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AERONOMICA ACTA

A - N° 180 - 1977

Stratospheric methane-measurements and predictions

by

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FORWORD

The results described in this note will be presented at the IAGA-IAMAP Assemblies in Seattle (September 1977) and will be published in Pure and Applied Geophysics.

AVANT-PROPOS

Les résultats décrits dans cette note seront présentés aux Assemblées de l'Association Internationale de Géomagnétisme et d'Aéronomie et de l'Association Internationale de Météorologie et de Physique de l'Atmosphère (Septembre 1977) et seront publiés dans la revue "Pure and Applied Geophysics".

VOORWOORD

De resultaten beschreven in dit werk, zullen voorgedragen worden ter gelegenheid van de Algemene vergadering van de Internationale Associatie voor Geomagnetisme en Aeronomie en van de Internationale Associatie voor Meteorologie en Atmosferische Fysica (IAGA-IAMAP) in Seattle (september 1977) en zullen gepubliceerd worden in "Pure and Applied Geophysics.

VORWORT

Die hier beschreibte Ergebnisse wirden zum IAGA-IAMAP Sammlung in Seattle (September 1977) vorgestelt. Dieses Artikel wird in "Pure and Applied Geophysics" veröffendlicht.

STRATOSPHERIC METHANE-MEASUREMENTS AND PREDICTIONS

by

M. ACKERMAN, D. FRIMOUT and C. MULLER

Abstract

A new determination of stratospheric methane from 22 km to 35 km altitude with implications on the abundance of this constituent at greater heights is presented. Previous measurements some of which showed large discrepancies with currently admitted values have been reinterpreted and brought into agreement. The results are in contradiction according to present theories with the in situ determined CH_4 abundances at the upper edge of the stratosphere.

Résumé

Une nouvelle détermination du méthane stratosphérique de 22 à 35 km d'altitude est présentée avec ses implications sur l'abondance de ce constituant aux altitude supérieures. Des mesures antérieures, parmi lesquelles d'importants désaccord existaient avec les valeurs courramment admises ont été réinterprétées et mise en accord. Les résultats sont en contradiction selon des théories actuelles avec les abondances déterminées in situ à la limite supérieure de la stratosphère.

Samenvatting

Dit werk bevat een nieuwe bepaling van de stratosferische methaan tussen 22 and 35 km hoogte, samen met de invloed ervan op de dichtheid van dit bestanddeel op grotere hoogten. De vroegere metingen, waarbij belangrijke onenigheid bestond met de algemeen aanvaarde waarden, worden opnieuw geïnterpreteerd en in overeenstemming gebracht. De bekomen resultaten zijn volgens de tegenwoordig aanvaarde theorieën, in tegenspraak met de in situ bepaalde dichtheden, aan de hogere limiet van de stratosfeer.

Zusammenfassung

Eine neue Bestimmung des stratosphärische Methanes zwischen 22 und 35 km Höhe vorgestelt ist mit seine Fölge über die CH_4 Konzentration zum höhere Höhe. Vorherige Beobachtungen sind wiedergestudiert und ein Vergleich zwischen diese geseigt ist. Die Ergebnisse wiedersprechen die in situ beobachtet Konzentration zum höhere Grens der Stratosphäre zufolge die jetzige Theorië.

INTRODUCTION

The first determinations of the abundance of CH_4 in the stratosphere were published by Baindridge and Heidt [1] in 1966. They showed a decrease of the mixing ratio above the tropopause and were based on in situ sampling with subsequent gas chromatography. Using infrared absorption measurements in the 7.7 μm band, Kyle *et al.* [2] also showed a decrease of the mixing ratio above the tropopause. Ackerman *et al.* [3] indicated also a decrease of concentration with altitude in the stratosphere as well as Cumming and Lowe [4] and Burkert *et al.* [5]. From aircraft borne spectrometer and interferometer data Farmer *et al.* [6] and Lowe and McKinnon [7] showed a decrease of the CH_4 mixing ratio from low to high latitude in the low stratosphere. The analysis of air samples collected by means of rockets in 1968 and in 1972 have lead to determinations of the methane abundance near the stratopause (Ehhalt *et al.* 1975 [8]).

Since CH_4 cannot be produced in the stratosphere, its abundance at various altitudes depends on the rate of its chemical destruction and the strength of vertical mixing. This latter property is a basic data for photochemical modeling of the stratosphere. Its knowledge allows for instance the evaluation of the rate of transport of aircraft effluents and other contaminants to the chemically ozone sensitive regions of the upper stratosphere. Several authors (Nicolet and Peetermans [9], Wofsy and McElroy [10], Hunten [11]) have attempted to deduce values of the vertical transport parameters using the available methane data. Chang [12] has analysed the various values and shown that the improvement of experimental data can reduce the present uncertainty and consequently the uncertainties in the models and in their predictions.

The present work is an attempt to reduce the uncertainty. It consists of the determination of the abundance of CH_4 from 22 to 40 km using high resolution infrared absorption spectroscopic measurements interpreted on the basis of the presently available laboratory spectroscopic data followed by a discussion of other results and of theoretical evaluations.

INSTRUMENTATION AND OBSERVATION

A 60 cm focal length grille spectrometer was flown on October 2, 1975 from the CNES range in Aire sur l'Adour to measure the vertical distribution of HCl in the stratosphere (Ackerman *et al.* [13]). Observations of the solar spectrum from an altitude of 35 km took place in the wavenumbers range from 2916 cm^{-1} to 2970 cm^{-1} which includes the P_5 to P_9 multiplets of the 3.3 μm band of CH_4 (fig. 1). The range of solar zenith angles from 80°.5 to 95°.5 was covered at 43° N and 2° E. The methane absorptions shown in figure 1 were always present in the spectra. Those due to P_9 are perturbed by solar absorption features and are not considered in this work. The measured equivalent widths of the multiplets are shown in figure 2 versus elevation angles for observation above the horizontal and listed in table 1 versus grazing altitude of the solar rays for observations below the horizontal.

INTERPRETATION OF THE DATA

a) Observations above the horizontal

Values of the number density and of the scale height have been assumed, to compute equivalent widths by dividing the atmosphere in layers of 1 km thickness to take into account the change of path length, pressure and temperature as a function of height in the successive layers above float altitudes according to the earth geometry and to the mid–latitude Spring- Fall model of the US Standard Atmosphere supplement, 1966. A Voigt profile has been introduced in the computation for each line of the multiplets of which the spectroscopic data taken from Toth *et al.* [14] and from MacClatchey *et al.* [15] are given in Table 2. The change of equivalent width with solar elevation angle for the four multiplets has been computed and is shown in figure 2 with the data. The shaded curves marked I represent the equivalent widths that should be observed if the number density at 35 km, was equal to $(1.46 \pm 0.12) \times 10^{11}$ cm^{-3} and if the scale height was equal to 4.54 km. These values correspond to the mixing ratio values published by Ehhalt *et al.* [8] and used in models to evaluate the strength of the vertical transport of methane. The range of values taken for the number density at 35 km is obtained from the mixing ratio value published by

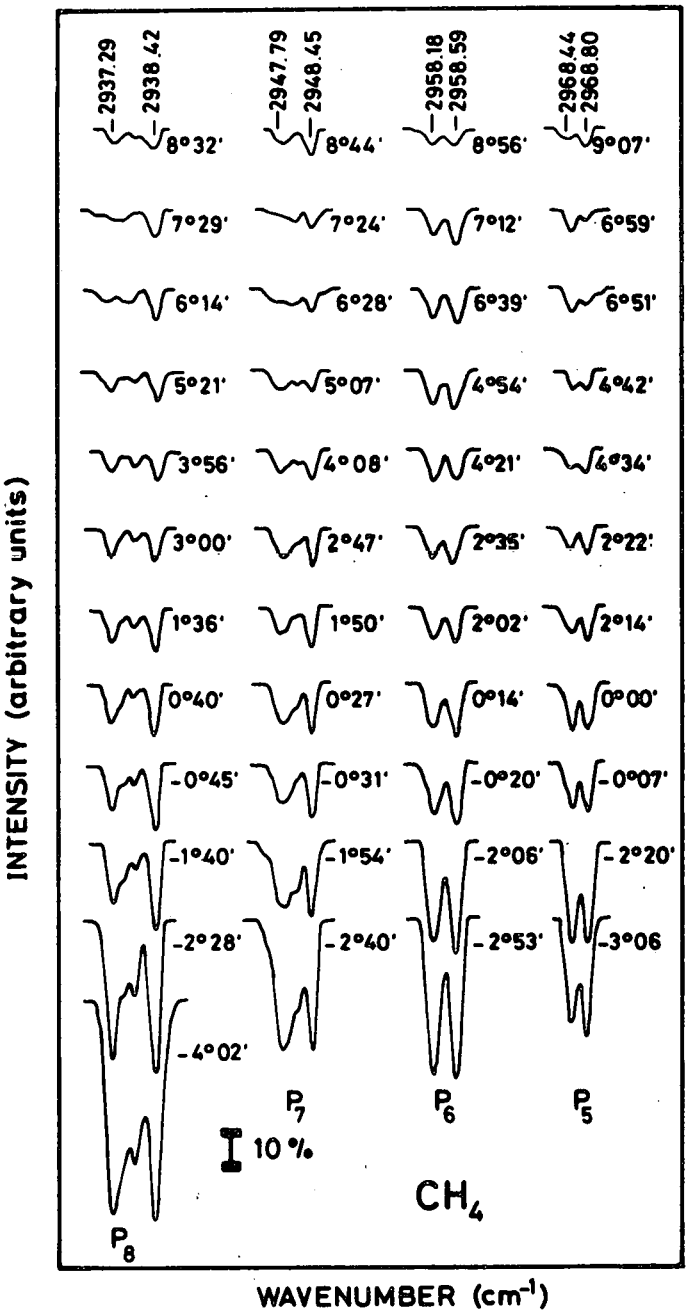

Fig. 1.- Portions of absorption spectra recorded on October 2, 1975, from 35 km altitude at 43°N and 2°E in the 3.3 μm CH_4 band. Multiplets P_5 to P_8 are shown with some identification wavenumbers in cm^{-1}. The angular values shown on the righthandside of each portion of spectrum are solar elevation and solar depression angles for positive and negative values respectively.

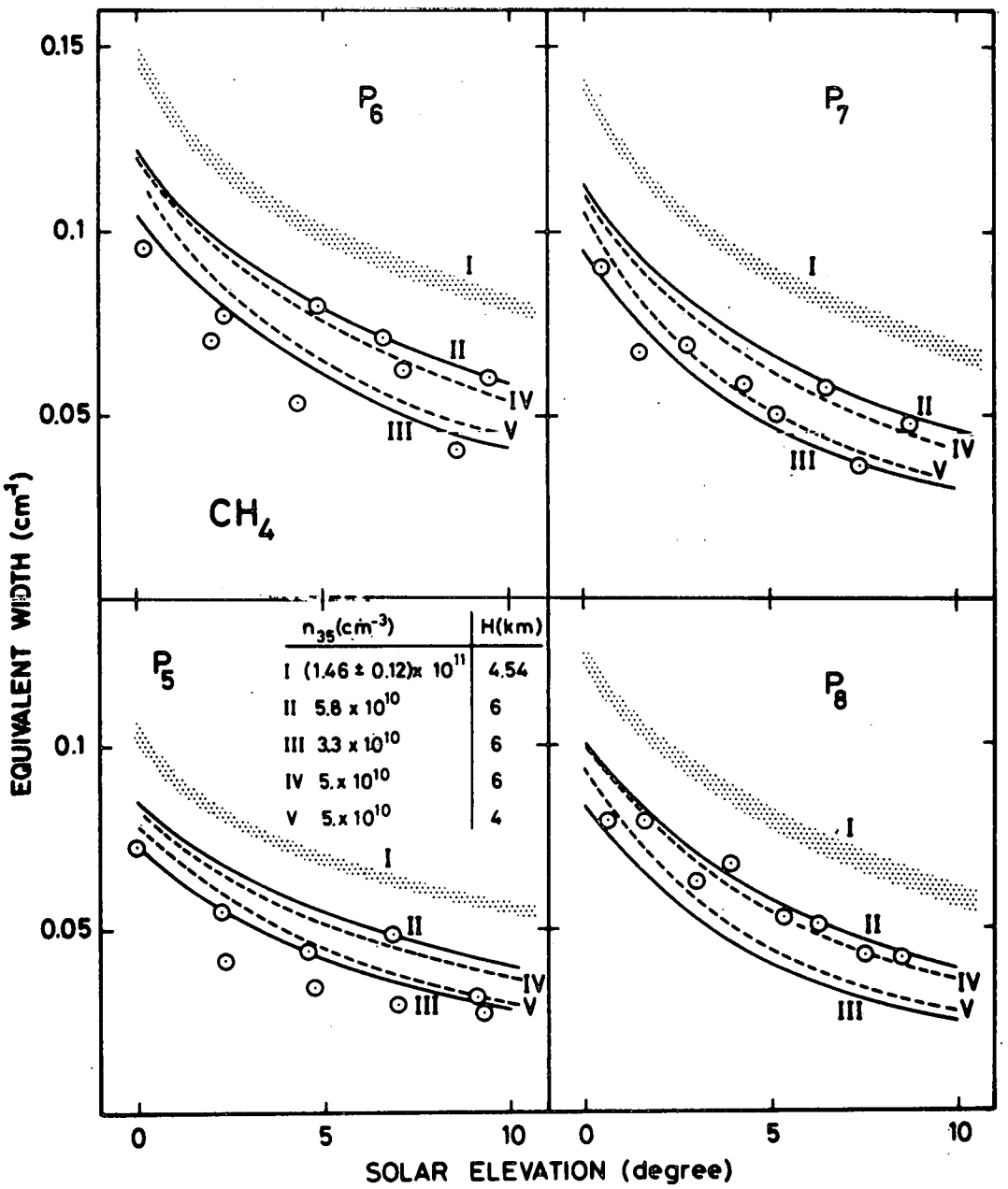

Fig. 2.- Equivalent width versus solar elevation angle. The circles represent the measurements. The shaded curves correspond to the mixing ratio values represented by the solid broken curve of figure 4. The other curves correspond to the CH_4 number densities at 35 km [$n_{35}(cm^{-3})$] and to the scale heights above this altitude H(km) indicated on the figure.

TABLE 1.- Equivalent widths in cm^{-1} of the 3.3 μm P branch multiplets of CH_4 versus minimum altitudes, z, reached by the solar rays.

z(km)	P_5	P_6	P_7	P_8
35	7.1×10^{-2}	1.06×10^{-1}	6.8×10^{-2}	8.5×10^{-2}
33	1.16×10^{-1}	1.64×10^{-1}	1.33×10^{-1}	1.10×10^{-1}
31	1.53×10^{-1}	2.19×10^{-1}	2.00×10^{-1}	1.52×10^{-1}
29	2.11×10^{-1}	2.76×10^{-1}	2.75×10^{-1}	2.10×10^{-1}
27			3.70×10^{-1}	2.82×10^{-1}
25				3.66×10^{-1}
23				4.91×10^{-1}
21				6.41×10^{-1}

TABLE 2.- Line positions λ , integrated absorption cross sections, S, full width at half height W and ground level Energies E for the CH_4 multiplets considered in the treatment of the data .

	$\lambda(cm^{-1})$	$S\ (cm^2.cm^{-1})$ 297°K	$W\ (cm^{-1})$	$E\ (cm^{-1})$
P_5	2968.885	7.06×10^{-20}	0.122	157
	2968.770	1.27×10^{-21}	0.094	157
	2968.738	7.06×10^{-20}	0.122	157
	2968.473	7.06×10^{-20}	0.122	157
	2968.404	7.06×10^{-20}	0.122	157
P_6	2958.683	4.40×10^{-20}	0.114	219
	2958.651	6.58×10^{-20}	0.118	219
	2958.537	1.10×10^{-19}	0.102	219
	2958.233	6.62×10^{-20}	0.118	219
	2958.120	6.42×10^{-20}	0.118	219
	2958.017	1.12×10^{-19}	0.102	219
P_7	2948.478	5.13×10^{-20}	0.114	293
	2948.421	5.00×10^{-20}	0.114	293
	2948.130	1.13×10^{-21}	0.102	219
	2948.107	8.47×10^{-20}	0.114	293
	2947.912	4.88×10^{-20}	0.114	293
	2947.810	3.28×10^{-20}	0.114	293
	2947.700	1.13×10^{-21}	0.102	219
	2947.668	5.00×10^{-20}	0.114	293
P_8	2938.248	6.46×10^{-20}	0.110	376
	2938.206	3.88×10^{-20}	0.110	376
	2938.206	2.59×10^{-20}	0.110	376
	2937.769	3.88×10^{-20}	0.110	376
	2937.494	3.88×10^{-20}	0.110	376
	2937.307	2.70×10^{-20}	0.110	376
	2937.234	3.95×10^{-20}	0.110	376

Ehhalt *et al.* [8] and from the extreme values of total number densities given in the US Standard Atmosphere Supplement, 1966. The computed equivalent widths do not fit the experimental data points. The computation has then been made for various sets of n_{35} and scale heights. Changing the scale height values from 4.5 km to 6.0 km has the most appreciable effect on the change of equivalent width with elevation angle at small angle. The scatter of the measured values does not allow to make a clear choice. However there is a tendency indicating that the scale height above 35 km is at least over a few kilometers altitude closer to 6 km so that the values corresponding to curves II and III of figure 2 have been represented in figures 3 and 4 where envelopes are shown at and above 35 km for the CH_4 number densities and mixing ratios respectively with the results of other investigators.

b) Observations below the horizon

The amount of methane above 35 km has been taken into account by choosing a scale height equal to 6 km and a number density of 4.5×10^{10} at 35 km, both values being the result of the preceeding section. The number densities below float altitude in successive layers of 2 km thickness have been determined from the equivalent widths listed in table 1. The same atmospheric model and spectroscopic data as in the previous sections have been introduced in the computation. The results are shown in figures 3 and 4 as number densities and volume mixing ratios respectively.

COMPARISON WITH OTHER RESULTS

For sets of spectroscopic data are available about stratospheric methane. They cover a period of 10 years since the measurements published by Kyle *et al.* [2] were performed in December 1967 at 33° North. The ν_4 band, from 1299 cm^{-1} to 1306 cm^{-1}, was observed in absorption during a balloon ascent for solar elevation angles from 31° to 5°. The authors give all information required to reinterpret their observations. After ten years the quality of spectroscopic parameters has greatly improved. This situation justifies a new analysis.

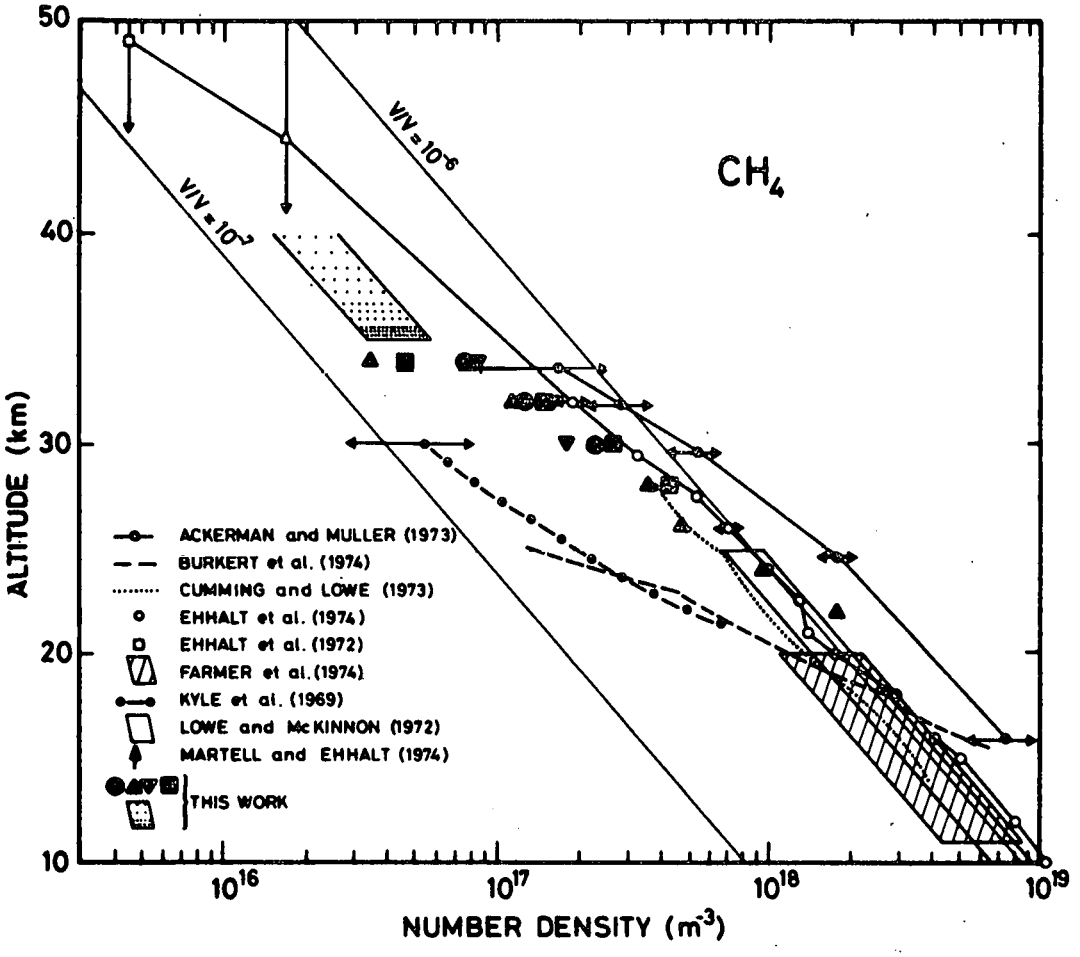

Fig. 3.- Methane number densities as published by various groups of authors and reported by Hard [19] with the values deduced from the observations reported in the present work. The arrowed vertical lines centered on the values between 40 and 50 km indicate the altitude range of vertical rocket sampling.

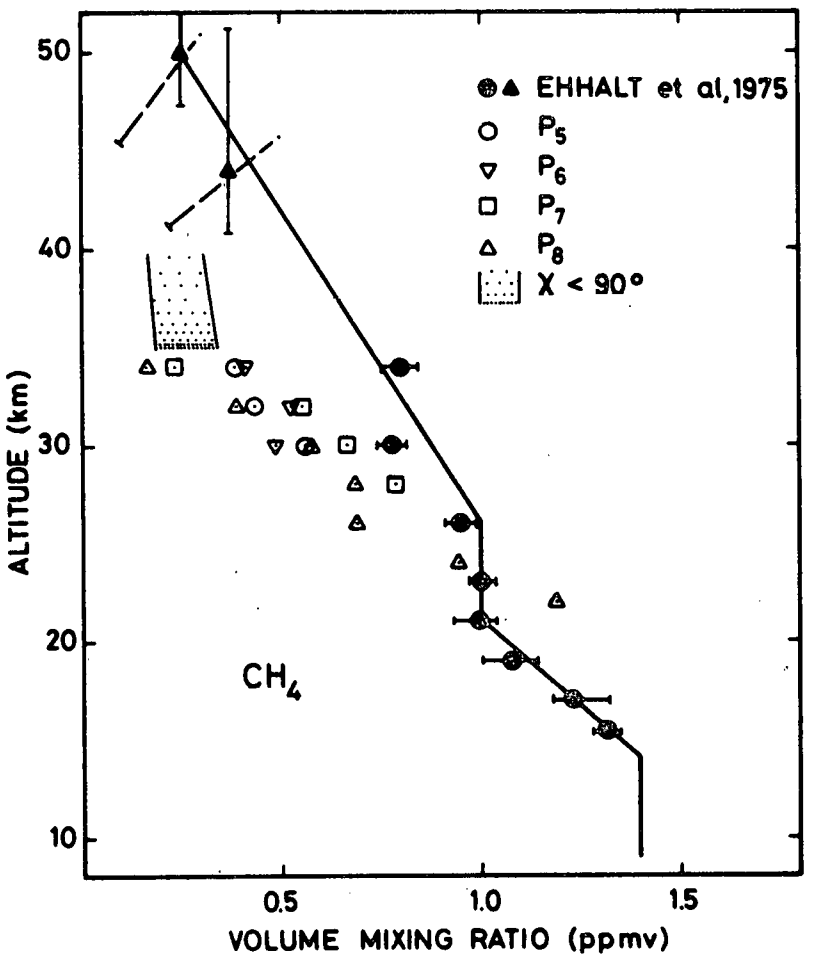

Fig. 4.- Methane mixing ratio as a function of altitude. The presently reported observations are shown with the values from Ehhalt *et al.* [8]. Tilted dashed bars are shown with the rocket determinations in order to keep this figure consistent with the previous one (figure 3).

This has been made, following the method already described previously on the basis of the spectroscopic data of Mc Clatchey *et al.* [15] listed in table 3. However, nitrous oxide absorbs in the region from 1299.1 cm^{-1} to 1307 cm^{-1} which is considered. For this reason, the analysis has been limited to the balloon float period. A number density of N_2O at 28 km equal to 6×10^{10} cm^{-3} has been assumed with a scale height of 3.7 km leading to a maximum contribution to the equivalent width equal to 0.1 cm^{-1}. The observations are then, as shown in figure 5, well represented if methane number density and scale height are respectively taken equal to 2×10^{11} cm^{-3} and 4 km. This represents an increase by a factor of almost 4 of the original values published by Kyle *et al.* [2] bringing them in agreement with others.

Enough flight data were given by Cumming and Lowe [4] in their publication to reinterpret their observation made at 47° N in August 1965 and at 28 km float altitude. A computation was made using the now available spectroscopic data on the components of the R_5 multiplet of the 3.3 μm ν_3 band. As shown in figure 6, a CH_4 number density and a scale height equal to 3×10^{11} cm^{-3} and 4.5 km respectively at 28 km, fit the data points and are in good agreement with the original result of the authors.

In the spectra obtained by Ackerman *et al.* [3] in October 1971 at 43° N, the Q branch of the 3.3 μm band of CH_4 is the most prominent feature which at the time of the publication could not be analysed due to the lack of availability of a powerfull enough computer. This has now partly been done. The equivalent width equal to 0.8 ± 0.1 cm^{-1} observed at 35 km for a zenith angle equal to 90° is represented by a CH_4 number density equal to $(4.5 \pm 1.5) \times 10^{10}$ cm^{-3} associated with a scale height equal to 4 km. This brings downward the values published in 1972 which have always appeard to be systematically to high.

DISCUSSION

Four sets of data obtained at various latitudes and seasons are now available at 30 km altitude for a period of ten years. The values derived on the basis of a consistent set of

TABLE 3.- Spectroscopic data used for the $\nu_4 CH_4$ band. The symbols have the same meaning as in Table 2.

λ (cm^{-1})	S_{297}($cm^2.cm^{-1}$)	W (cm^{-1})	E (cm^{-1})
1299.638	2.35×10^{-20}	0.112	293.10
1299.678	1.71×10^{-21}	0.098	950.27
1299.903	2.35×10^{-20}	0.112	293.11
1299.903	8.32×10^{-21}	0.104	575.14
1300.282	6.21×10^{-21}	0.130	10.48
1300.467	8.33×10^{-21}	0.104	575.23
1300.467	1.71×10^{-21}	0.098	950.30
1300.748	2.99×10^{-22}	0.096	1251.7
1301.208	2.05×10^{-21}	0.100	814.61
1301.290	4.48×10^{-22}	0.096	1251.8
1301.371	1.94×10^{-20}	0.112	219.90
1301.500	8.37×10^{-21}	0.106	470.77
1301.550	2.92×10^{-20}	0.116	219.92
1301.550	3.07×10^{-21}	0.100	814.97
1301.825	1.25×10^{-20}	0.106	470.78
1302.040	4.86×10^{-20}	0.100	219.90
1302.040	9.01×10^{-22}	0.098	1095.6
1302.451	5.21×10^{-21}	0.102	689.93
1302.774	1.78×10^{-20}	0.110	376.80
1302.774	3.35×10^{-20}	0.120	157.11
1302.774	2.85×10^{-21}	0.098	950.35
1302.945	2.09×10^{-20}	0.106	470.81
1303.198	1.39×10^{-20}	0.104	575.19
1303.290	3.67×10^{-22}	0.122	000.00
1303.373	3.35×10^{-20}	0.120	157.12
1303.567	3.93×10^{-20}	0.112	293.13
1303.709	5.13×10^{-21}	0.100	815.05
1303.709	5.90×10^{-20}	0.092	104.77
1303.709	7.49×10^{-22}	0.096	1252.0
1303.951	1.78×10^{-20}	0.110	376.71
1304.223	3.54×10^{-20}	0.124	104.77
1304.332	5.22×10^{-21}	0.102	689.99
1304.463	2.36×10^{-20}	0.112	293.15
1304.602	9.03×10^{-22}	0.098	1095.6

TABLE 3.- continued.

λ (cm^{-1})	S_{297}($cm^2.cm^{-1}$)	W (cm^{-1})	E (cm^{-1})
1304.602	2.36×10^{-20}	0.108	104.77
1304.602	8.35×10^{-21}	0.104	575.15
1304.847	1.71×10^{-21}	0.098	950.45
1304.847	3.38×10^{-20}	0.124	62.87
1305.002	2.92×10^{-20}	0.116	219.90
1305.002	1.57×10^{-20}	0.112	293.15
1305.092	1.26×10^{-20}	0.106	470.83
1305.286	3.08×10^{-21}	0.100	814.83
1305.286	5.57×10^{-21}	0.104	575.02
1305.413	3.38×10^{-20}	0.124	62.87
1305.454	1.88×10^{-20}	0.102	31.43
1305.454	4.50×10^{-22}	0.096	1252.0
1305.563	2.24×10^{-20}	0.120	157.13
1305.563	1.14×10^{-21}	0.098	950.47
1305.635	2.92×10^{-20}	0.116	219.93
1305.635	1.19×10^{-20}	0.110	376.71
1305.688	2.81×10^{-20}	0.130	31.44
1305.809	3.48×10^{-21}	0.102	690.01
1305.809	1.87×10^{-20}	0.130	10.48
1305.809	1.26×10^{-20}	0.106	470.84
1305.905	3.36×10^{-20}	0.120	157.13
1305.989	3.55×10^{-20}	0.124	104.77
1305.989	6.03×10^{-22}	0.098	1095.2
1305.989	3.08×10^{-21}	0.100	814.61
1306.021	1.78×10^{-20}	0.110	376.76
1306.106	2.36×10^{-20}	0.112	296.16
1306.106	5.64×10^{-20}	0.112	62.87
1306.254	4.88×10^{-20}	0.100	219.93
1306.254	4.50×10^{-22}	0.096	1252.0
1306.254	8.36×10^{-21}	0.104	575.02
1306.254	5.23×10^{-21}	0.102	690.02
1306.428	2.10×10^{-20}	0.106	470.85
1306.428	1.72×10^{-21}	0.098	950.49
1306.627	9.04×10^{-22}	0.098	1095.2
1306.627	5.14×10^{-21}	0.100	814.61
1306.832	7.51×10^{-22}	0.096	1252.0

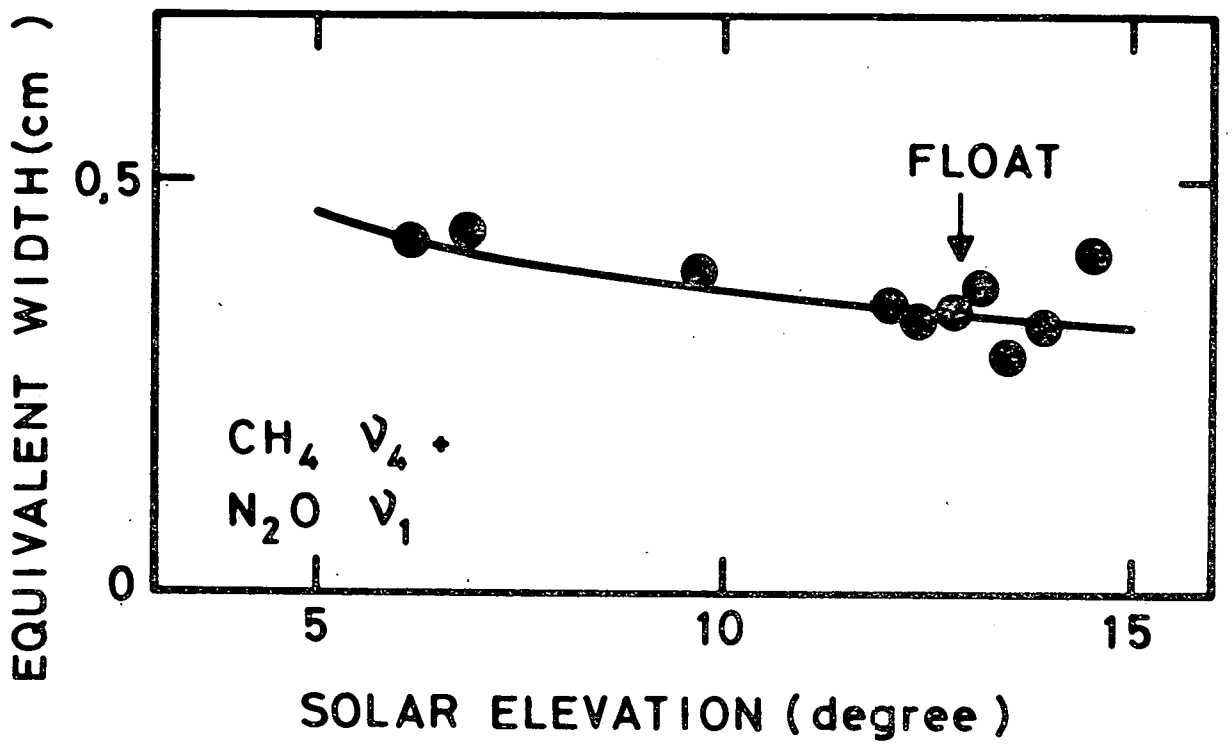

Fig. 5.- Equivalent width observed at balloon float altitude by Kyle *et al.* [2] before sunset versus solar elevation angle. The curve corresponds to a methane number density at 30 km equal to 2×10^{11} cm^{-3} associated with a scale height of 4 km. The N_2O absorption of 0.1 cm^{-1} equivalent widths has been taken into account, corresponding to an N_2O number density at 30 km equal to 6×10^{10} cm^{-3} associated with a scale height of 3.7 km.

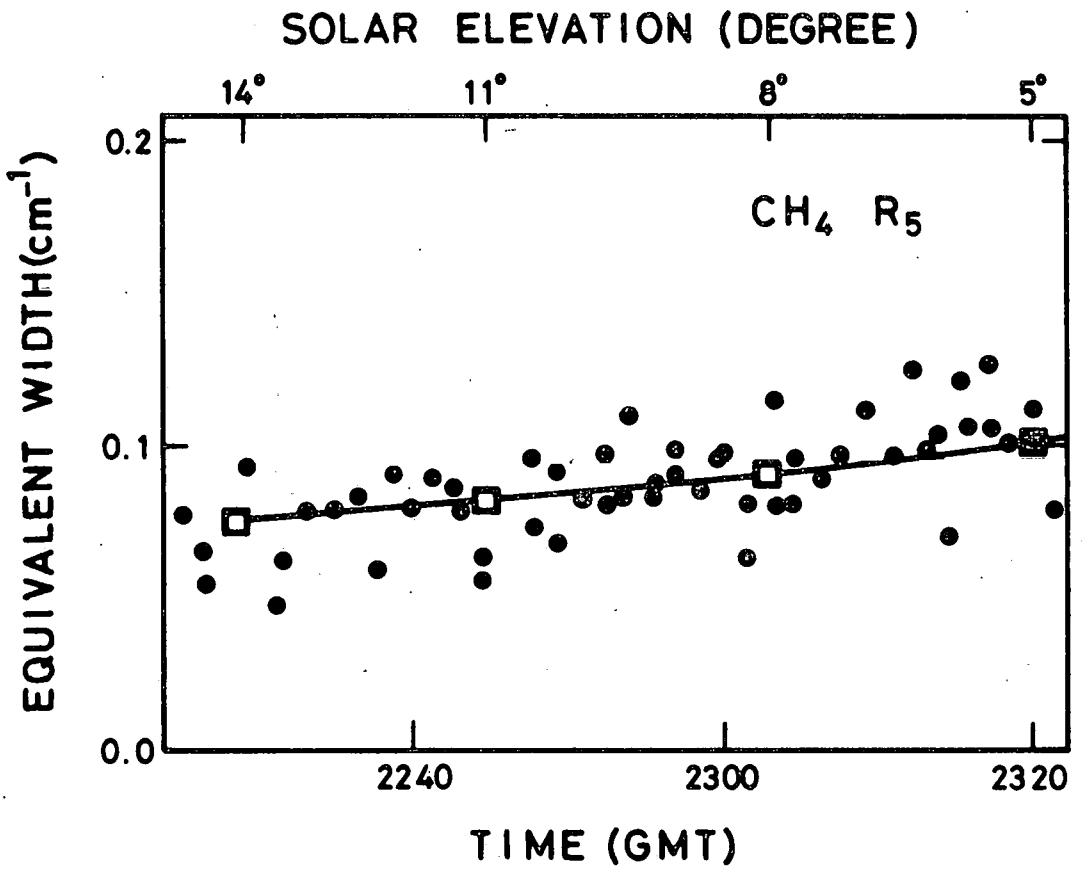

Fig. 6.- Equivalent width due to the R_5CH_4 multiplet observed by Cumming and Lowe [4] versus time during the float period of the gondola. The circles and the solid line are from the original publication, The squares correspond to the reinterpretation with a CH_4 number density at 28 km altitude equal to 3×10^{11} associated with a scale height equal to 4.5 km, both being in good agreement with the original interpretation.

spectroscopic parameters are listed in table 4 with in situ sampling results. No significance in terms of geographic, time or season variability can be attributed to the differences appearing between the various values since the uncertainties are most probably larger than theses differences. Methane number density at 30 km appears to be very stable within experimental error limits.

An envelope of the new methane mixing ratios presented here is shown in figure 7 with values predicted by Chang [12] on the basis of a unified chemical sheme with different vertical distributions of vertical transport coefficients. Curve B appears to fit the experimental data in the worst fashion while curves A and C bring the best agreement within the uncertainty limits. Values of the vertical transport coefficient have been evaluated on the basis of the number densities of CH_4, OH and O^1D shown in table 5. The rate constants for the reactions

$$O^1D + CH_4 \rightarrow \text{products}$$

and

$$OH + CH_4 \rightarrow CH_3 + OH$$

published by Nicolet [20], namely 3×10^{-3} cm^3 sec^{-1} and 3.5×10^{-12} $e^{-1800/T}$ cm^{-3} sec^{-1} respectively, have been used.

The uncertainty shown on figure 8 in the altitude range around 25 km is the consequence of the rather abrupt change of methane scale height in the middle stratosphere.

Low stratospheric methane abundances will have various consequences on model calculations of other species. They will have the effect of reducing the HCl/ClO ratio, as an example.

TABLE 4.- Methane number densities at 30 km altitude.

CH_4 number density (cm^{-3})	Time	Latitude	Ref.
1.9×10^{11}	August 1965	47^0 N	[4]
2×10^{11}	December 1967	33^0 N	[2]
2×10^{11}	October 1971	43^0 N	[3]
2.2×10^{11}	October 1975	43^0 N	This work
3×10^{11}	---	32^0 N	[8]

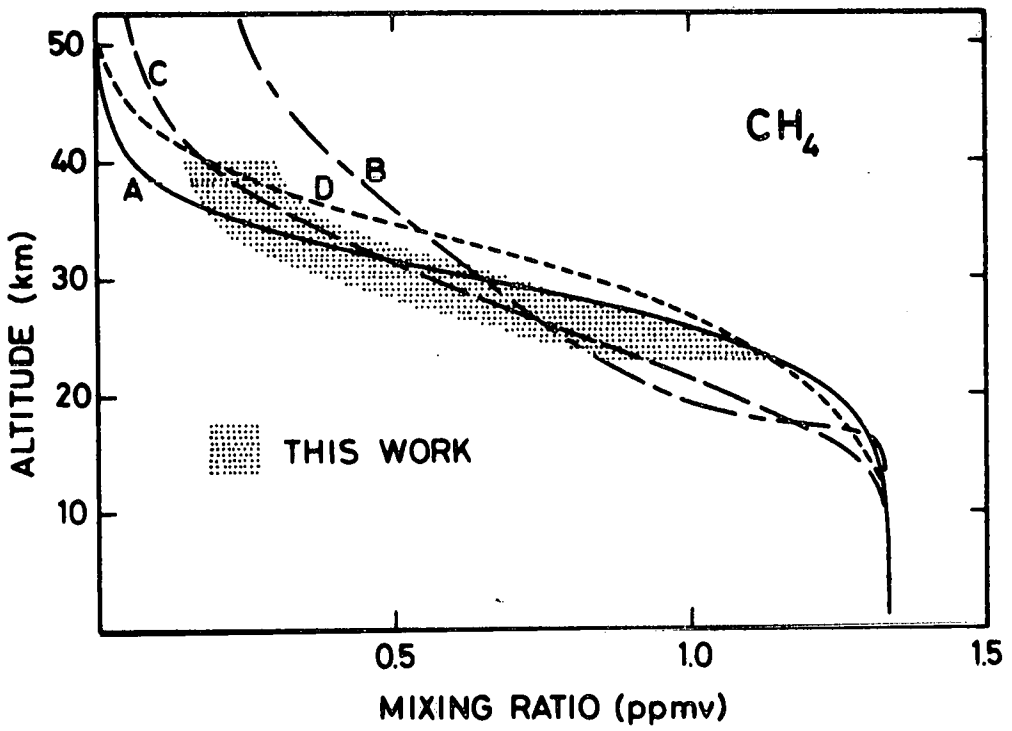

Fig. 7.- Vertical distributions of the CH_4 volume mixing ratio computed by Chang [12]. The envelope represents the new observations presented here.

TABLE 5.- Data used in conjunction with the mid-latitude Spring-Fall model of U.S. Standard Atmosphere supplement, 1966, to evaluate the vertical transport coefficient, K.

Altitude km	$n(O^1D)$ cm^{-3}	$n(OH)$ cm^{-3}	$n(CH_4)$ cm^{-3}
12	2.4×10^{-2}	2.1×10^{5}	9.09×10^{12}
14	6.2	2.3	6.49
16	1.5×10^{-1}	2.5	4.43
18	3.4	3.0	2.96
20	9.0	3.6	1.96
22	1.6×10^{0}	4.4	1.35
24	3.3	5.5	9.46×10^{11}
26	6.5	7.0	6.27
28	1.2×10^{1}	9.0	3.80
30	2.0	1.4×10^{6}	2.15
32	3.1	1.7	1.21
34	4.8	2.5	7.00×10^{10}
36	6.8	3.8	4.23
38	9.2	5.4	2.69
40	1.4×10^{2}	7.0	1.91
42	1.6	8.4	1.18
44	2.0	9.6	6.58×10^{9}
46	2.6	1.2×10^{7}	2.49

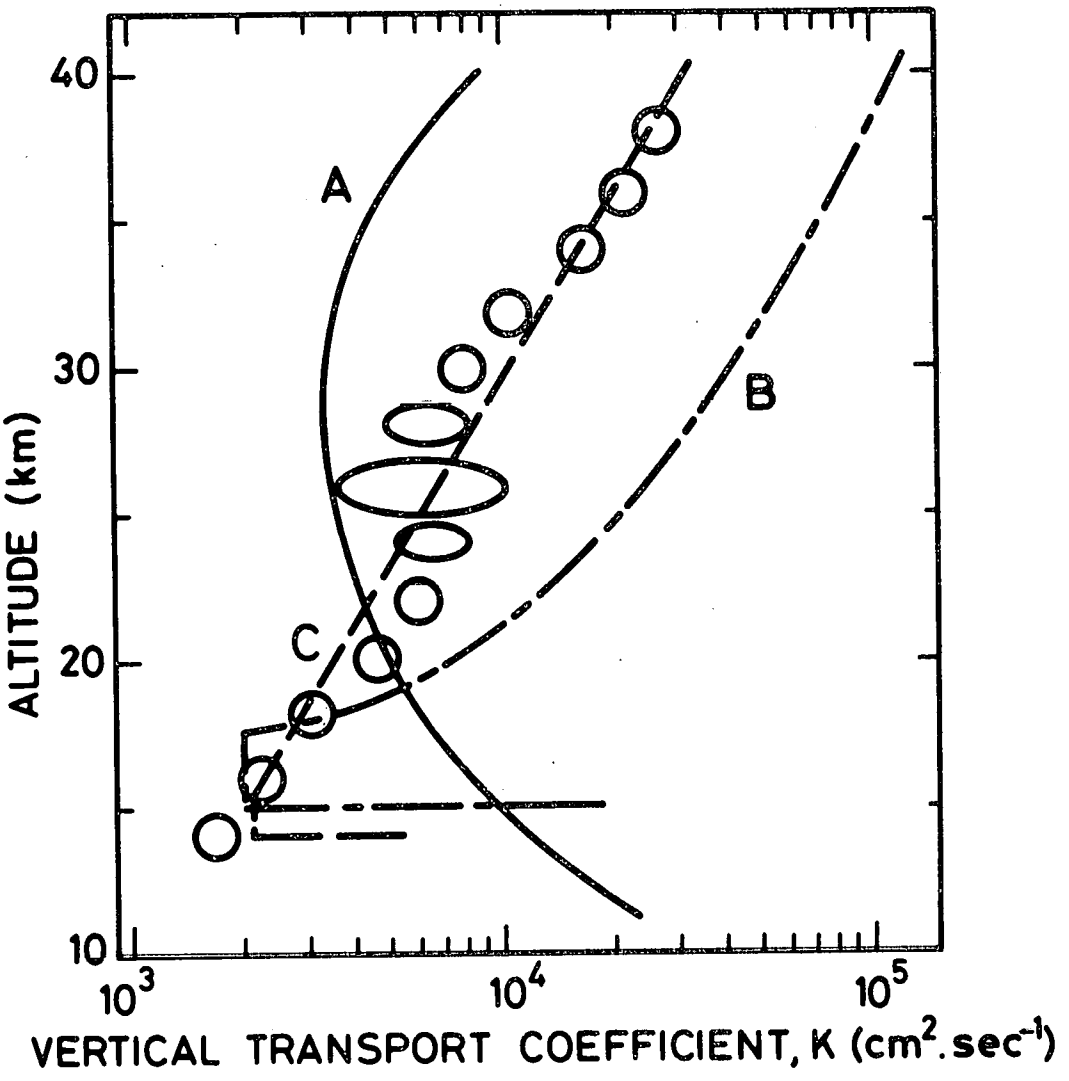

Fig. 8.- Vertical distribution of vertical transport coefficient computed on the basis of the data presented in table 5 (circles). Curves A, B and C are from references [12], [10] and [11] respectively. The uncertainty represented around 25 km results from the change of CH_4 scale height at these altitudes.

CONCLUSION

New stratospheric methane measurements have been presented with previous measurements reinterpreted on the basis of a consistent set of spectroscopic parameters. Discrepancies with values obtained at the upper edge of the stratosphere by means of in situ sampling calls for new measurements, particularly at those altitudes.

AKNOWLEDGEMENT

Thanks are due to M. Rosseeuw for computer programming.

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