

## Stratospheric Methane and Nitrogen Dioxide from Infrared Spectra

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*Abstract* – Values of the mixing ratio by volume of stratospheric NO<sub>2</sub> and CH<sub>4</sub> deduced from infrared spectra taken by means of balloon-borne spectrometers are presented. Possible evidence for the presence of formaldehyde in the stratosphere is also given.

### *I. Introduction*

Most of the information on minor stratospheric constituents has been deduced from infrared spectra. Until recently this technique has been applied to absorbers having volume-mixing ratios of the order of  $10^{-7}$  or higher. The measurements based on absorption infrared spectrometry performed by means of balloon-borne spectrometers operating in the 30 km altitude range at solar zenith angles larger than  $90^\circ$  are allowed to reach concentrations lower by two orders of magnitude. This method offers several advantages: changes in absorption can be related to short-term variation of the optical thickness, ensuring the absence of contamination by the instrumentation; the absorption takes place mostly at constant temperature, absorber concentration and pressure, leading to an easier quantitative interpretation. Information on the vertical distribution of minor constituents can be obtained by this method since the optical depth is maximum at the altitude of the solar grazing rays. As shown in Fig. 1, 75% of the optical depth is located within a small altitude range of the order of 3 km.

The method has been quantitatively applied to some minor constituents. Results on stratospheric methane and nitrogen dioxide are presented here.

### *II. Methane*

Methane was first observed in the atmosphere by MIGEOTTE [19] and is known as a permanent constituent of the atmosphere. The most significant sink is the reaction with O(<sup>1</sup>D) or OH which leads to the CH<sub>3</sub> radical, as discussed by NICOLET and PEETERMANS [21].

The distribution of CH<sub>4</sub> in the stratosphere is thus essentially determined by its transport properties and precise measurements can give valuable information about the stratospheric eddy diffusion coefficients.

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The tropospheric  $\text{CH}_4$  measurements have been reviewed by FINK *et al.* [10]. The stratospheric mixing ratio has been shown (BAINBRIDGE and HEIDT [3]) to decrease above the tropopause; a rocket sampling near the stratopause led to a value of  $3 \times 10^{-7}$  for a vertical column ranging between 42 and 62 km (EHHALT *et al.* [9]).

A vertical distribution of methane can be deduced from measurements of the solar spectrum taken from a balloon-borne spectrometer for grazing altitudes of the solar rays ranging from 15.9 to 33.6 km. The flight studied here took place on 22 October 1971 between 13.10 and 18.16 G.M.T. The absorption took 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.

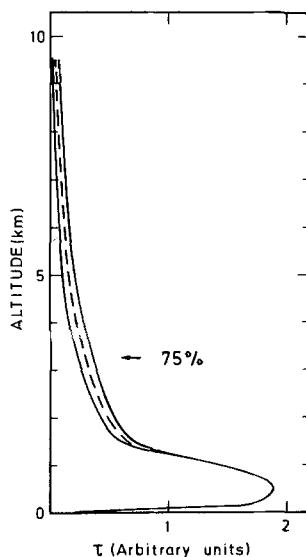


Figure 1

Optical depth ( $\tau$ ) in arbitrary units versus altitude in kilometers above the solar grazing ray smallest altitude for a constituent in mixing

Absorptions for the  $\nu_3$  and  $\nu_2 + \nu_4$   $\text{CH}_4$  bands were observed and have been analysed by means of a line calculation using the data of KYLE [16]. These give the positions, line strengths, energy of the fundamental level and identification of the lines. Confirmation of the relative line intensities has been given by MCMAHON *et al.* [18] and objections that can be made against the use of KYLE's data have been summarised by TAYLOR [25] for their application to the study of the  $\nu_4$  band in the jovian atmosphere.

The values for the  $\text{CH}_4$  half-width used here are those of YAMAMOTO and HIRONO [30] for  $\text{N}_2$  broadening. These are not very different from the constant value of  $0.05 \text{ cm}^{-1}$  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 [7] is not very significant.

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

$$S(T) = S_0 \left( \frac{T_0}{T} \right)^m \exp \left( -1.4388 \frac{E''(T_0 - T)}{T_0 T} \right) \quad (1)$$

$$\alpha = \alpha_0 \left( \frac{P}{P_0} \right) \cdot \left( \frac{T_0}{T} \right)^n \quad (2)$$

where  $E''$  is the rotational energy of the fundamental level and where the index 0 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 [26] 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

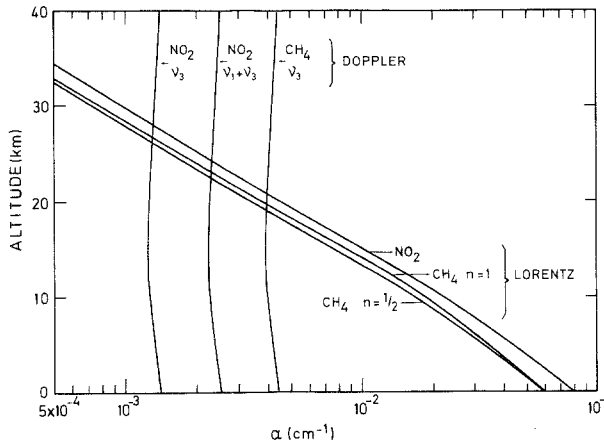


Figure 2  
Lorentz and Doppler half-width as a function of altitude for the  $\text{CH}_4$  and  $\text{NO}_2$  bands studied

derived by MCMAHON *et al.* [18], but Fig. 2 shows that in the narrow range of stratospheric temperatures the difference between the two dependencies may not lead to significant errors. The exponent  $m$  corresponds to the temperature dependence of the rotational partition function.

Figure 2 shows also the Doppler half-width for the  $\nu_3$  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 [24] and DRAYSON [8].

Another effect would be a deviation from the Lorentz line shape in the wings, as noted by TAYLOR [25] on the basis of BENEDICT's correction for  $\text{CO}_2$ , but if this effect is

important in the jovian atmosphere, it must be considered as negligible in the earth's stratosphere, the value given by WINTERS *et al.* [27] for the beginning of this effect being  $5 \text{ cm}^{-1}$  or about 70 s.t.p. 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 [17]; at each

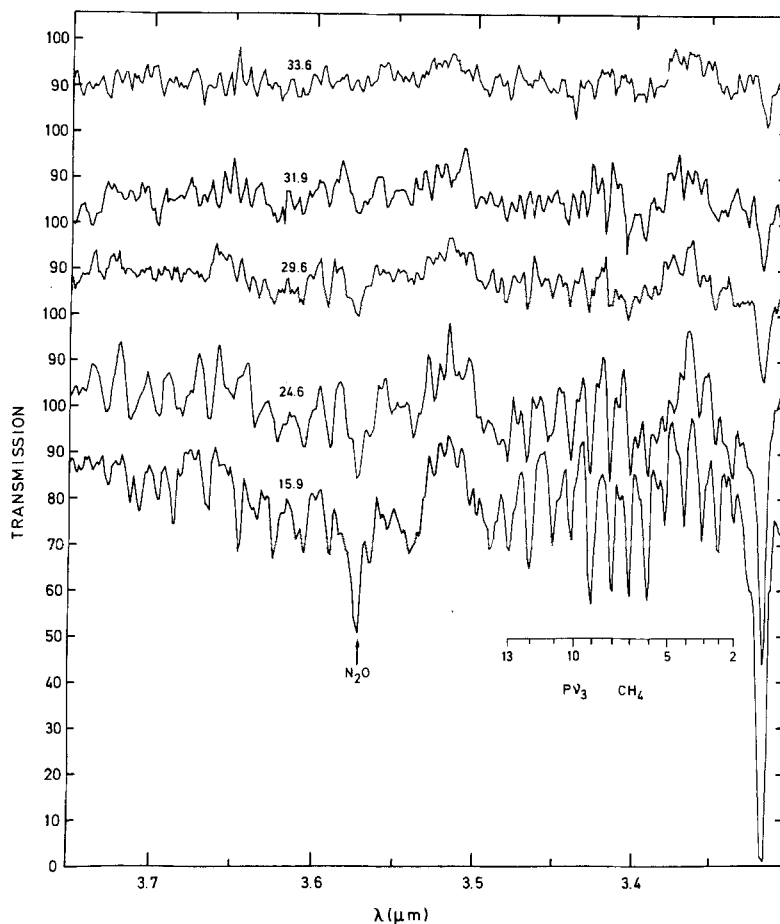


Figure 3

Spectra observed from an altitude of 34 km at solar zenith angles of  $90.5^\circ$ ,  $91.5^\circ$ ,  $92.4^\circ$ ,  $93.3^\circ$  and  $94.5^\circ$  corresponding to the altitudes of grazing solar rays indicated for each spectrum

step, all lines situated in an interval adjacent of the computing point are added. The absorption coefficients are then multiplied by the optical paths and the transmission can be computed. The integration net obtained is used to perform a convolution by a triangular slit function of  $2.5 \text{ cm}^{-1}$  half-width.

Figure 3 shows the spectra recorded at float altitude between  $3.3$  and  $3.75 \mu\text{m}$  for zenith angles of  $90.5^\circ$ ,  $91.5^\circ$ ,  $92.4^\circ$ ,  $93.3^\circ$  and  $94.5^\circ$ . The solar grazing rays altitudes are

indicated for each spectrum. The strong  $\nu_3$  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  $\nu_3$  band belong to the medium  $2\nu_2$   $\text{H}_2\text{O}$  band at  $3.17 \mu$  (HOUGHTON *et al.* [15]), even in tropospheric conditions, they do not contaminate the high J lines that were used for the measurements. The weak  $\nu_2 + \nu_4$   $\text{CH}_4$  band absorbs too weakly to be responsible for all the absorption observed between  $3.5$  and  $3.75 \mu$ . Part of this absorption can be attributed to the  $\nu_2 + \nu_3$   $\text{N}_2\text{O}$  band, to the  $\nu_2 + 2\nu_3$  and  $\nu_1 + \nu_2 + \nu_3$  bands of

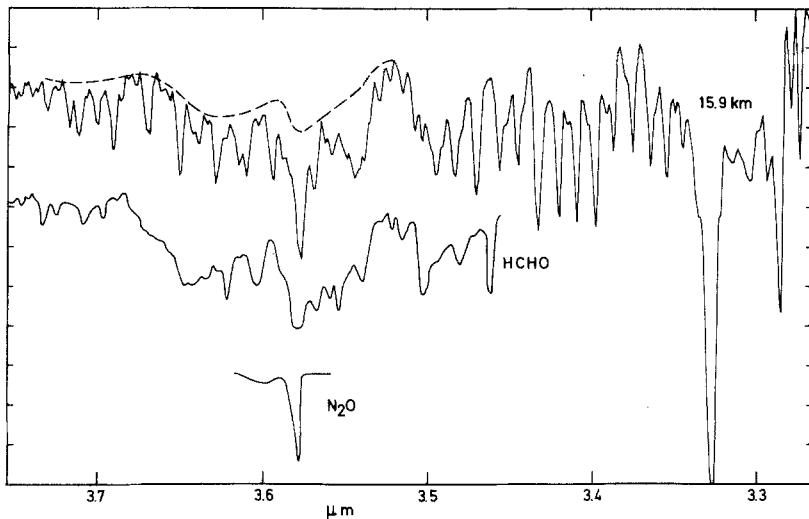


Figure 4

Spectrum taken at a solar zenith angle of  $94.5^\circ$  with laboratory spectra of  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$ . The atmospheric absorption observed from  $3.55$  to  $3.70 \mu\text{m}$  could be explained by  $\text{CH}_2\text{O}$

ozone and to the  $\nu_1$  fundamental of heavy water; but the main absorption possibly responsible for the structure observed on the lowest altitude spectrum is formaldehyde, as shown in Fig. 4, where laboratory spectra of HCHO and  $\text{N}_2\text{O}$  are shown with stratospheric spectra. The two resonant  $\nu_1$  and  $\nu_5$  bands constitute one of the strongest absorptions observed on the formaldehyde spectrum (PIERSON *et al.* [23]). A value of the mixing ratio can hardly be established now because of the lack of data concerning

Table 1  
*Stratospheric  $\text{CH}_4$  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	$(7.5 \pm 4) \times 10^{-7}$

the line strengths. High resolution spectrum and rotational constants of  $\text{CH}_2\text{O}$  are given by YAMADA *et al.* [28]. An upper limit of  $10^{-8}$  can be deduced from the spectrum given by PIERSON *et al.* [23]. Formaldehyde absorption seems to be present in all spectra.

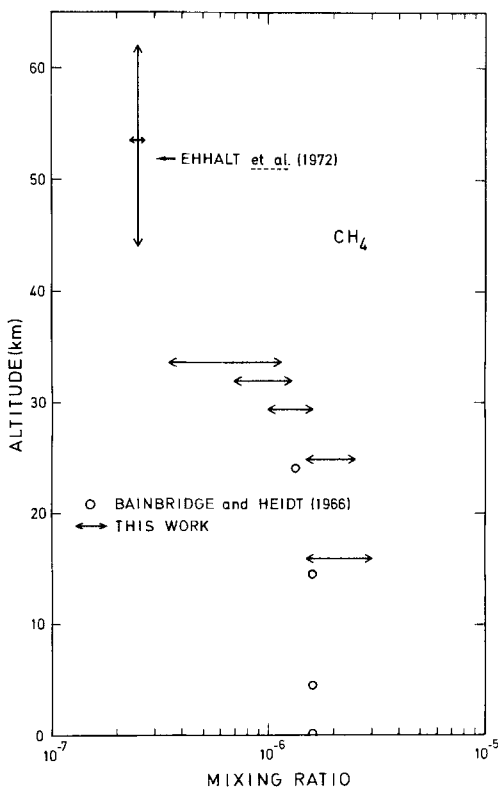


Figure 5  
Measurements of  $\text{CH}_4$  mixing ratios versus altitude

The values found for the methane mixing ratios are indicated in Table I. Figure 5 compares these values with the balloon sampling results of BAINBRIDGE and HEIDT [3] for a stratopause located at 14.5 km, the results of the rocket sampling of EHHALT *et al.* [9] is also indicated. A methane scale height of  $3.4 \pm 0.5$  km above the altitude of 25 km can be deduced from our measurements.

### III. Nitrogen dioxide

Some forty years ago, GOETZ [12] was searching experimental evidence for the presence of nitrogen dioxide in the atmosphere. Stratospheric absorption due to  $\text{NO}_2$  has been identified (ACKERMAN and FRIMOUT [2], GOLDMAN *et al.* [11], ACKERMAN [1]) in infrared spectra of the solar radiation recorded from balloon-borne gondolas floating

at mid-latitudes in the altitude range of 30 km when the solar zenith angle was larger than  $91^\circ$ .

A quantitative interpretation of the available data leading to stratospheric mixing ratios of  $\text{NO}_2$  from the edge of the tropopause at 12 km up to 28 km is reported here. Synthetic spectra have been computed on the basis of the spectroscopic constants given for  $\text{NO}_2$  by OLMAN and HAUSE [22] and BLANK *et al.* [5] using a Lorentz line full width of  $0.16 \text{ cm}^{-1}$  in s.t.p. conditions. The choice of this value is based on the work of YAMAMOTO and AOKI, [29]. Figure 2 shows that a Lorentz line profile could be adopted for all observations. The line intensity was determined by comparing the integrated

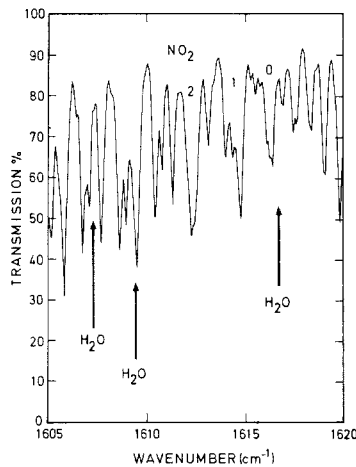


Figure 6

Synthetic absorption spectrum of a portion of the  $\nu_3$  band of  $\text{NO}_2$  computed on the basis of the available spectroscopic data and calibrated in absolute values by means of the laboratory measurements of GUTTMAN. Optical thickness,  $0.014 \text{ atm cm}$ ; total pressure,  $1.18 \text{ atm}$ ; temperature,  $298 \text{ }^\circ\text{K}$ . The position of water vapor lines is indicated, one of them overlapping the  $\text{NO}_2$  absorption marked 0. Absorptions 1 and 2 are unaffected by water vapor and appear clearly in the atmospheric spectra

synthetic spectra with the integrated absorption measured in the laboratory by GUTTMAN [13]. Figure 6 shows the transmission versus wave number of a portion of the  $\nu_3$  band computed for the laboratory conditions used by GUTTMAN [13]. The positions of water vapor lines are shown at the wave numbers given by BENEDICT and CALFEE [4]. One of these overlap the  $\text{NO}_2$  absorption feature numbered 0 on the figure. Absorptions numbered 1 and 2 are very well isolated. This part of the spectrum, particularly well marked in the atmospheric recordings, has mainly been used for the quantitative interpretation. Observed and computed spectra are shown in Fig. 7. It has to be pointed out that the water vapor line overlapping the  $\text{NO}_2$  feature marked 0 in Fig. 6 increased with solar depression angle while the  $\text{NO}_2$  absorption remains more or less constant. The  $\nu_1 + \nu_3$  band (ACKERMAN and FRIMOUT [2], ACKERMAN [1]) underlies very clearly the P branch of the  $\nu_3$   $\text{CH}_4$  band as it appears in Fig. 8, showing spectra recorded at

sunset from an altitude of 29 km on 8 October, 1970, by means of a balloon-borne instrument launched from Aire sur l'Adour (Landes, France). The synthetic spectrum degraded by a triangular slit function of  $6 \text{ cm}^{-1}$  half-width, and matching the spectrum for an altitude of the solar grazing rays of 12.5 km, is compared with this one in Fig. 9.

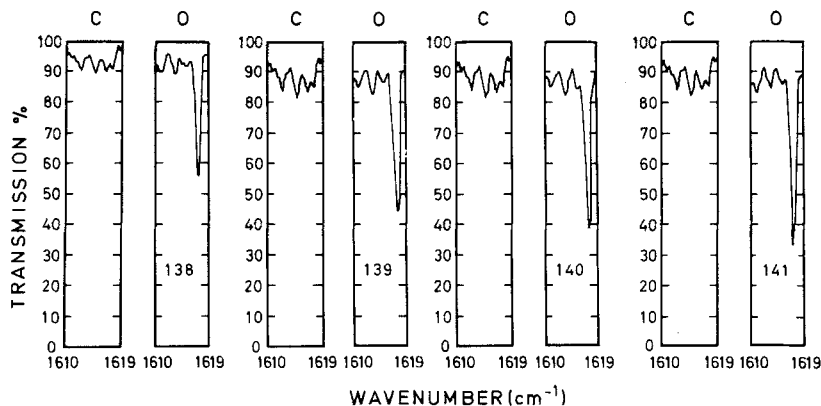


Figure 7

Observed (O) and computed (C)  $\text{NO}_2$  spectra. The water vapor line overlapping the  $\text{NO}_2$  absorption feature numbered 0 in Fig. 6 appears clearly in the stratospheric spectra. The numbers refer to the numbering given by GOLDMAN *et al.* [11]. A triangular slit function of  $0.5 \text{ cm}^{-1}$  has been used to degrade the synthetic spectra

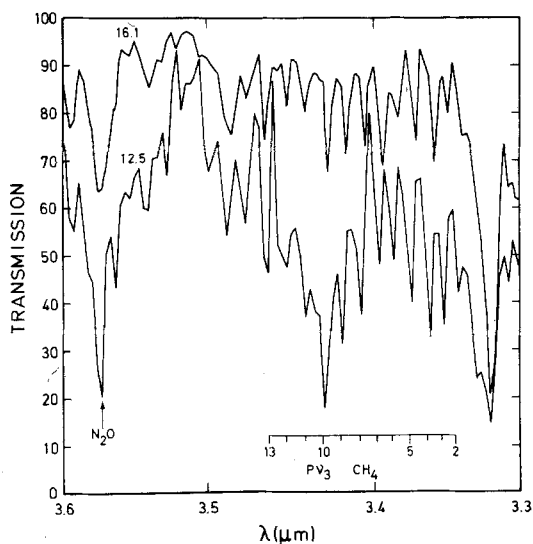


Figure 8

Stratospheric spectra of the  $\text{NO}_2 \nu_1 + \nu_3$  band underlying the  $\nu_3 \text{CH}_4$  band for two minimum altitudes of the grazing solar ray indicated in kilometers



The mixing ratios, by volume, shown in Table II and in Fig. 10 refer to the altitudes of the solar grazing rays and have been deduced from the  $\text{NO}_2$  concentrations determined from the spectra and from the total concentration given in the Mid-Latitude, Spring-Fall model of U.S. Standard Atmosphere Supplements, 1966. The quoted errors correspond

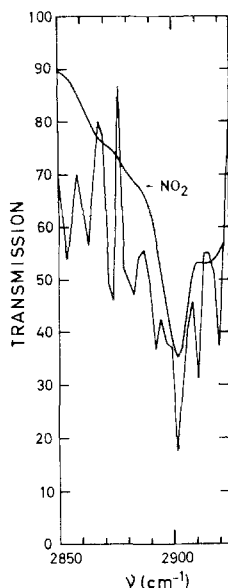


Figure 9

Comparison between observed and computed spectra of the  $\nu_1 + \nu_3$   $\text{NO}_2$  band

Table II

$\text{NO}_2$  mixing ratios

Balloon altitude (km)	Solar zenith angle	Grazing solar rays altitude (km)	$\text{NO}_2$ mixing ratio (by volume)	Observed band	Reference to spectra
29	94.1	12.5	$(3.4 \pm 1) \times 10^{-9}$	$\nu_1 + \nu_3$	[1, 2]
34	94.3	16.1	$< 2.3 \times 10^{-9}$	$\nu_1 + \nu_3$	[1, 2]
29.7	92.8	21.9	$(8.3 \pm 1.5) \times 10^{-10}$	$\nu_3$	[11]
29.7	92.4	23.9	$(1.7 \pm .5) \times 10^{-9}$	$\nu_3$	[11]
29.7	92.0	25.7	$(3.8 \pm 1.3) \times 10^{-9}$	$\nu_3$	[11]
29.7	91.5	27.5	$(7.8 \pm 1.5) \times 10^{-9}$	$\nu_3$	[11]
29.7	91.2	28.3	$(4.0 \pm 1.5) \times 10^{-9}$	$\nu_3$	[11]

to lower and upper values of the amount of absorber in the optical path leading to computer-generated spectra that could be distinguished from the observed atmospheric spectra. The relatively high value observed at the lowest altitude is thought to be due to a tropospheric influence. Using the experimental data, it has to be kept in mind that they were obtained in separate experiments performed at two different locations and at

different moments. The mixing ratio appears to increase from 20 to 28 km, showing the presence of a stratospheric layer of  $\text{NO}_2$ . This peculiarity might be the reason why no evidence for  $\text{NO}_2$  has been found up to now in submillimetre stratospheric emission spectra (HARRIES *et al.* [14]) taken from an altitude of 12 km at a zenith angle of  $75^\circ$ .

Following the theoretical investigation made by NICOLET [20] on the role of  $\text{NO}_2$  on the stratospheric ozone, the values listed in the table indicate an influence of natural

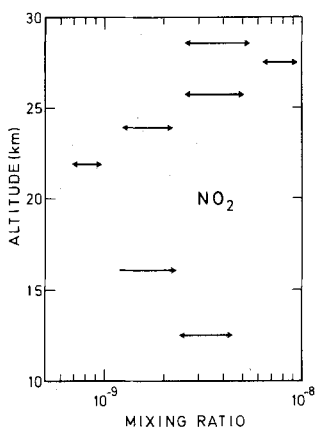


Figure 10

$\text{NO}_2$  mixing ratio by volume versus altitude

nitrogen dioxide on  $\text{O}_3$ . In sunset conditions, as is the case for these determinations,  $\text{NO}_2$  mixing ratios can be taken, within experimental error, equal to  $\text{NO}_x$ .

#### IV. Conclusion

The data presented in this article appear to be useful to gain information on stratospheric vertical transport (NICOLET and PEETERMANS [21]) and on the stratospheric nitrogen oxygen compounds (BRASSEUR and CIESLIK [6]). More measurements are, of course, needed to improve the picture now available, not only in the atmosphere but also in the laboratory.

#### Acknowledgement

We express our thanks to Dr. M. NICOLET for his help and suggestions throughout this work.

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