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FOREWORD

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AVANT-PROPOS

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SIMULTANEOUS MEASUREMENTS OF NO AND NO_2 IN THE STRATOSPHERE

by

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Abstract

Simultaneous measurements of NO and NO_2 in the stratosphere leading to an NO_x determination have been performed by means of infrared absorption spectrometry using the sun as a source in the 5.2 μm band of NO and in the 6.2 μm band of NO_2. The observed abundance of NO_x peaks at 26 km where it is equal to $(4.2 \pm 1) \times 10^9$ cm^{-3}. The volume mixing ratio of NO_x was observed to vary from 1.3×10^{-9} at 20 km to 1.3×10^{-8} at 34 km.

Résumé

Des mesures simultanées de NO et NO_2 dans la stratosphère conduisant à une détermination de NO_x ont été effectuées par spectrométrie d'absorption en utilisant le soleil comme source dans les bandes de 5,2 μm de NO et de 6.2 μm de NO_2. La concentration de NO_x présente un maximum de 26 km où elle vaut $(4,2 \pm 1) \times 10^9$ cm^{-3}. Le rapport de mélange volumique observé varie de $1,3 \times 10^{-9}$ à 20 km à $1,3 \times 10^{-8}$ à 34 km.

Samenvatting

    De gelijktijdige meting van NO en NO_2 in de stratosfeer, leidend tot de bepaling van NO_x, werden uitgevoerd door absorptie spectrometrie, waarbij de zon als bron gebruikt werd, van de banden op 5,2 μm voor NO en van 6,2 μm voor NO_2. De concentratie van NO_x vertoont een maximum bij 26 km waar de waarde $(4,2 \pm 1) \times 10^9$ cm^{-3} is. De volumetrische mengverhouding die werd waargenomen, varieert van $1,3 \times 10^{-9}$ bij 20 km tot $1,3 \times 10^{-8}$ bij 34 km.

Zusammenfassung

    Gleichzeitige stratosphärische Messungen von NO und NO_2, die eine Bestimmung von NO_x geben, wurden durch Absorptionsspektrometrie mit der Sonne als Lichtquelle in den 5,2 μm Banden von NO und in den 6,2 μm Banden von NO_2 durchgeführt. Die NO_x Konzentration erreicht ein Maximum von $(4,2 \pm 1) \times 10^9$ cm^{-3} auf einer Höhe von 26 km. Das beobachtete NO_x Mischungsverhältuis ändert sich von $1,3 \times 10^{-9}$ auf einer Höhe von 20 km zu $1,3 \times 10^{-8}$ auf einer Höhe von 34 km.

I. INTRODUCTION

Since the first detection of nitric oxide in the stratosphere (Toth *et al.*, 1973, Girard *et al.*, 1973 and Ridley *et al.* 1973) useful information about the vertical distribution of this constituent have been derived by absorption spectrometry using the sun as a source (Ackerman *et al.*, 1973) and by chemiluminescence (Ridley *et al.*, 1974). More recently the variation of NO versus time at 28 km after sunrise has been observed by spin flit Raman laser spectrometry by Patel *et al*, (1974) and observations from a very high flying aircraft have been performed by Loewenstein *et al.*, (1974).

Separate determinations of the abundance of NO_2 have been derived from absorption spectra (Ackerman and Muller, 1972, 1973, Farmer, 1974, Fontanella *et al.* 1974) from emission spectra (Harries 1973) and from photometric observations in the visible (Brewer *et al.*, 1973).

As it is known that NO and NO_2 are photochemically linked through the reaction of nitric oxide with ozone and the photodissociation of NO_2 by solar radiation with a time constant that is very short compared with day length, it is most useful to determine both constituents simultaneously. This appears even more crucial when it is realized that the rate of conversion of NO into NO_2 at sunset and of NO_2 into NO at sunrise is altitude dependent due to the variation with height of the attenuation of solar radiation by Rayleigh scattering and by ozone and NO_2 absorptions and due to the variation with height of the abundance of ozone as an NO scavenger.

A first step towards the determination of the natural variability of NO_x requires the simultaneous measurement of NO and NO_2. Such a measurement is presented here. The method involves absorption spectrometry, using the sun as a source, in two narrow spectral ranges : 1913 - 1923 cm^{-1} in the 5.2 μm band of NO and 1593 - 1603 cm^{-1} in the 6.2 μm band of NO_2.

2. EXPERIMENTAL DETAILS

A grille spectrometer (Girard, 1963) associated with a telescope and a sun pointer has been used to record the spectra.

The spectrometer uses a Littrow mounting with an off-axis parabolic mirror whose focal length is 60 cm. Its Jobin-Yvon grating ruled at 60 grooves per mm over an area of 130 x 68,6 mm is blazed at 70°. It is used in the 5th and in the 6th orders associated with two band pass interference filters. At every inversion of the grating drive the filter wheel switches from one filter to the other in order to scan the two wavelength ranges shown in figure 1. The grille is deposited on an 18 x 18 mm calcium fluoride window and the minimum step is 0.2 mm. The resolution approaches the theoretical limit. The signal is chopped at 360 Hz by vibrating the collimating mirror at 180 Herz, which is the resonance frequency of the mechanical mounting included in the servo system stabilizing the vibration amplitude. The spectral calibrations are performed by means of H_2O and CO_2 absorption lines and by the simultaneous recording of the spectra and of position grating marks. To maintain the instrumental performance during flight the optical path inside the spectrometer is servo controlled to balance the mechanical deformations due to temperature and attitude alterations. Two auxiliary grilles located along side of the main grille were used for this purpose. The first was illuminated by a filament lamp, with ray paths close to the path of the solar radiation to be measured. The light flux was received on a germanium photodiode after reflection on the second grille. The parabolic mirror vibrating at a frequency f induces a photodiode signal at frequencies f and 2 f. The f component called error signal is used to keep the instrument properly tuned. A gold doped germanium detector was used at solid nitrogen temperature. The detector signals were preamplified and telemetered to the ground through three channels having different sentivities. The linearity of the system was controlled in flight by means of calibration voltages as shown in figure 1.

A 4.2 m focal length modified Cassegrain telescope of 32 cm diameter was used to image the sun on the grille.
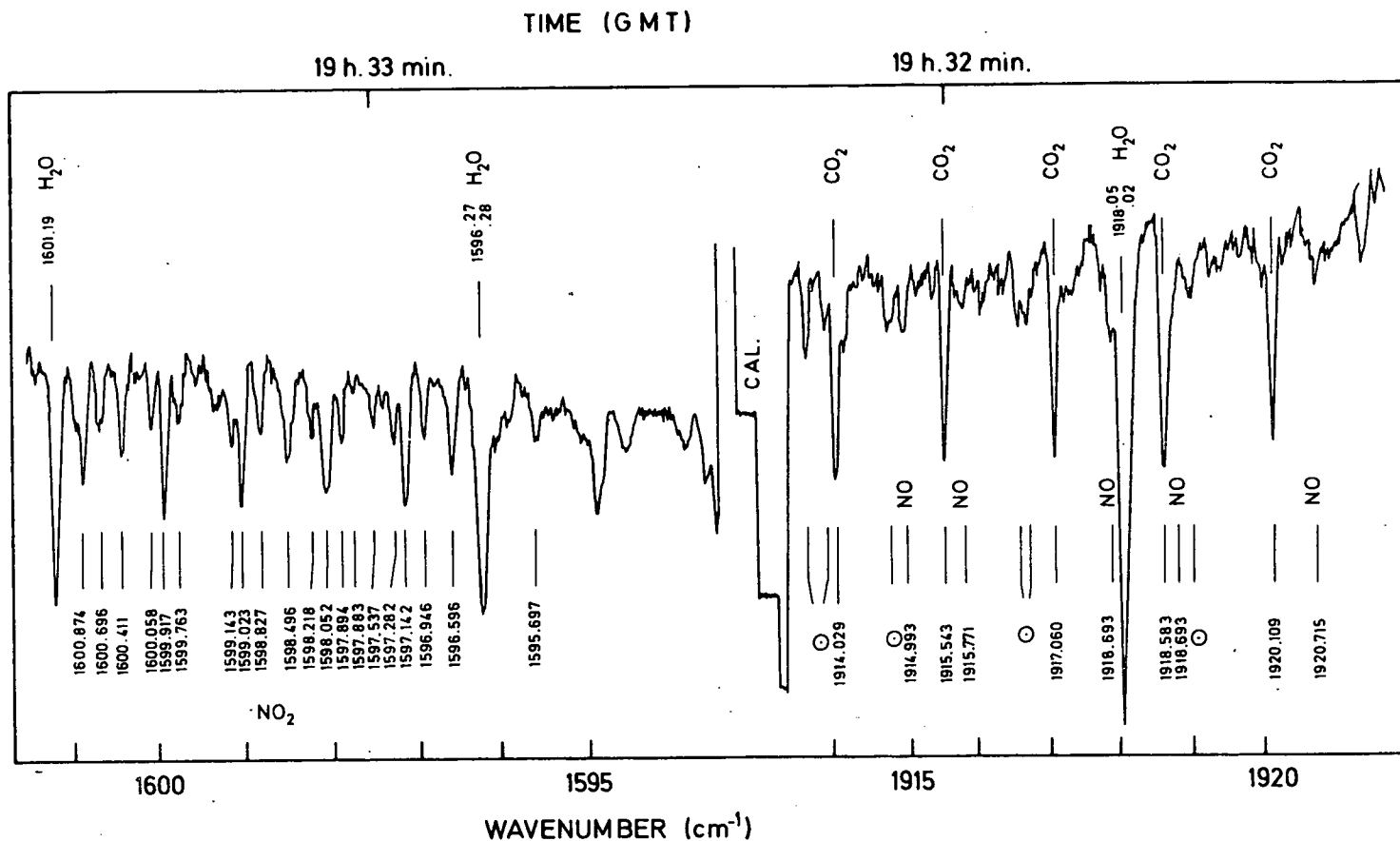
Fig. 1.- Portion of recording versus time of the solar radiation partially absorbed by the atmosphere on May 13, 1974. Time is running from the right to the left. The spectral region of the 5.2 μm NO band is scanned. Then, the inversion of the motion of the grating takes place. Simultaneously the voltage calibration sequence marked CAL is initiated and the filter wheel is rotated to select the spectral range in the 6.2 μm NO_2 band that is further scanned. CO_2, H_2O, NO and NO_2 lines are identified. Solar absorption features are also indicated. The NO lines at 1914.993 cm^{-1} and at 1920.715 cm^{-1} appear to be uncontaminated by any absorption and give equivalent widths in agreement with each other. The first has been preferred for the interpretation since it is more intense and has been observed in May 1973 and in May 1974.

The sun pointing system controls the attitude of the spectrometer telescope assembly. The whole gondola is uncoupled from the balloon on the three axis. In a first mode the gondola is oriented along a fixed axis referred to the earth. The couples are provided by inertia wheels desaturated by means of moving masses. At the end of the acquisition mode a rendez-vous is realized with the sun. A timer switches then to the tracking mode involving optical sun sensors. The pointing accuracy is better than 30 arc seconds.

Temperatures and ambient pressure were also telemetered as described in more detail by Ackerman *et al.* (1973).

3. THE FLIGHT

The gondola was flown on May 13, 1974 from the CNES range in Aire sur l'Adour (France). A Winzen 11.6 million cubic foot balloon carried the payload up to 38.5 km after 3 hours of ascent. As usual at that period of the winds inversion, the balloon remained practically at the same geographic coordinates during the measurements namely 0° 25' East and 43° 35' North. The recording of spectra started at a solar zenith angle equal to 86° showing the solar continuum and small absorption lines due to H_2O. Solar absorption lines were also present in the 1900 cm^{-1} range (Kunde 1967). Sample spectra obtained at solar zenith angles larger than 90° are shown in figure 1. The two spectral ranges scanned in sequence show telluric absorption features due to NO_2, NO, H_2O and CO_2.

4. INTERPRETATION OF THE DATA

The identification of the lines has been based on the laboratory measurements of Hurlock *et al* (1974) and of Dana and Fontanella (1973) for NO_2, on the compilation made by Cieslik and Muller (1974) for NO and on the compilation of Mac Clatchey *et al* (1973) for H_2O and for CO_2. The quantitative evaluation of the amount of NO and NO_2 on the optical path has been based on the measured equivalent widths and on the absorption cross sections whose values are listed in table 1 and have been adapted for the stratospheric

TABLE 1 : Integrated absorption cross sections, s, used in the interpretation of the data.

Constituent	↓	Wavenumber (cm^{-1})	s(300 K) (cm^2 cm^{-1} mol.$^{-1}$)
NO		1914.993	9.56×10^{-20}
NO$_2$		1600.411	3.18×10^{-19}
NO$_2$		1600.058	1.70×10^{-19}
NO$_2$		1596.946	2.11×10^{-19}

temperatures. For NO the line at 1914.993 cm^{-1} has been chosen for the sake of comparison of the results of this flight with those of a previous flight for which preliminary data have already been published (Ackerman *et al.* 1973).

Figures 2a and 2b show the evolution of the absorption due to this NO line while the minimum altitude reached by the solar rays decreases in the cases of the May 1973 and May 1974 flights respectively. Figure 3 shows the evolution of NO_2 absorption lines during the increase of solar depression angles corresponding to lower and lower minimum altitudes of the solar rays. The equivalent width is shown in figure 4 for NO and NO_2 versus minimum altitude reached by the solar radiation in the atmosphere. These values are used in the inversion process involving the division of the atmosphere in layers of 2 km thickness. The correct amount of absorber is introduced in the successive layers in order to repfoduce the observed integrated absorptions by means of an iterative Newton-Raphson process (Hartree, 1958). The Voigt line profile is represented by the approximation derived by Whiting (1968).

5. RESULTS AND DISCUSSION

The deduced vertical distributions are shown in figure 5 and 6 for NO and NO_2 respectively. Numerical values are listed in Table 2 for NO, NO_2, $NO + NO_2$ and for the NO_2 over NO ratio. The sum of NO and NO_2 is plotted versus altitude in figure 7. The limits of uncertainties indicated in Table 2 and in figures 5 to 7 are given to take into account the uncertainty in determining the equivalent widths from the spectra, amplified by the inversion process leading to the vertical distributions of number densities. They do not include the effects on the inversion process that could be due to the conversion of NO into NO_2 by reaction with ozone when the photodissociation of the latter decreases. Theoretical considerations (Brasseur and Nicolet, 1973) indicate that for an average ozone profile the NO_2 over NO ratio should exhibit a broad maximum of its day time value close to one in the 20 to 30 km altitude range. The observed values listed versus altitude in table 2 indicate that the measurements still correspond to day time ratios down to at least 25 km. The sunset conversion process has no significant effect on the values given here for ($NO + NO_2$)
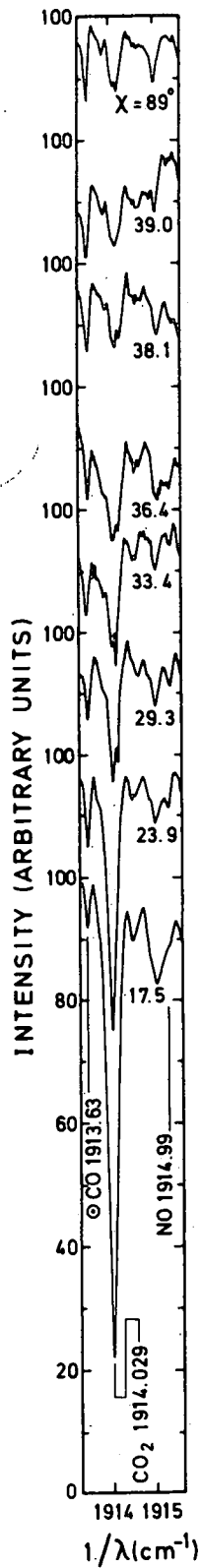
Fig. 2a.- Intensity of solar radiation versus wavenumber during the experiment performed on May 14, 1973 (Ackerman *et al.* 1973) at 40 km altitude. The spectral region from 1913.5 cm^{-1} to 1915.3 cm^{-1} recorded during sunset is shown. The upper spectrum corresponds to a solar zenith angle, χ, equal to 89°. For each of the other spectra χ was larger than 90° and the minimum altitude reached by the solar radiation in the atmosphere is indicated. The NO line at 1914.993 cm^{-1} appears clearly, well separated from the solar absorption line at 1914.73 cm^{-1}. It is well separated from the closest CO_2 lines due to the $(12^2 02)-(01^1 01)$ transitions that occur at 1914.541 cm^{-1} and 1915.328 cm^{-1}.
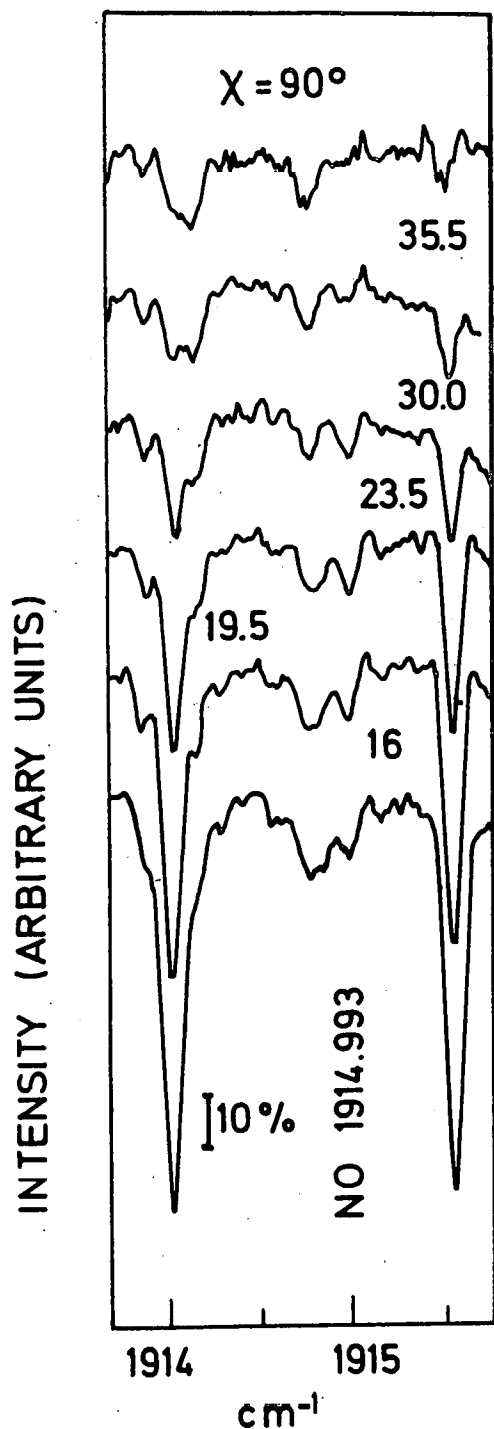
Fig. 2b.- I n t e n s i t y of solar radiation recorded versus wavenumber during the experiment performed on May 13, 1974 at 38,5 km altitude. An intensity change corresponding to 10% of absorption at the position of the NO line at 1914.993 cm^{-1} is indicated. The other main absorptions are identified in figure 1. The rate of growth is obviously different for the NO line and for the CO_2 lines while the minimum altitude reached by the solar radiation is the atmosphere decreases. The altitude is indicated in km for each spectrum excepted for the upper one obtained at a solar zenith angle χ equal to 90°.

NO$_2$

$\chi = 89.5°$

34.7

28.4

21.8

18.0

1600.411

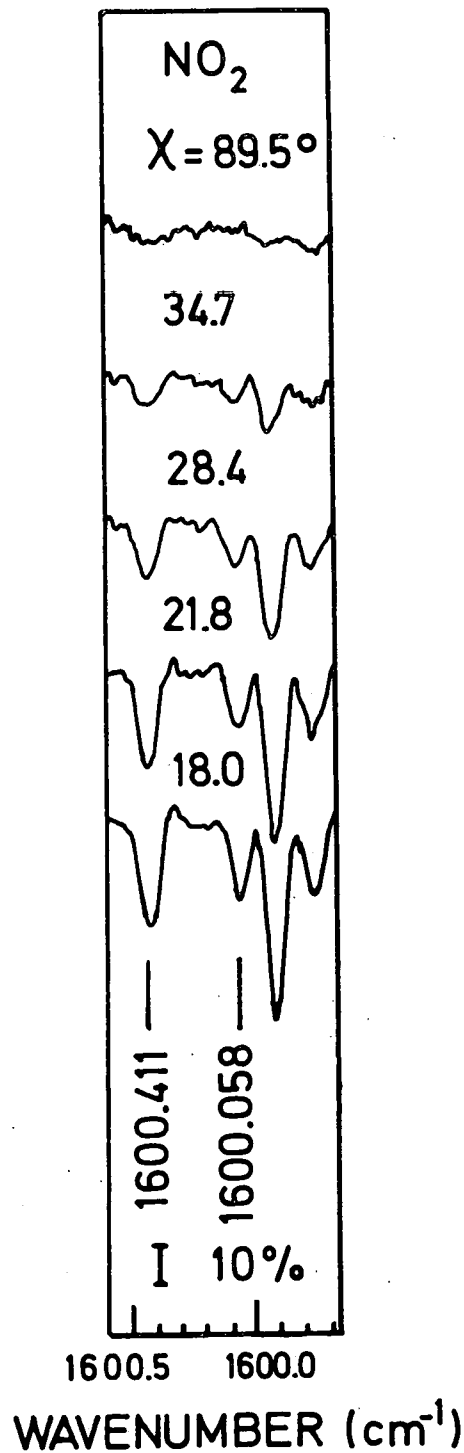1600.058

I 10%

1600.5   1600.0

WAVENUMBER (cm^{-1})

Fig. 3.- Intensity of solar radiation recorded versus wavenumber during the experiment performed on May 13, 1974. The spectral region shown is in the range of the 6.2 μm band of NO$_2$. The lines are identified in figure 1. The upper spectrum corresponds to a solar zenith angle, χ, equal to 89.5°. For each of the other spectra χ was larger than 90° and the minimum altitude reached by the solar radiation in the atmosphere is indicated in km. Two of the lines selected for the quantitative interpretation are indicated. An intensity change corresponding to 10% of absorption is shown.
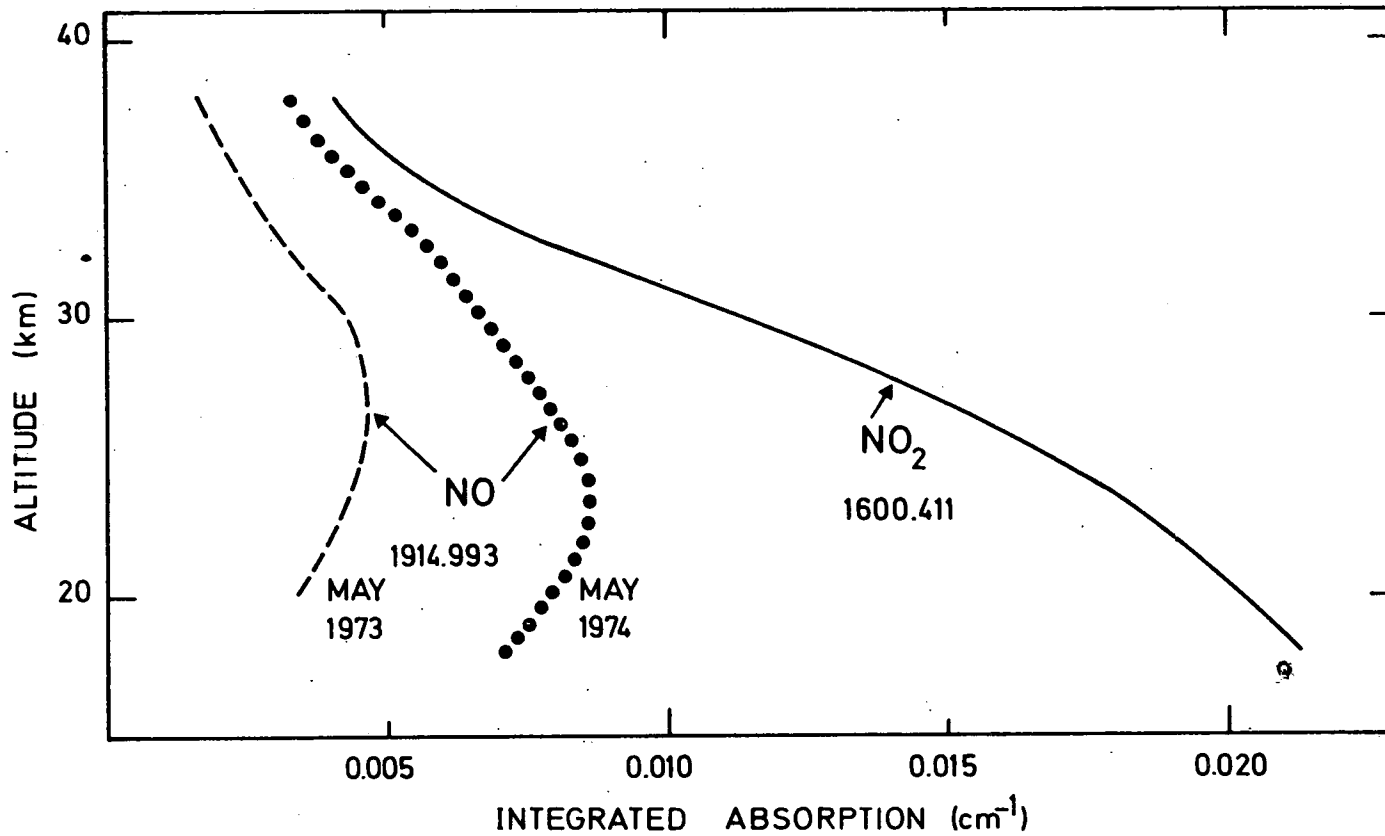
Fig. 4.- Integrated absorption expressed in cm⁻¹ deduced from the equivalent widths measured that have been used in the inversion process to determine the number densities. Each value corresponds to a minimum altitude expressed in km reached by the solar radiation in the atmosphere. The NO curves for May 1973 and May 1974 are very different even if their overall shapes are similar. The overall shape of the NO_2 curve differs much from the ones observed for NO.
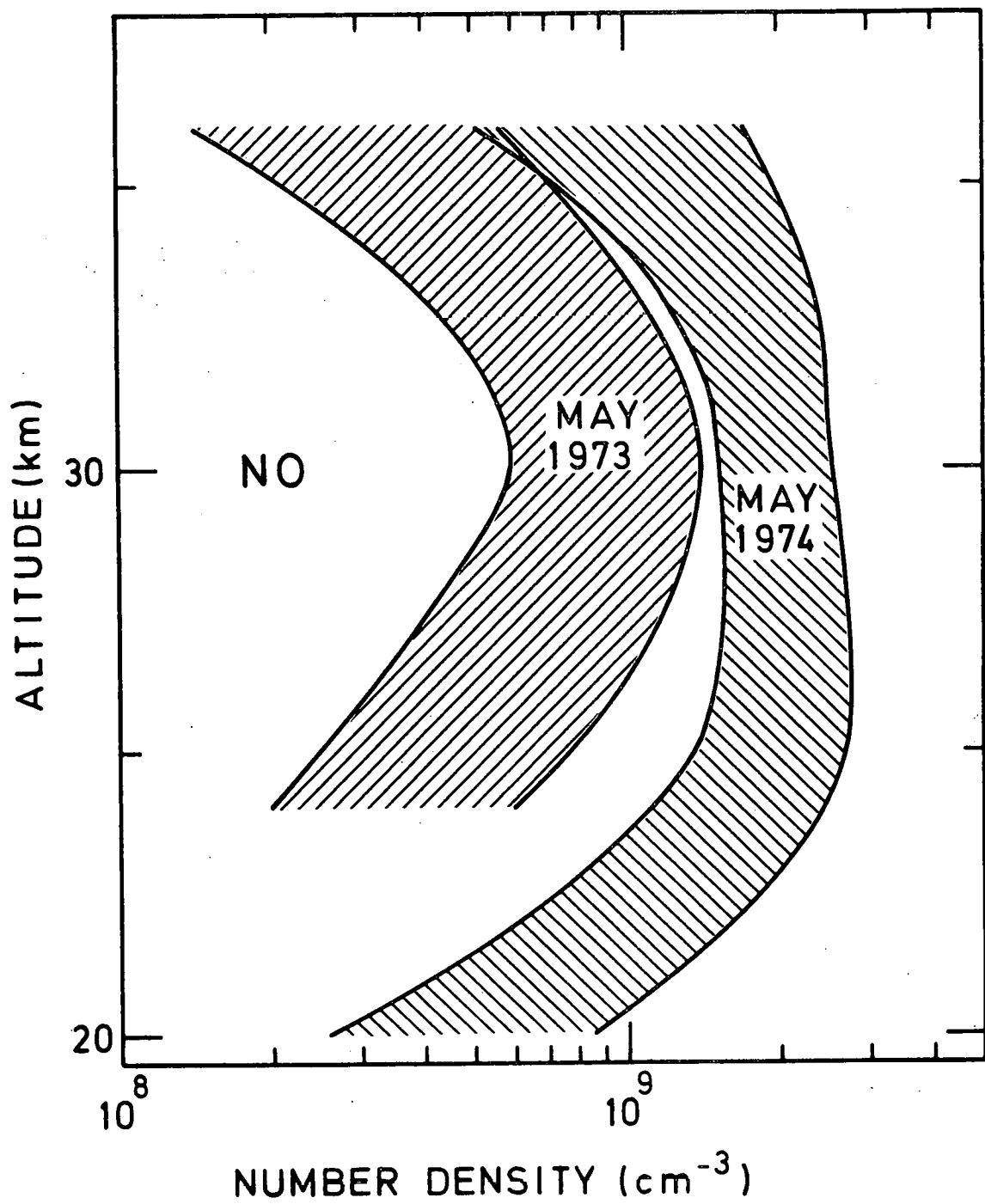
Fig. 5.- Number density of NO versus altitude obtained by the inversion process. The differences between the values obtained in May 1973 and in May 1974 is outside the uncertainty limit discussed in the text. They do not only relate to the abundances but also to the shape of the vertical distributions.
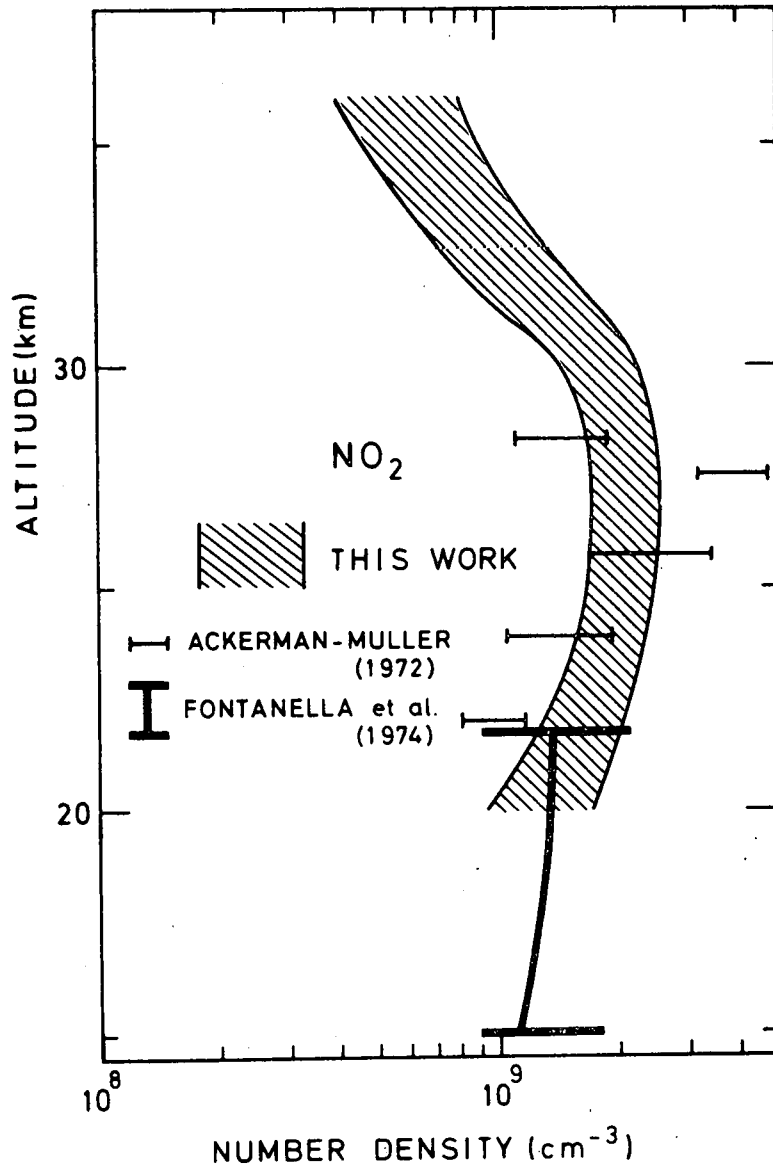
Fig. 6.- Number density of NO_2 versus altitude obtained by the inversion process. The results are in good agreement with the values reported by Ackerman and Muller (1972, 1973) and by Fontanella et al. (1974). They are lower than those obtained by Brewer et al. (1973).

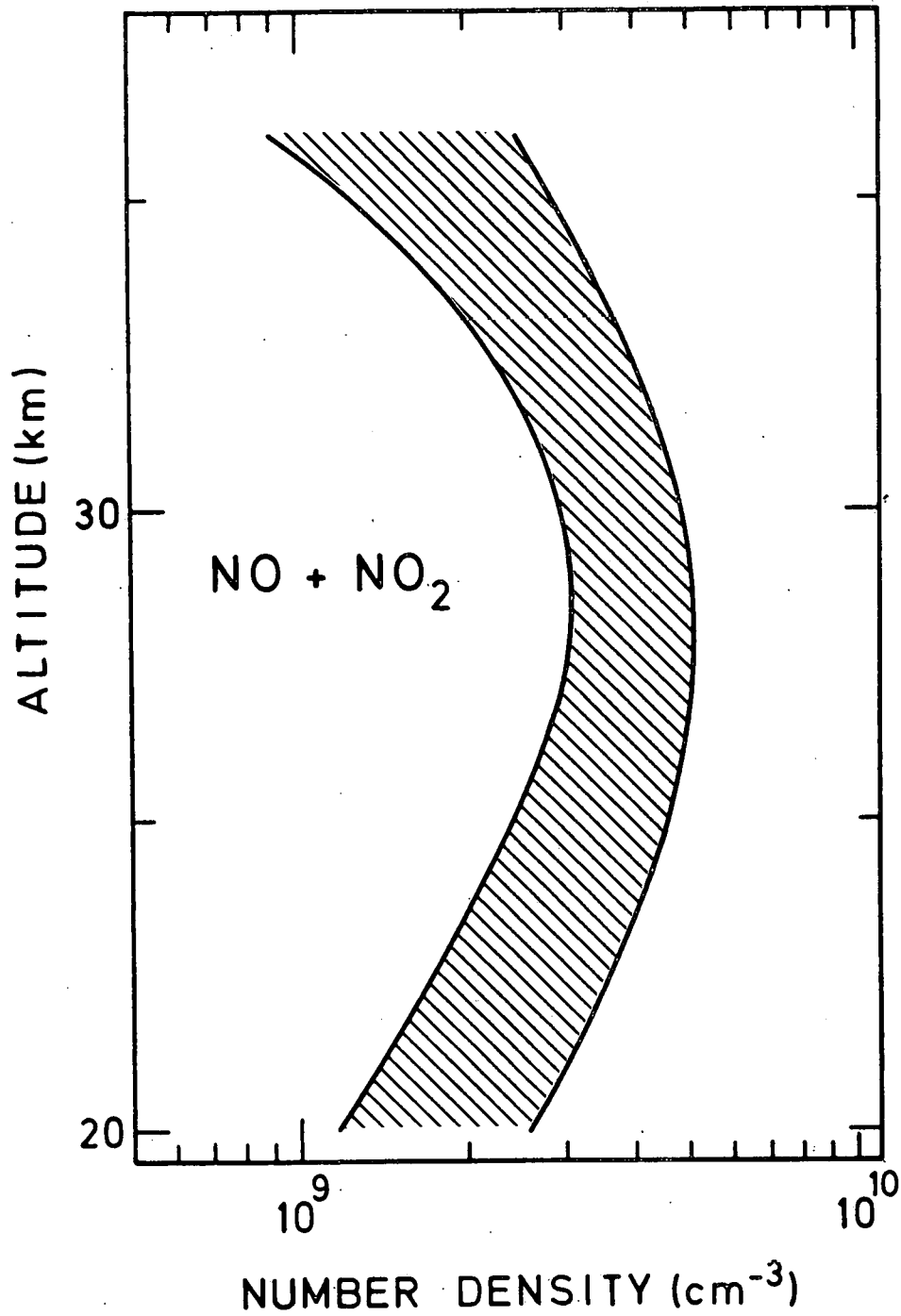Fig. 7.- Sum of the number densities of NO and NO_2 deduced from the experiment of May 13, 1974, versus altitude. The vertical distribution shown here corresponds to a decrease by a factor of 10 of the NO_x volume mixing ratio from 34 to 20 km.

TABLE 2 : NO and NO_2 results

Z(km)	NO(May 1973) 10^8 cm^{-3}	NO(May 1974) 10^8 cm^{-3}	NO_2(May 1974) 10^8 cm^{-3}	NO + NO_2(May 1974) 10^8 cm^{-3}	NO_2/NO(May 1974)
36	3.5 ± 2	11 ± 6	6 ± 2	17 ± 8	0.55
34	6.0 ± 3	16 ± 6	8 ± 2.5	24 ± 8.5	0.50
30	10 ± 4	20 ± 5	19 ± 4	39 ± 9	0.95
26	6 ± 3	21 ± 6	21 ± 4	42 ± 10	1.0
24	4 ± 2	18 ± 7	20 ± 4	38 ± 11	1.1
20	-	5.5 ± 3	13.5 ± 4	19 ± 7	3

over the whole altitude range considered within the given limits of uncertainties. The range of uncertainty is larger for the NO measurements of May 1973 than for those of May 1974. This is due to the smaller equivalent widths observed in the first case for which no value is given for altitudes lower than 24 km where the uncertainty appears to be too large.

It is unambiguous that the NO densities derived from the May 1974 experiment are larger than those measured in May 1973 by means of the same instrumentation used under the same conditions. No precise deduction can however be drawn at present from this point, since the NO_2 over NO ratio depends on the ozone profile, which is not available to the authors for comparison at the two periods. For this reason it is not possible to attribute the observed difference to a variation in time of the NO_2 over NO ratio or to an increase of the sum of both components that could for instance, be related to transport processes or to other phenomena. It should however be mentionned that the tropopause altitude over the Gulf of Biscay was higher ($\sim$ 13 km) in the case of the May 1973 experiment than in the case of the May 1974 one ($\sim$ 9 km). The NO_2 vertical distribution is in rather good agreement with the values deduced by Ackerman and Muller in 1972 and by Fontanella *et al.* (1974). All of them seem to be within the limits of the possible natural variability.

The vertical distribution of the sum of NO and NO_2 shown in figure 7 exhibits a well marked maximum centered at about 27 km. The total amont in a vertical column between 20 and 37 km is equal to $(5.3 \pm 1.5) \times 10^{15}$ molecules per cm^2. This amount would correspond to an apparent volume mixing ratio above 20 km equal to $(4.9 \pm 1.5) \times 10^{-9}$. In fact this number can be a factor of 3 too small compared with the real maximum mixing ratio observed and listed in table 3 where two sets of mixing ratios of the sum of three odd nitrogen molecules, NO_2, NO and HNO_3 are also given. The numbers for HNO_3 are from in situ measurements (Lazrus and Gandrud, 1974) in one set and from spectroscopic measurements (Fontanella *et al*, 1974; Murcray *et al.*, 1974) in the other. In the first case the volume mixing ratio of the odd nitrogen molecules decreases by a factor of 4 from 30 to 20 km while in the second case it remains practically constant and equal to $(1.2 \pm 0.2) \times 10^{8}$ over the whole altitude range considered. Similar values, slightly varying or constant with height in the middle stratosphere have been derived or used in various models (Brasseur and Nicolet 1973; Dütsch, 1973; Mac Elroy *et al.*, 1974; Crutzen, 1973; Isaksen,

TABLE 3 : Volume mixing ratios.

Z(km)	NO + NO$_2$	NO + NO$_2$ + HNO$_3$*	NO + NO$_2$ + HNO$_3$**
	M	M	M
36	1.2×10^{-8}	1.3×10^{-8}	1.3×10^{-8}
34	1.3	1.4	1.4
30	1.1	1.3	1.4
26	6.4×10^{-9}	1.0	1.2
24	4.2	7.9×10^{-9}	1.0
20	1.3	3.3	1.0

*HNO$_3$ values taken from Lazrus and Gandrud (1974).

**HNO$_3$ values taken from Murcray *et al* (1974) and Fontanella *et al* (1974).

1973). This emphasises the need for resolving the discrepency between the in situ and spectroscopic measurements of nitric acid that is considered in all the models above mentioned as the main loss agent for stratospheric oxides of nitrogen.

6. CONCLUSIONS

The variation with altitude of the concentration of NO_x appears to be firmly established by these first measurements. A considerable variation of NO at the same local time and season is observed in comparison of the results with those of a previous experiment one year earlier.

The main role played by nitric acid in the balance of odd nitrogen molecules in the lower stratosphere has been experimentally demonstrated. This should obviously be taken into account in models dedicated to realistic practical predictions of future trends of atmospheric constituents. Such models ought particularly to represent among many other aspects, the observed natural variations of various kinds from *ab initio* computations.

The measurements presented here can be considered as a first order attempt to determine the stratospheric abundance of odd nitrogen molecules. A more complete picture could be drawn if other constituents including at least O_3 and HNO_3 were also measured simultaneously with NO and NO_2.

It should eventually be noticed that possible uncertainties on the molecular absorption cross sections have not been taken into account in the absolute values given here and that more laboratory data are needed in this field.

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