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3 - Avenue Circulaire

B - 1180 BRUXELLES

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Stratospheric methane from infrared spectra

by M. ACKERMAN and C. MULLER

BELGISCH INSTITUUT VOOR RUIMTE-AERONOMIE

3 - Ringlaan

B - 1180 BRUSSEL

FOREWORD

This is the text of a communication presented at the symposium on "Sources, sinks, and concentrations of carbon monoxide and methane in the earth's environment", St. Petersburg Beach, Fla., August 15-17, 1972.

AVANT-PROPOS

Ce texte est celui d'une communication présentée au symposium : "Sources, sinks, and concentrations of carbon monoxide and methane in the earth's environment", St. Petersburg Beach, Fla., 15-17 août 1972.

VOORWOORD

De hiernavolgende tekst werd meegedeeld op het symposium : "Sources, sinks, and concentrations of carbon monoxide and methane in the earth's environment", St. Petersburg Beach, Fla., 15-17 augustus, 1972.

VORWORT

Dieser Text ist eine Mitteilung die während das Symposium "Sources, sinks, and concentrations of carbon monoxide and methane in the earth's environment" (St. Petersburg Beach, Fla., 15-17 August 1972) vorgetragen würde.

STRATOSPHERIC METHANE FROM INFRARED SPECTRA

by

M. ACKERMAN and C. MULLER

Abstract

Solar spectra recorded by means of a balloon borne spectrometer over the 3 to 4 μm wavelength range at solar zenith angles between 75° and 95° from an altitude of 34 km are presented. The mixing ratio of methane between 16 and 33 km which is deduced from the measurements decreases in the stratosphere. These observational results confirm the conclusion drawn from sampling experiments made by Bainbridge and Heidt up to 23 km and show that the mixing ratio decreases by a factor of about 3 between the tropopause at 13.5 km and the altitude of 33 km in the stratosphere.

Résumé

Des spectres solaires ont été enregistrés au moyen d'un spectromètre embarqué à bord d'une nacelle stratosphérique dans la domaine de longueur d'onde compris entre 3 et 4 μm pour des distances zénithales allant de 75° à 95° et depuis une altitude de 34 km. Le rapport de mélange du méthane entre 16 et 33 km est déduit des mesures qui indiquent sa décroissance avec l'altitude. Ceci confirme le résultat obtenu à partir d'expériences d'échantillonnage in situ faites par Bainbridge et Heidt jusqu'à l'altitude de 23 km et montre que le rapport de mélange du méthane décroît d'à peu près un facteur 3 de la tropopause (13.5 km) jusqu'à l'altitude de 33 km dans la stratosphère.

Samenvatting

Door middel van een spectrometer, aan boord van een stratosfeergondel op een hoogte van 34 km, werden zonn spectra opgenomen over het golflengtegebied tussen 3 en 4 μm , voor zenithale afstanden gaande van 75° tot 95°. De mengverhouding van metaan tussen 16 en 33 km welke afgeleid wordt uit deze metingen neemt af in de stratosfeer. De resultaten van deze waarnemingen bevestigen het besluit dat Bainbridge en Heidt trokken uit hun proefnemingen met monsternamen tot op 23 km hoogte en tonen aan dat de mengverhouding afneemt met een faktor 3 ongeveer tussen de tropopauze op 13.5 km en een hoogte van 33 km in de stratosfeer.

Zusammenfassung

Mit Hilfe einer Spektrometer, eingebaut in einer stratosphärischen Ballonenkorb, wurden Sonnenspektren zwischen 3 und 4 μm , für Zenitdistanzen zwischen 75° en 95°, auf einer Höhe von 34 km registriert. Das Durchmischungsverhältnis des Methanes weicht ab zwischen 16 und 33 km. Diese Messungen stimmen mit der in situ Stichproben von Bainbridge und Heidt bis auf einer Höhe von 23 km. Das Durchmischungsverhältnis nimmt ein Faktor 3 ab zwischen der Tropopause (13.5 km) und der Höhe von 33 km in der Stratosphäre.

Methane has been first observed in the atmosphere by Migeotte ⁽¹⁾ and is since known as a permanent constituent of the atmosphere. The most significant sink is the reaction with $O(^1D)$ or OH which leads to the CH_3 radical ⁽²⁾ as discussed by Nicolet and Peetermans ⁽²⁾.

The distribution of CH_4 in the stratosphere is thus essentially determined by its transport properties and precise measurements can bring valuable informations about the stratospheric eddy diffusion coefficients.

The tropospheric CH_4 measurements have been reviewed by Fink *et al* ⁽³⁾. The stratospheric mixing ratio has been shown ⁽⁴⁾ to decrease above the tropopause ; a rocket sampling near the stratopause leads to a value of 3×10^{-7} for a vertical column comprised between 42 and 62 km ⁽⁵⁾.

A vertical distribution of methane can be deduced from measurements of the solar spectrum from a balloon borne spectrometer for grazing altitudes of the solar rays ranging from 15.9 to 33.6 km. The instrumentation and the results of a previous flight have already been presented ⁽⁶⁾. The flight studied here took place the 22th of October 1971 between 13h 10 and 18h 16 G.M.T. The absorption was taking place over South-Western France and the Atlantic ocean. The tropopause level was 13.5 km and an anticyclonic zone was located on the gulf of Biscay.

Absorptions from the ν_3 and $\nu_2 + \nu_4$ CH_4 bands were observed and have been analysed by means of a line by line calculation using the data of Kyle ⁽⁷⁾. Those give the positions, line strengths, energy of the fundamental level and identification of the lines. Confirmation of the relative line intensities has been brought by McMahon *et al* ⁽⁸⁾ and the objections that can be made against the use of Kyle's data have been summarised by Taylor ⁽⁹⁾ for their application to the study of the ν_4 band in the jovian atmosphere.

The values for the half-width used here are those of Yamamoto and Hirono ⁽¹⁰⁾ for N_2 broadening. These are not very different from the constant value of 0.05 cm^{-1} S.T.P. used by Kyle and offer the advantage of giving a rotational variation. It should be noted that the influence of the line width on the integrated absorbance measured by Burch and Williams ⁽¹¹⁾ is not very significant.

Zenith angles greater than 90° permit to divide the atmosphere in two layers that were chosen of 3 km thickness with the pressure and temperature of their lower boundaries. The first layer only, for an uniformly mixed constituent takes into account about 75% of the optical depth.

The line strengths and half-widths were adapted in temperature and pressure using the formulae :

$$S(T) = S_o \left(\frac{T_o}{T} \right)^{3/2} \exp \left(-1.4388 \frac{E'' (T_o - T)}{T_o T} \right)$$

$$a = a_o \left(\frac{P}{P_o} \right) \left(\frac{T_o}{T} \right)^n$$

where E'' is the rotational energy of the fundamental level and where the index o indicates the conditions of pressure and temperature given in the data. The exponent n was chosen equal to 1/2 which is close to the value used by Varanasi and Tejwani⁽¹²⁾ which for $\text{CH}_4 - \text{H}_2$ broadening varies from 0.55 to 0.5. A value of n close to 1 has been derived by McMahan *et al*⁽⁸⁾, but figure 1 shows that in the narrow range of stratospheric temperatures, the difference between the two dependances may not lead to significant errors.

Figure 1 shows also the Doppler-half-width for the ν_3 band as a function of the altitude. It can be seen that the Lorentz and Doppler half-widths come to equality at an altitude of about 20 km. Above this, a Voigt profile should be used but it can be seen that saturation effect occurs near the center of the lines even for higher altitude and that the most significant absorption for the calculation of the spectra occurs in the overlapping lorentzian wings. This effect, applicable to methane only because of the great optical depth, has been discussed by Plass and Fivel⁽¹³⁾ and Drayson⁽¹⁴⁾.

An other effect would be a deviation from the Lorentz line shape in the wings as pointed by Taylor⁽⁹⁾ on the basis of the Benedict's correction for CO_2 but if this effect

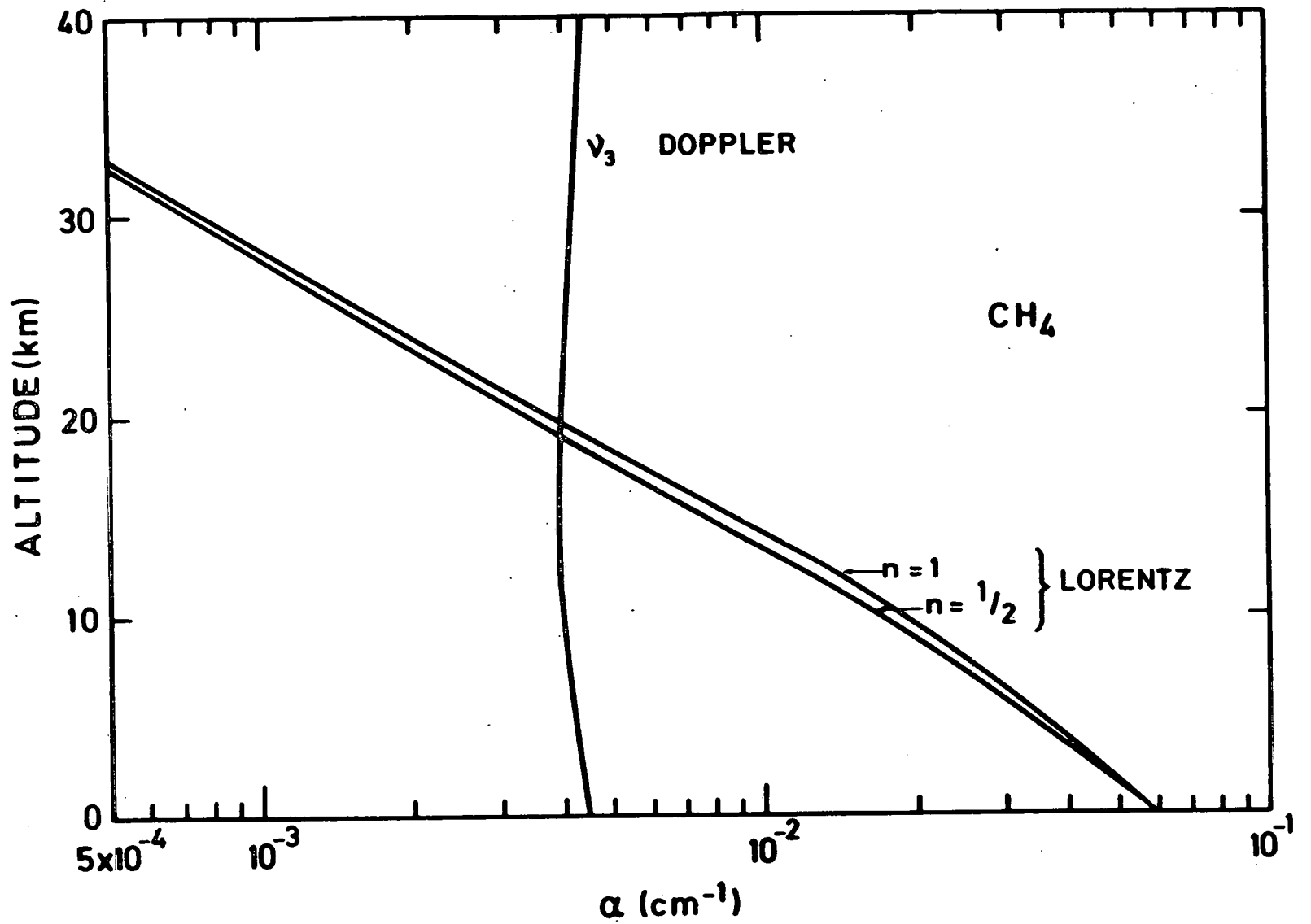


Fig. 1.- Methane half-width as a function of the altitude. For the Lorentz width, two temperature factors are considered : $n = 1$ and $n = 2$.

would be important in the jovian atmosphere, it must be considered as negligible in the earth's stratosphere, the value given by Winters *et al* ⁽¹⁵⁾ for the beginning of this effect being 5 cm^{-1} or about 70 STP half-widths.

To reduce the computing time, three computation steps are used of which the smallest is smaller than the half-line width to obey the condition of Kyle ⁽¹⁶⁾ ; at each step, all lines situated in an interval adjacent to the computing point are added. The absorption coefficients are then multiplied by the optical paths and the transmission can be computed. The obtained integration net is used to perform a convolution by a triangular slit function of 2.5 cm^{-1} half-width.

Figure 2 shows the spectra recorded at float altitude between 3.3 and $3.75 \mu\text{m}$ for zenith angles of 90.5° ; 91.5° ; 92.4° ; 93.3° and 94.5° . The solar grazing rays altitudes are indicated for each spectrum. The strong ν_3 band was used to determine the methane concentration on the optical paths. The weak lines that can be observed between the P lines of the ν_3 band belong to the medium $2 \nu_2$ H_2O band at 3.17μ , even in tropospheric conditions, they do not contaminate the high J lines that were used for the measurements. The weak $\nu_2 + \nu_4$ CH_4 band absorbs too weakly to be responsible of all the absorption observed between 3.5 and 3.75μ . Part of this absorption can be attributed to the $\nu_2 + \nu_3$ N_2O band, to the $\nu_2 + 2 \nu_3$ and $\nu_1 + \nu_2 + \nu_3$ bands of ozone and to the ν_1 fundamental of heavy water ; but the main absorption possibly responsible of the structure observed on the lowest altitude spectrum is formaldehyde as shown in Figure 3 where laboratory spectra of HCHO and N_2O are shown with stratospheric spectra. The two resonant ν_1 and ν_5 bands constitute one of the strongest absorptions observed on the formaldehyde spectrum ⁽¹⁸⁾. A value of the mixing ratio can hardly be established now because of the lack of data concerning the line strengths. High resolution spectrum and rotational constants of CH_2O are given by Yamada *et al* ⁽¹⁹⁾. An upper limit of 10^{-8} can be deduced from the spectrum given by Pierson *et al* ⁽¹⁸⁾. Formaldehyde absorption seems to be present in all spectra.

The values found for the methane mixing ratios are indicated in table I. Figure 4 compares these values with the balloon sampling results of Bainbridge and Heidt ⁽¹⁴⁾ for a stratopause located at 14.5 km , the results of the rocket sampling of Ehhardt *et al* ⁽⁵⁾ (1972) is also indicated. A methane scale height of $3.4 \pm 0.5 \text{ km}$ above the altitude of 25 km can be deduced from our measurements.

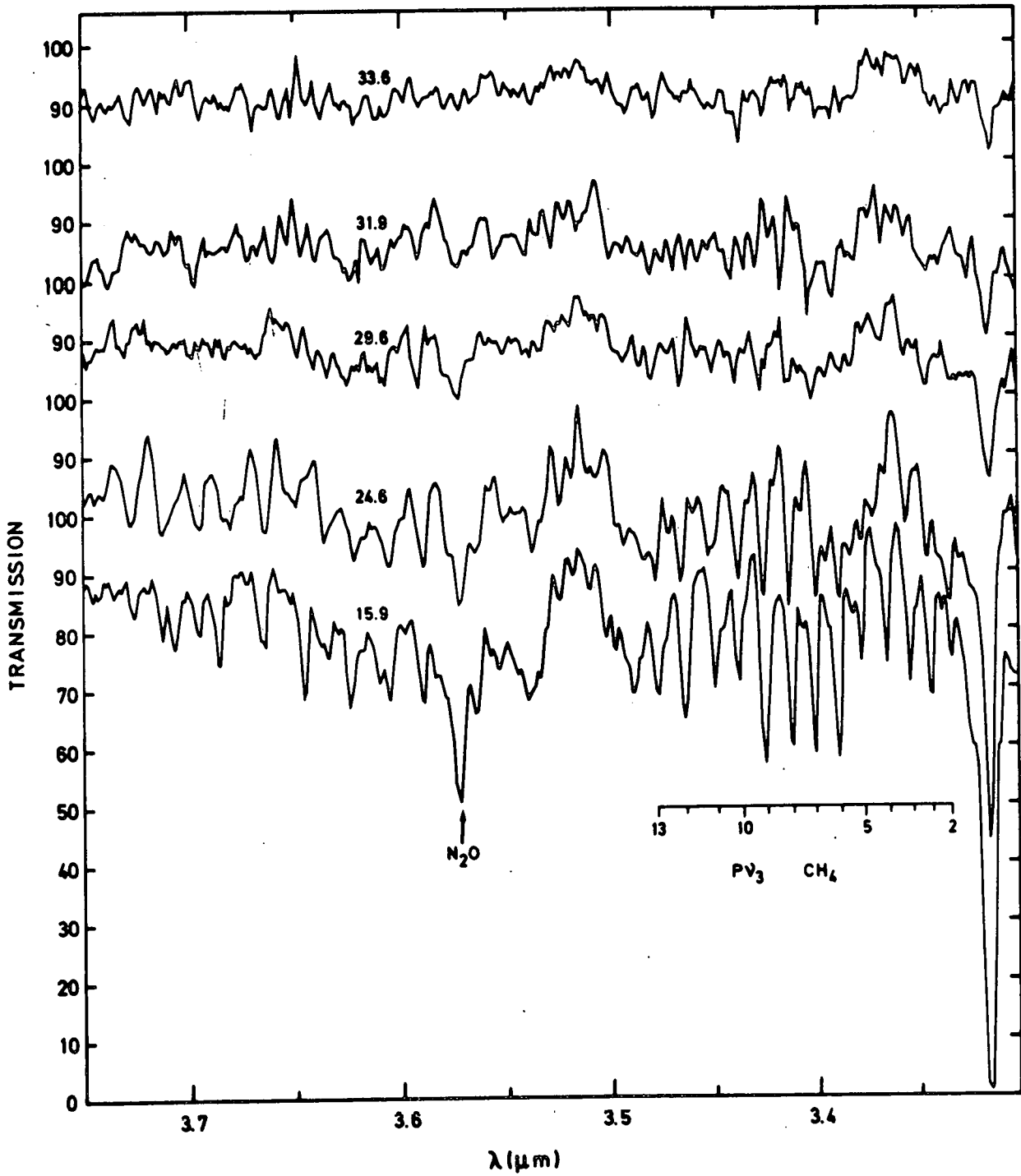


Fig. 2.- Spectra observed from an altitude of 34 km at solar zenith angles of 90.5°, 91.5°, 92.4°, 93.3°, and 94.5° corresponding to the altitudes of grazing solar rays indicated for each spectrum.

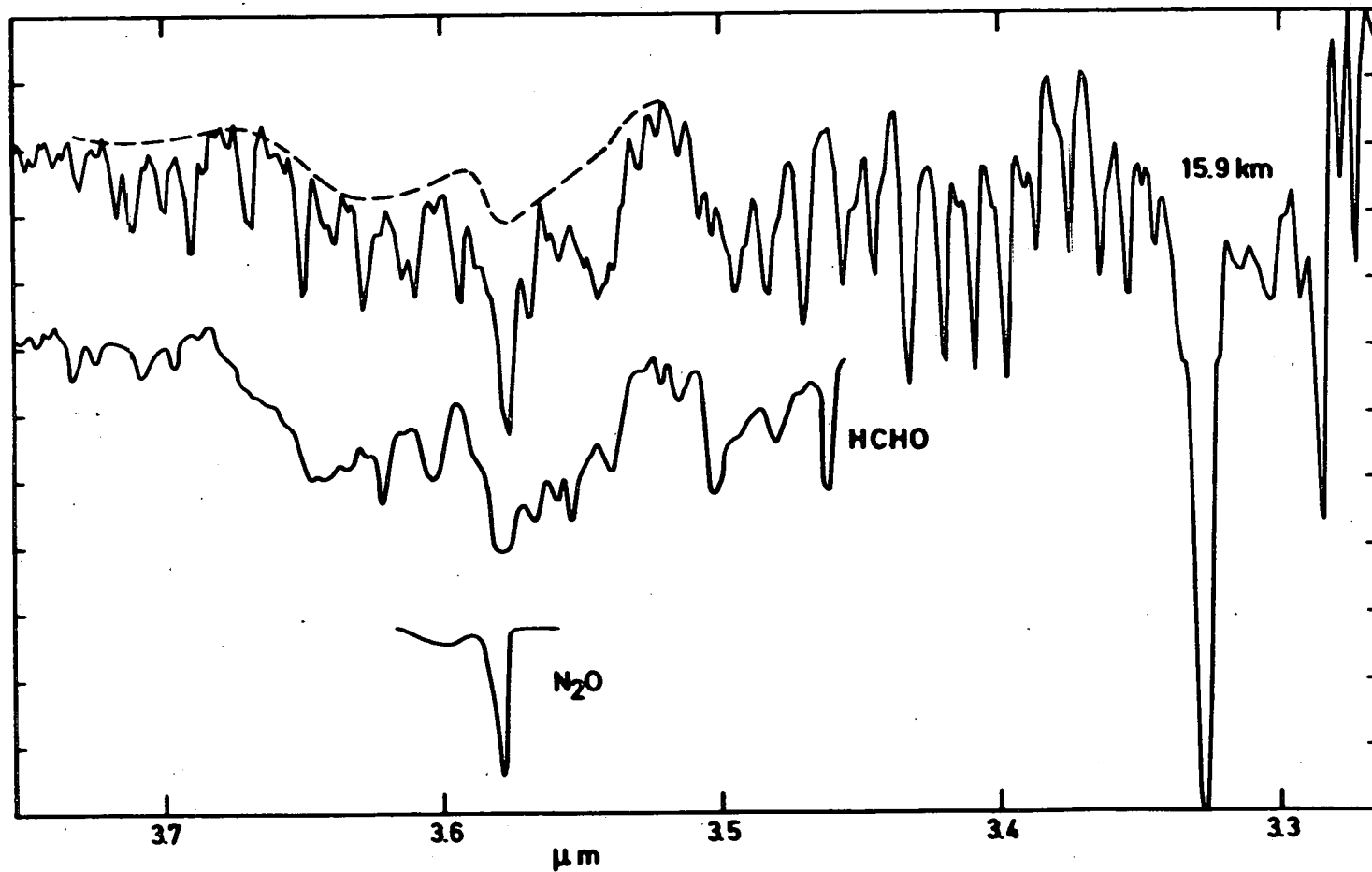


Fig. 3.- Spectrum taken at a solar zenith angle of 94.5° with laboratory spectra of N_2O and CH_2O . The atmospheric absorption observed from 3.55 to 3.70 μm could be explained by CH_2O .

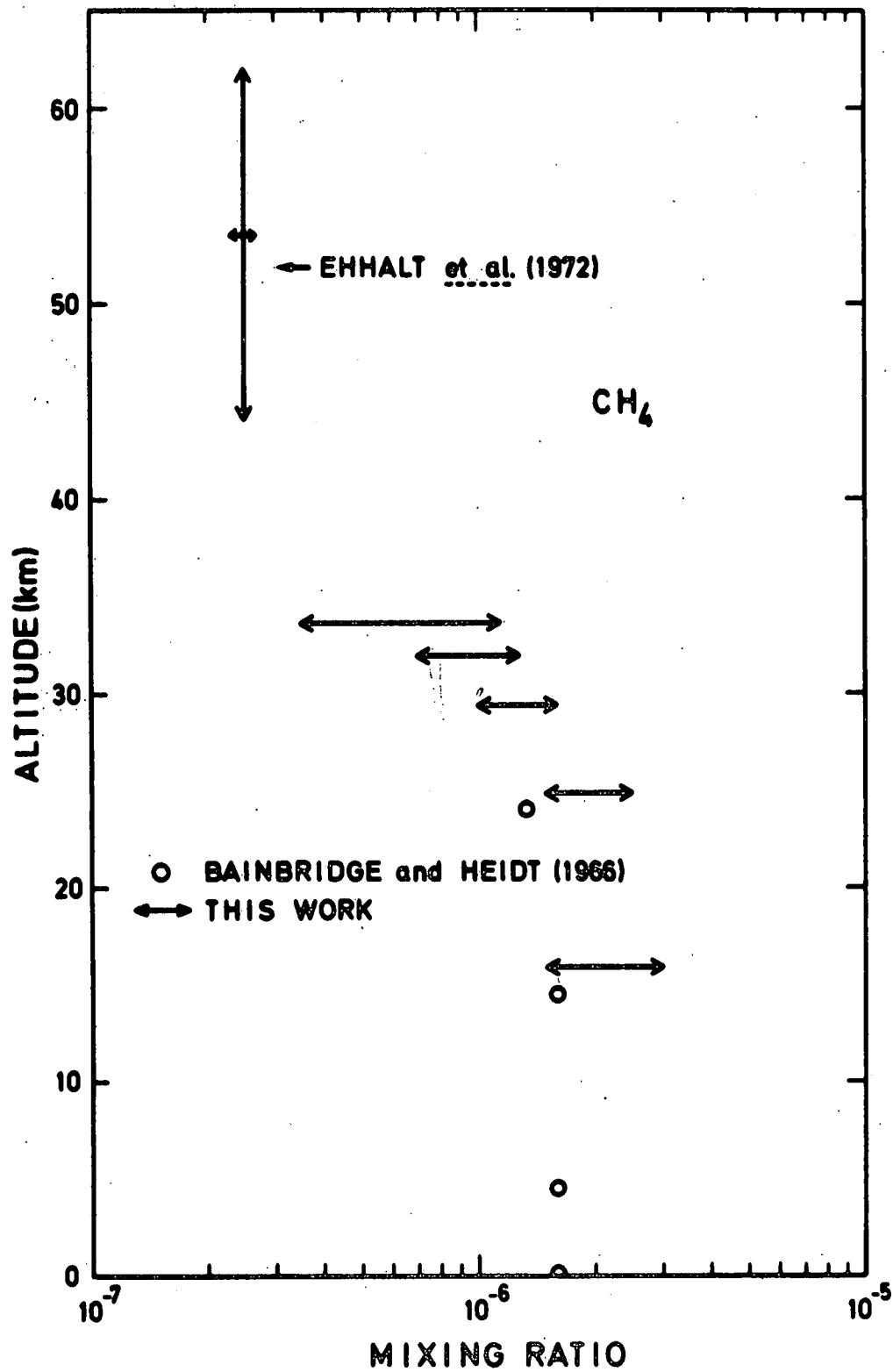


Fig. 4.- Measurements of CH₄ mixing ratios versus altitude.

TABLE I : Stratospheric CH₄ mixing ratios.

Z (km)	Mixing ratios
15.9	$(2.2 \pm 0.7) \times 10^{-6}$
24.6	$(2.2 \pm 0.3) \times 10^{-6}$
29.6	$(1.3 \pm 0.3) \times 10^{-6}$
31.9	$(1.0 \pm 0.3) \times 10^{-6}$
33.6	$(7.5 \pm 4) \times 10^{-7}$

More precise and higher altitudes measurements are necessary to draw final conclusions about the diffusion coefficients and the chemical reactions involved in the destruction of methane.

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