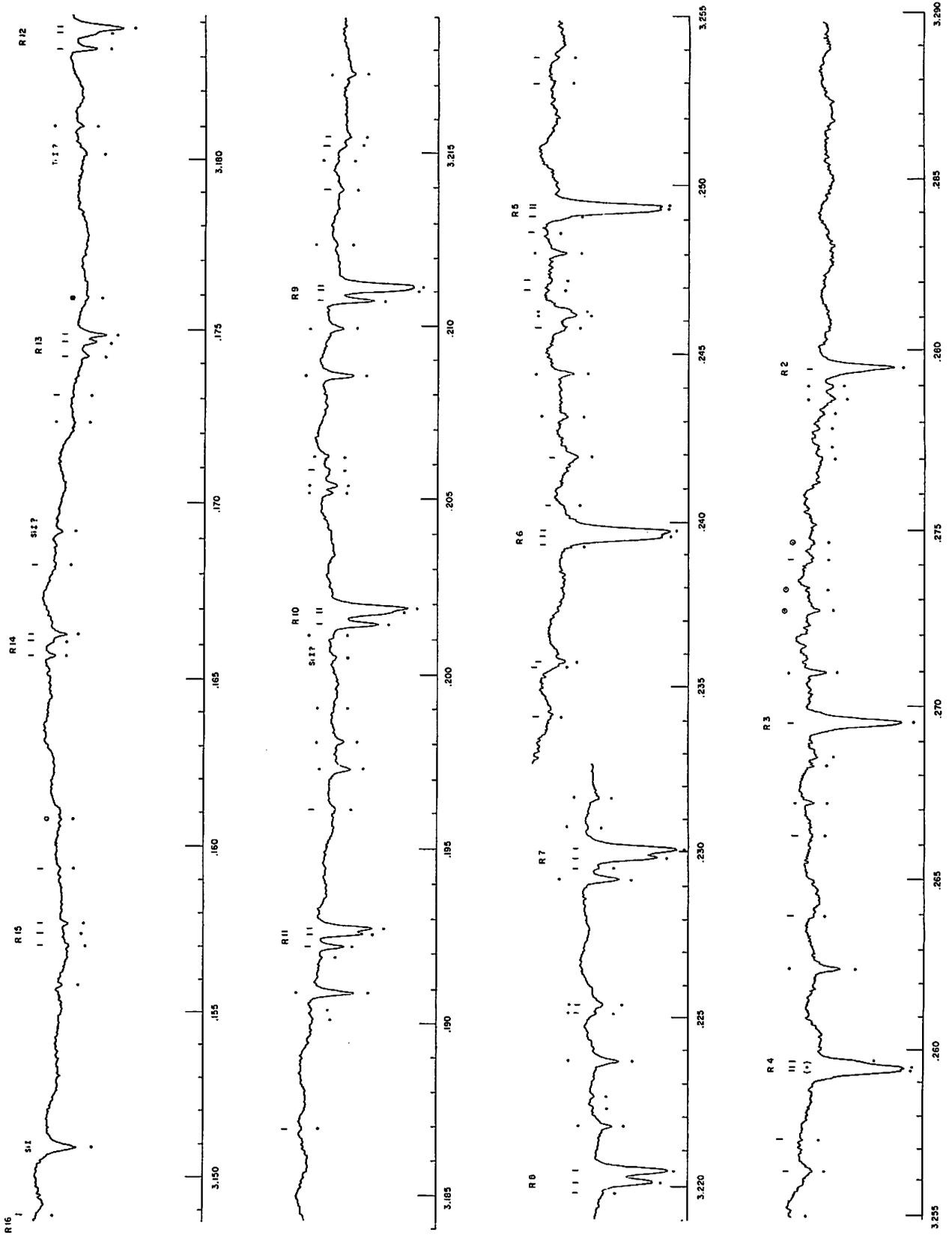


Fig. 2 Solar Spectrum,  $\lambda$  3.149-3.290  $\mu$ , in four strips, with 4-meter Spectrometer (cf. Table 1).

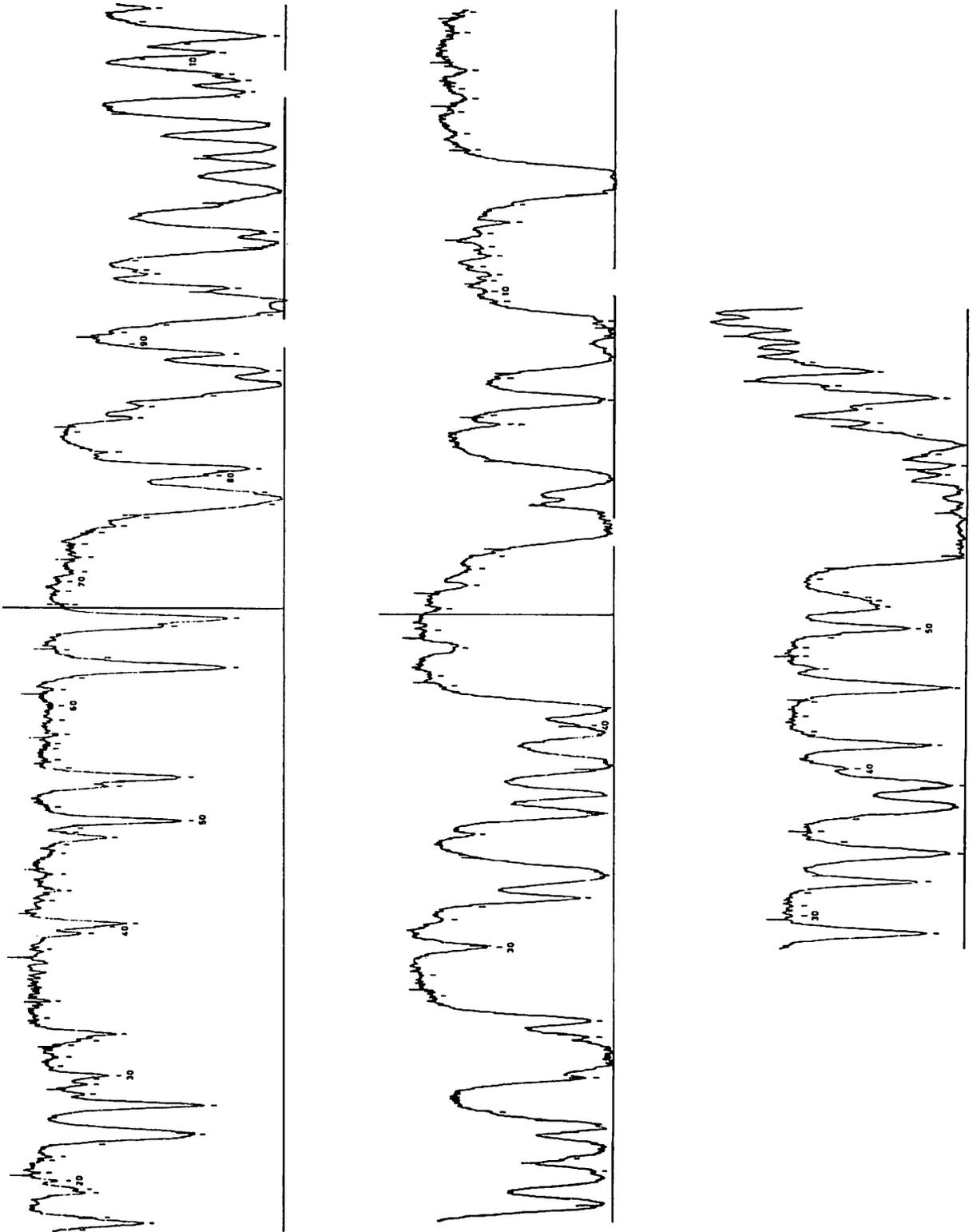


Fig. 3 Five sections of Migeotte Atlas (1956) matching 4-meter records of Fig. 1 (bottom) and Fig. 2 (upper four).

## ADDENDUM

Laboratory Spectra of the  $\nu_3$  Band of  $\text{CH}_4$ 

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. 1Ad and 2Ad is the same as in Figs. 1A a, 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  $295^\circ$  K vs.  $220^\circ$  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

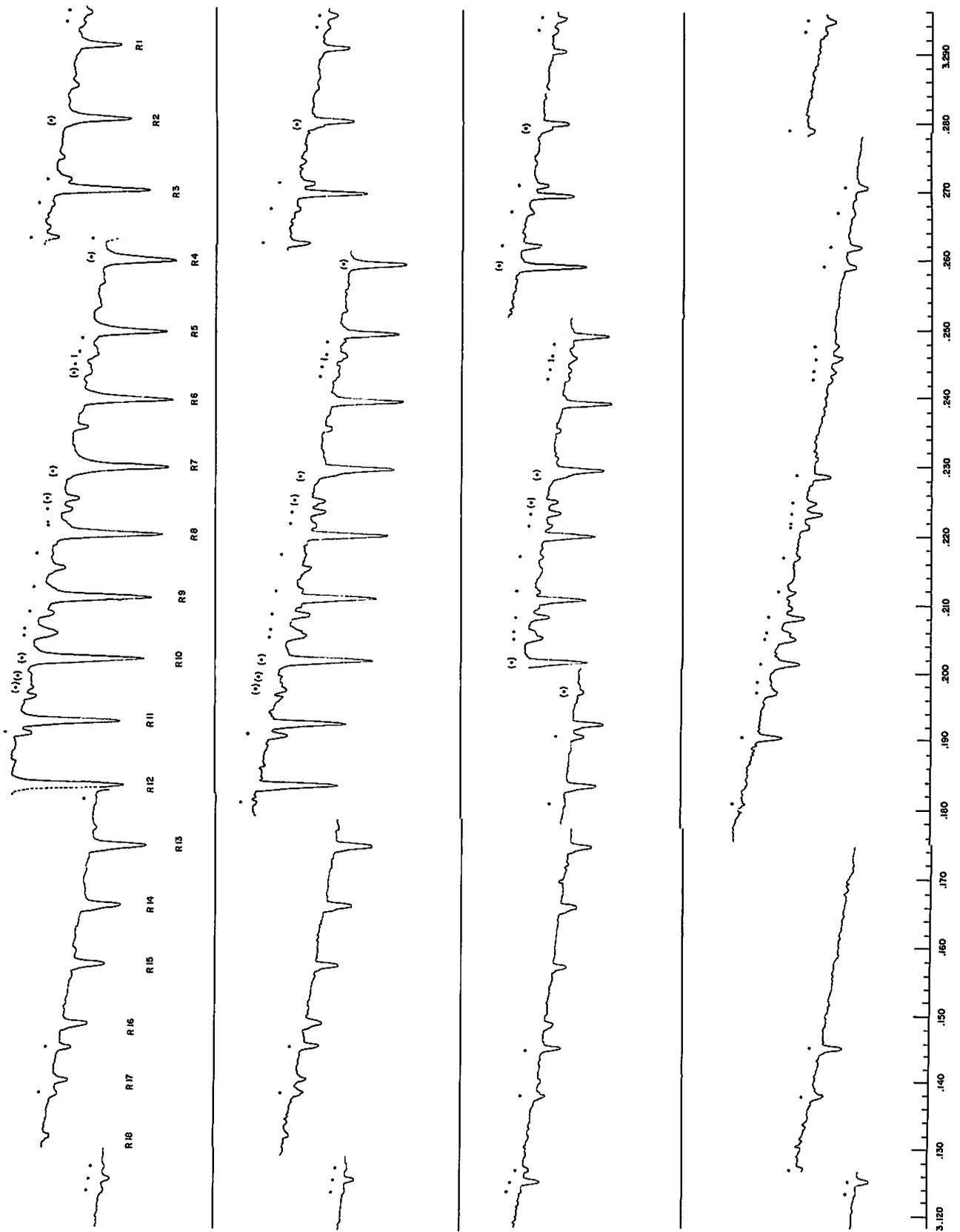
- Migeotte, M., Neven, L., Swensson, J., and Vigroux, E., *An Atlas of Nitrous, Methane and Ozone Infrared Absorption Bands*, Liège 1957, Part I. *The Photometric Records*, Liège 1958, Part II. *Measures and Identifications*.

TABLE 1  
LABORATORY RECORDS OF  $\nu_3$  BAND OF  $\text{CH}_4$ ,  
4-M SPECTROMETER, 4- $\mu$  GRATING (300 LINES/MM),  
2.4- $\mu$  FILTER, PbS DETECTOR ( $-78^\circ\text{C}$ )

FIG.	$\text{CH}_4$ P(CM)	GAIN	SLIT (MM)	$\tau$ (SEC.)
1A	a	9 4-5, 4-6, 5-2, 5-3	1.0	0.24
	b	4 4-5, 4-6, 5-2, 5-3	1.0	0.12
	c	2 4-6, 5-1, 5-2, 5-3	1.0	0.12
	d	0 4-5, 4-6, 5-2, 5-3	1.0	0.12
2A	a	9 5-3, 5-4, 5-5, 5-6	1.0	0.24
	b	4 5-4, 5-5, 5-6	1.0	0.12–0.24
	c	2 5-3, 5-4, 5-5, 5-6	1.0	0.12–0.24
	d	0 5-3, 5-4, 5-5, 5-6	1.0	0.12–0.24
3A	a	8 6-1, 6-2	0.10	0.24
	b	0 6-1, 6-2	0.10	0.24
	c	8 6-2	0.10–0.15	0.24
	d	0 6-2	0.10	0.24
4A	a	8 6-2	0.15	0.24
	b	0 6-2	0.10–0.20	0.24
	c	8 6-2	0.15	0.24
	d	0 6-2	0.20	0.24
5A	a	8 6-2, 6-3	0.15	0.24
	b	0 6-2, 6-3	0.20	0.24
	c	8 6-3	0.15	0.24
	d	0 6-3	0.20	0.24
6A	a	8 6-4	0.17	0.36*
	b	0 6-4, 6-5	0.17	0.36*
	c	8 6-5	0.17–0.30	0.36*
	d	0 6-5	0.30	0.36*

\*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  $\mu$ . 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. →



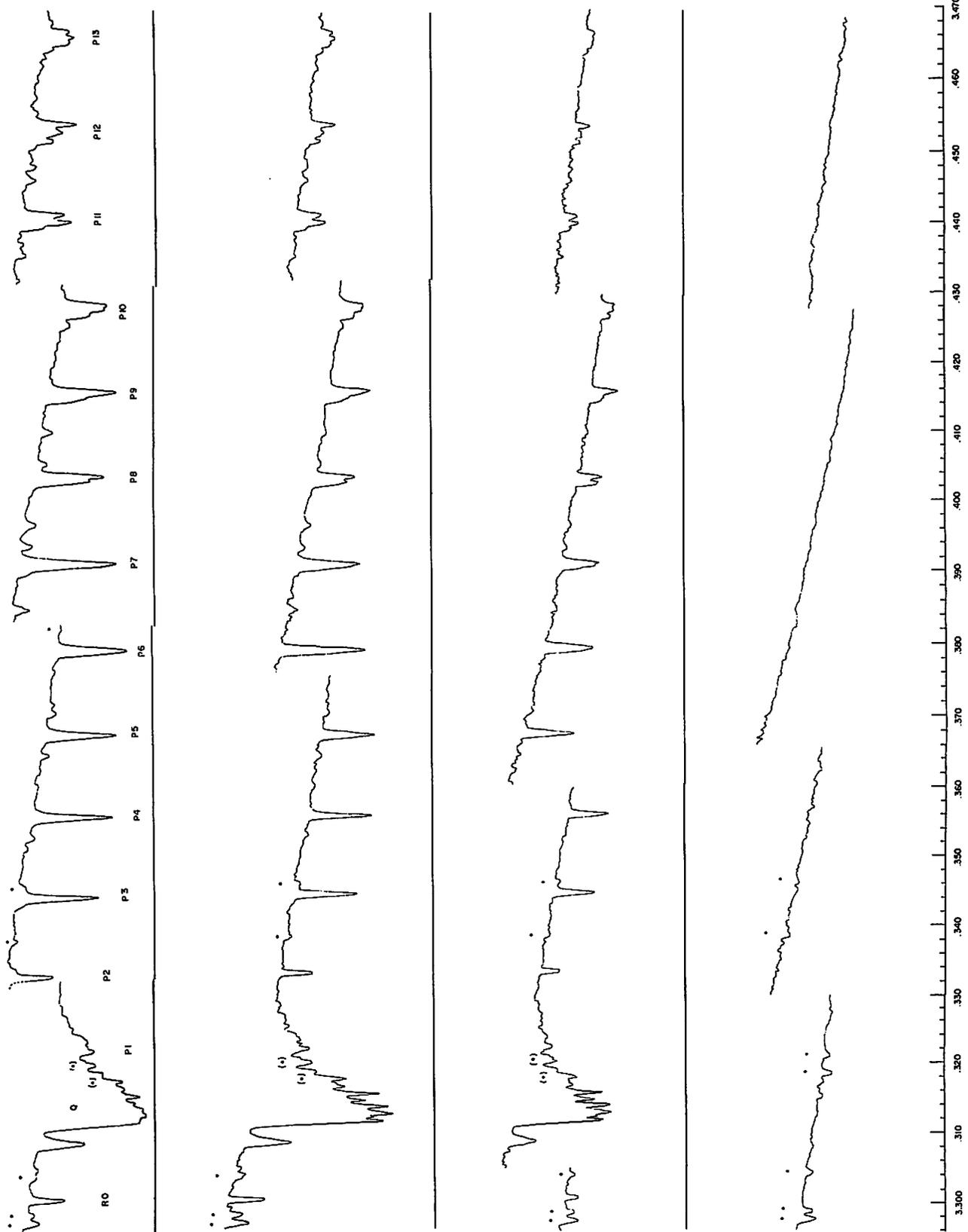


Fig. 2A Laboratory spectrum of methane, matching Fig. 1a and 1b in resolution, 3.296–3.469  $\mu$ . Three amounts are used: *a*, 12 mm atm; *b*, 5.3 mm atm; and *c* 2.6 mm atm. The corresponding water-vapor spectrum is found in *d*.



Fig. 3A Laboratory spectrum of methane, 10.5 mm atm, p = 8 cm, 3.148-3.219 μ, with water-vapor comparisons added.

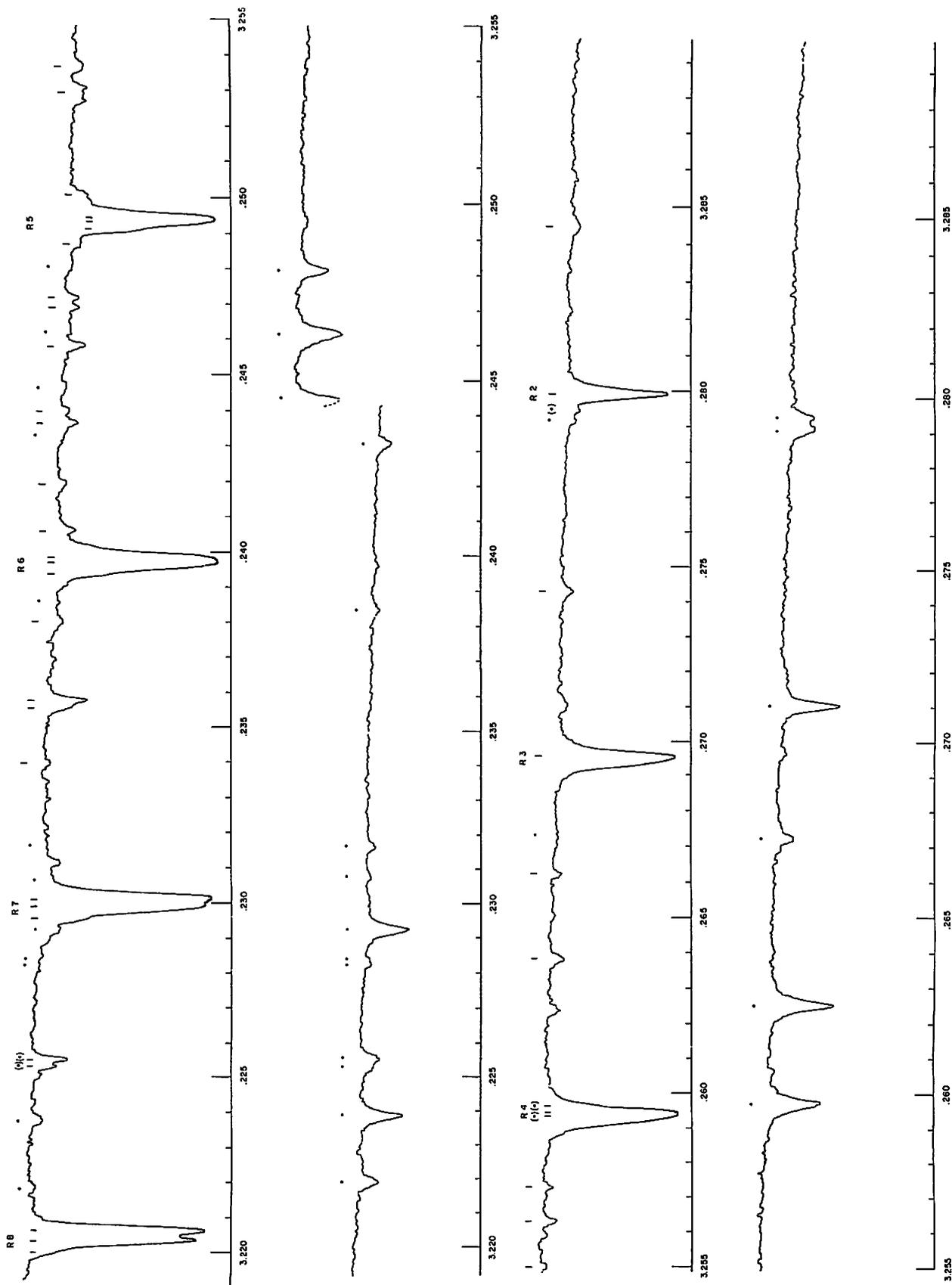


Fig. 4A Laboratory spectrum of methane, 10.5 mm atm,  $p = 8$  cm, 3.219–3.290  $\mu$ , with water-vapor comparisons added.

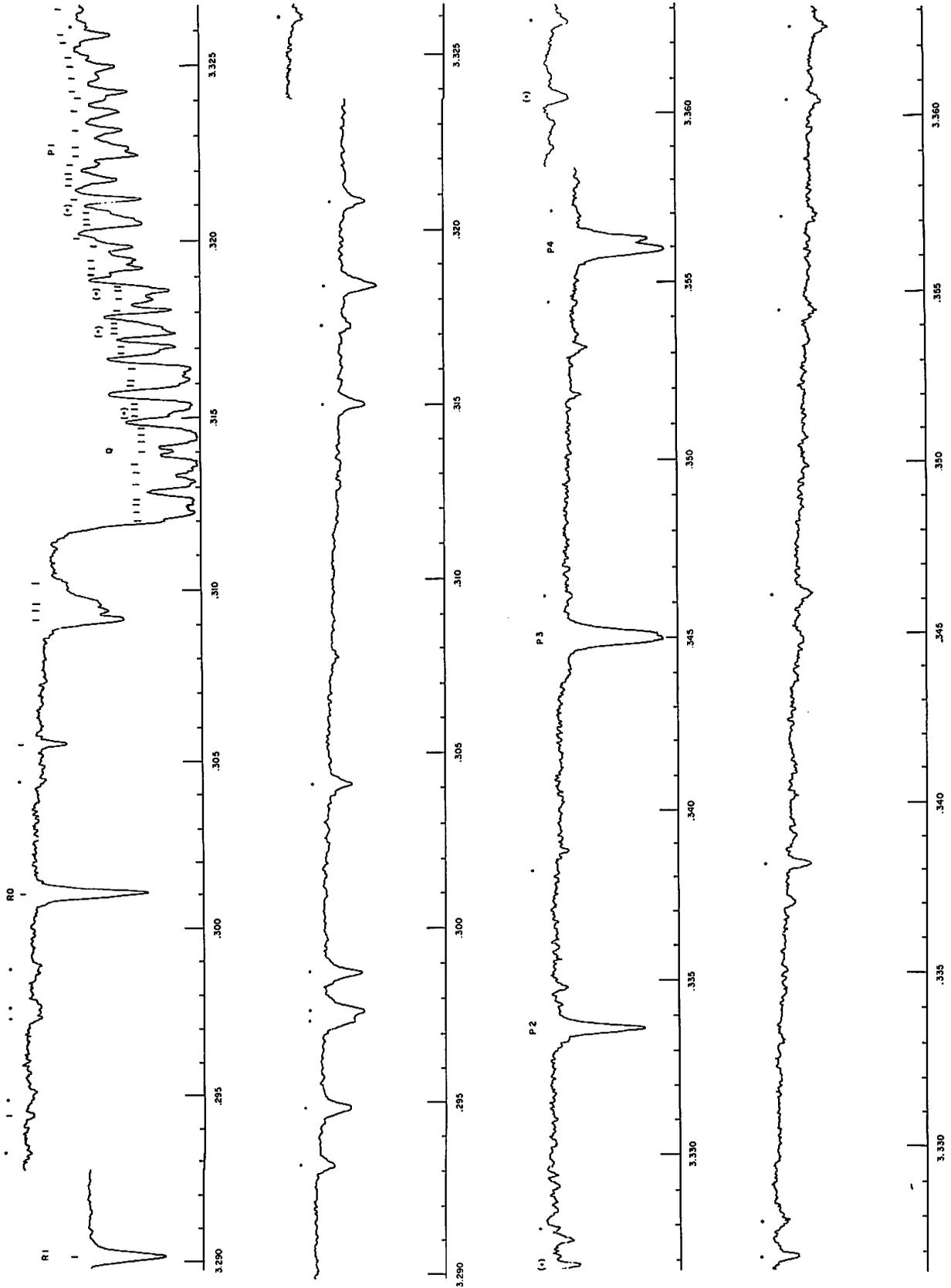


Fig. 54 Laboratory spectrum of methane, 10.5 mm atm, p = 8 cm, 3.290-3.363  $\mu$ , with water-vapor comparisons added.

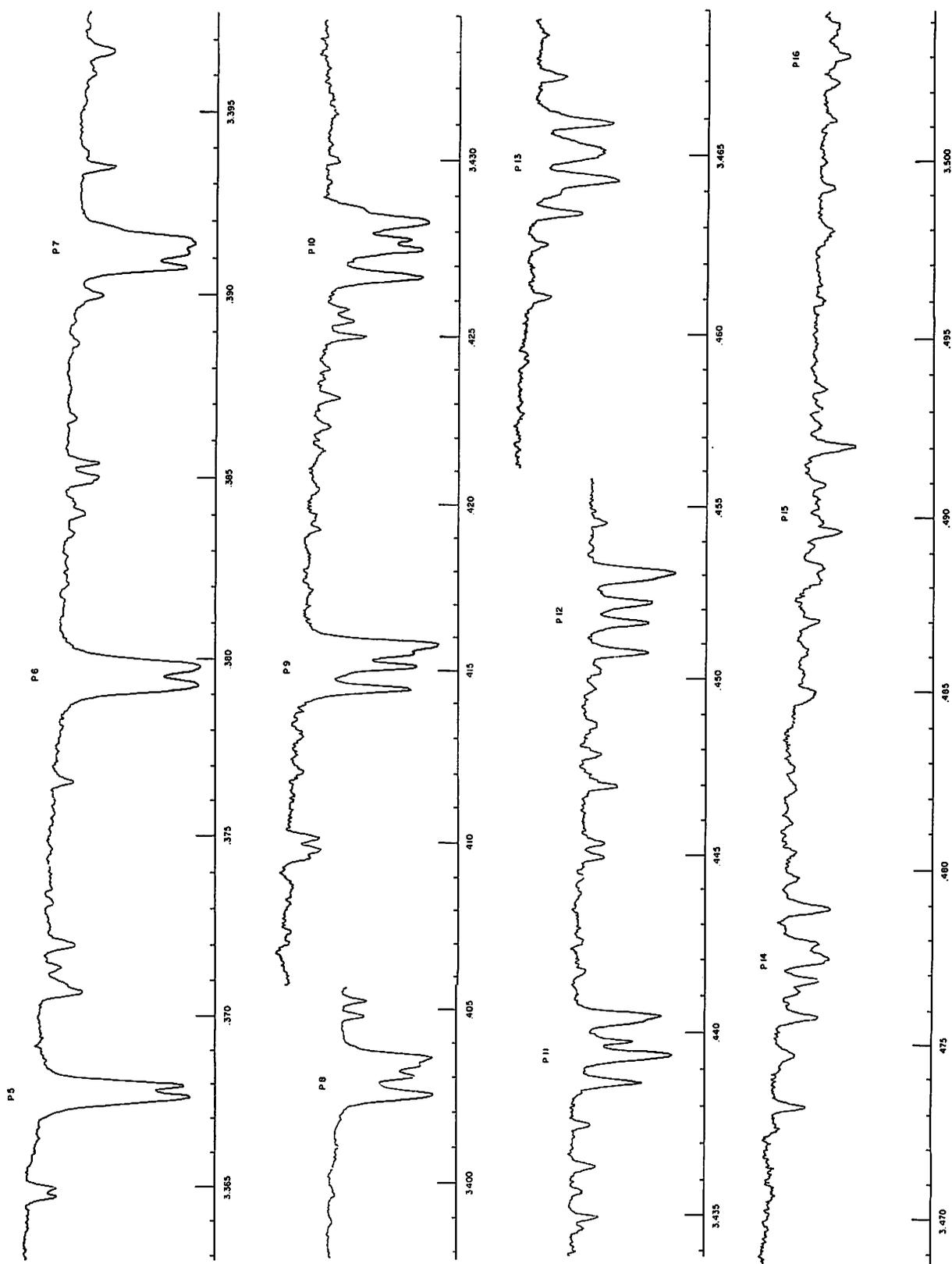


Fig. 6A Laboratory spectrum of methane, 10.5 mm atm,  $p = 8$  cm, 3.363-3.504  $\mu$ . No observable water absorptions.