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FOREWORD

This paper has been presented at the Symposium on Aeronomic Processes in the Stratosphere and Mesosphere of the IAGA General Scientific Assembly held in Kyoto, September 1973. It will appear in the Canadian Journal of Chemistry.

AVANT-PROPOS

Ce texte a été présenté au "Symposium on Aeronomic Processes in the Stratosphere and Mesosphere of the IAGA General Scientific Assembly" tenu à Kyoto en septembre 1973. Il sera publié dans le "Canadian Journal of Chemistry".

VOORWOORD

Deze tekst werd voorgedragen tijdens de "Symposium on Aeronomic Processes in the Stratosphere and Mesosphere of the IAGA General Scientific Assembly" in september 1973 te Kyoto. Hij zal in "Canadian Journal of Chemistry" uitgegeven worden.

VORWORT

Dieser Text wurde zum "Symposium on Aeronomic Processes in the Stratosphere and Mesosphere of the IAGA General Scientific Assembly", September 1973 in Kyoto vorgestellt. Er wird in "Canadian Journal of Chemistry" herausgegeben werden.

RECENT STRATOSPHERIC SPECTRA OF NO AND NO_2

by

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Summary

NO and NO_2 spectra obtained by means of a grill spectrometer from a balloon gondola and from Concorde are presented. The corresponding stratospheric abundance of these species are deduced.

Résumé

Des spectres de NO et de NO_2 obtenus au moyen d'un spectromètre à grille embarqué à bord d'une nacelle et de Concorde sont présentés. L'abondance correspondante de ces composés dans la stratosphère en est déduite.

Samenvatting

De NO en NO_2 spectra bekomen bij middel van een Rasterspectrometer, gemonteerd in een schuitje en aan boord van Concorde zijn voorgesteld. De overeenstemmende stratosferische hoeveelheden van deze komponenten zijn er uit afgeleid.

Zusamenfassung

NO und NO_2 Spektra die von einer Ballongondel und von Concorde mit einem Gitterspektrometer erhalten sind, sind vorgestellt worden. Die entsprechende Konzentrationen dieser Bestandteille der Stratosphäre sind abgerechnet worden.

INTRODUCTION

The interest in the stratospheric chemistry has grown since a few years. The lowest stratosphere had particularly been neglected from this point of view and was recognized as a region where the photochemistry was unimportant. This statement was based on the long life time of ozone below its peak even if most of the ozone molecules have a relatively short life time in the whole atmosphere. It is now recognized that active chemical processes take place throughout the stratosphere. They involve species of which the mixing ratios by volume are lower than one part per million. The analytical methods necessary to measure these constituents are not numerous and have to be selected by taking into account both the properties of the molecules to be measured and of the atmosphere itself.

Infrared spectroscopy appears to be particularly well suited to satisfy both aspects by presenting a high specificity and by being well adapted to the atmospheric dimensions. These qualities have since a long time been recognized by many authors exploiting them by means of ground based instruments. Infrared spectrometers acquire even more versatility when operated from space plateforms.

Determinations of NO and NO_2 are necessary to define their possible role in the stratospheric photochemistry. Absorption spectra of nitrogen oxides obtained from a balloon gondola and from an aircraft (Concorde 001) will be discussed here.

INSTRUMENTATION AND EXPERIMENTS

The spectra discussed have been obtained in absorption using the setting sun as a source. The method presents advantages that have already been pointed out [1]. A complete description of the spectrometers will be given elsewhere for the balloon borne as well as for the aircraft borne [2] equipment. In the case of the balloon experiment it can be summarized as follows. The postulated amount of absorber on the optical path being small and a relatively fast wavelength scanning being necessary the spectrometer used had to present the double advantage of large ligth input combined with high resolving power. It was one of the grid spectrometers developed by Girard [3]. The instrument of 60 cm focal length was equiped with a 6 cm x 6 cm "Yvon et Jobin" grating ruled at 60 grooves per mm and used

in the 6th order. The foreoptics was a 4.2 m focal length modified Cassegrain telescope of 32 cm diameter. The detector was a liquid nitrogen cooled "SAT" InSb photo element. An instrumental profile of 0.1 cm^{-1} half width was achieved with a square grid of 18 x 18 mm having a step of 0.2 mm. The instrument was mounted on a sun seeker equiped with the electronics used for the synchronous detection of the detector output, with the voltage controlled oscillators and with the transmitter used in the telemetry radio link. The 320 kg gondola was launched from Aire sur l'Adour in the afternoon of May 14, 1973 with an 11.6 x 10^6 cubic feet "Winzen" balloon.

The instrument used on Concorde 001 was similar. Due to the limited dimension of the CaF_2 window (10 cm diameter) adapted to the skin of the aircraft the light input was smaller giving a somewhat smaller signal to noise ratio. While the body of the balloon spectrometer was open to the ambient air, the aircraft instrument was flushed with dry nitrogen. A sun seeker was mounted to bend the solar radiation at right angle and to track the sun over amplitudes of azimuth and elevation angles of about ten degrees. The spectra discussed here where obtained on constant heading trajectories travelled over at mach two between the northwest of Spain and the west of Cornwall.

RESULTS

a) Nitric oxyde

The recording of the solar spectrum from the balloon gondola at an altitude of 40 km started when the solar zenith angle was 86°. The spectra showed then little structure partly attributed to solar CO absorption lines [4]. As shown in figure 1 telluric absorptions become more and more pronounced for solar zenith angles larger than 90° due to the increase of optical path reaching lower and lower altitudes in the stratosphere. Absorption lines of NO, CO_2 and H_2O were mostly present. CO_2 and H_2O lines were identified on the basis of the AFCRL infrared compilation [5]. For NO other laboratory data were used [6]. The amount of NO on the optical path was deduced from the integrated line absorption cross sections for 220 °K listed in table 1 [7]. The number density of NO versus altitude was infered from the total amounts measured and represented in figure 2 by division of the atmosphere in successive layers of three kilometers thickness. The deduced values are given in table 2 with

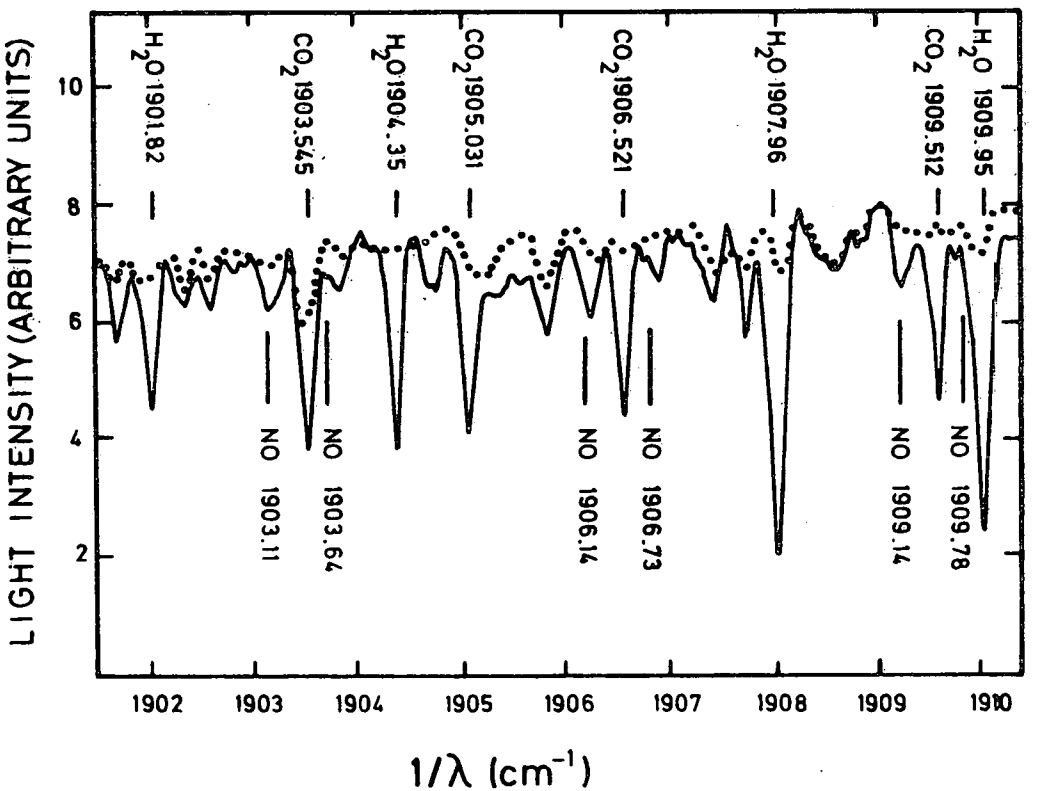

Fig. 1.- Intensity of solar radiation recorded at 40 kilometers altitude versus wavenumber in reciprocal centimeter. The dotted line represents the spectrum at a solar zenith angle of 86^{0}. The continuous line represents the spectrum at a zenith angle of 94^{0}. The absorption lines due to stratospheric NO, CO_2 and H_2O are indicated.

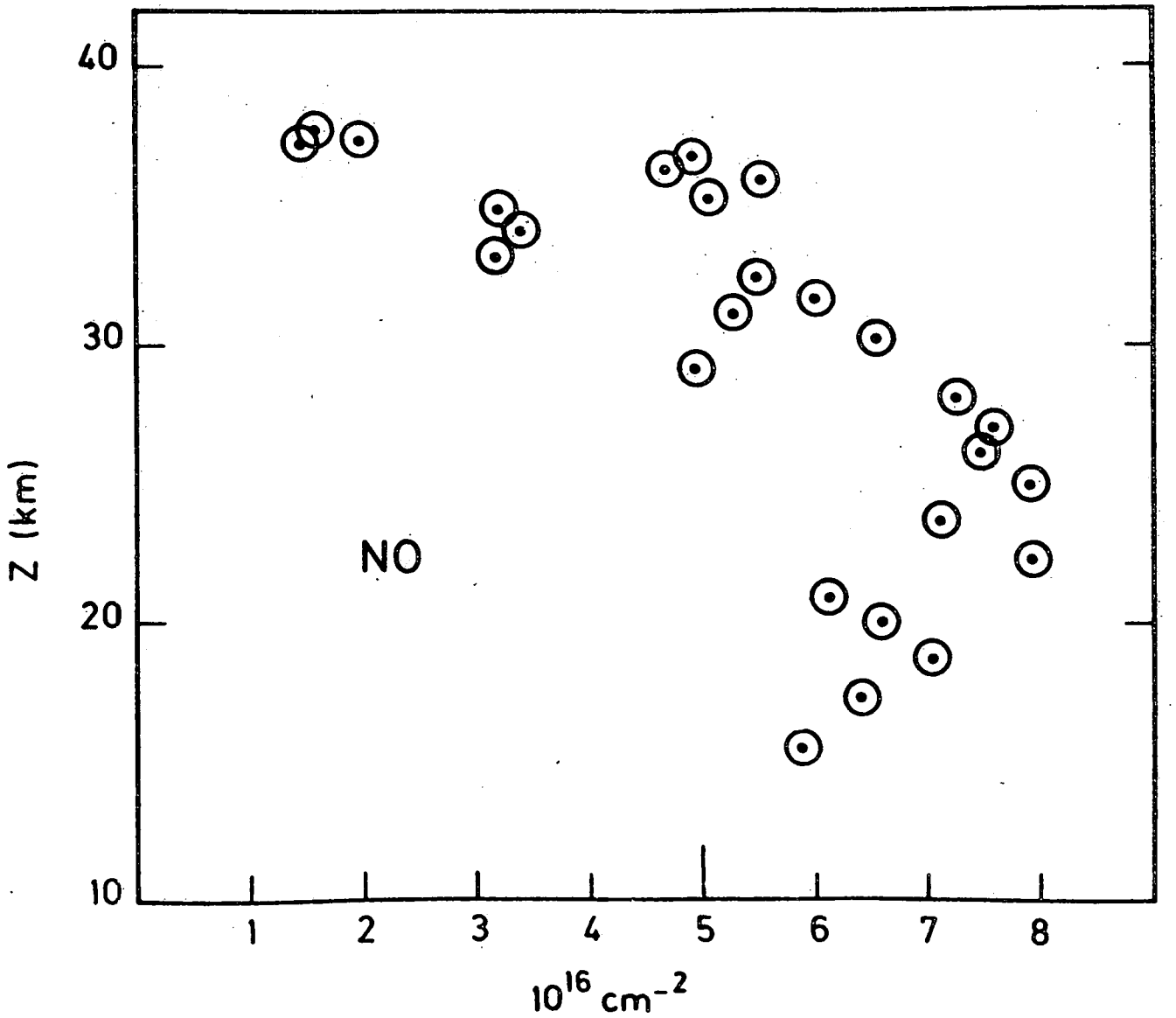

Fig. 2.- Total number of NO molecules observed from the balloon gondola on the optical path versus grazing altitude of solar rays.

the corresponding mixing ratios. The limits of error indicated correspond to the maximum scattering of the original data points taken for grazing ray altitudes from 38 to 15 kilometers. The results are represented in Figure 3 with other experimental data. On June 6, 1973, the aircraft spectrometer previously flown on board of a Caravelle airplane [8], has been used on board of the Concorde prototype 001 in the same spectral region and with the same resolving power. The integrated amounts of NO measured in this latter case along the optical path from 15.2 km are respectively at solar zenith angles of 88° and 90° equal to $(3 \pm 1) \times 10^{16}$ and $(5.5 \pm 1) \times 10^{16}$ molecules per cm^2. The results are within experimental uncertainities in agreement with the data presented in figure 2.

b) Nitrogen dioxide

Spectra of NO_2 in the 1617 cm^{-1} band have been obtained from Concorde at an altitude of 16 km on July 6, 1973. The zenith angle changed during the flight from 88 to 91°. The spectrum for this latter case is shown in figure 4. The NO_2 lines have been identified according to recent data [13] based on molecular constants that are in close agreement wich those used by Ackerman and Muller [1, 14] to determine a vertical distribution of NO_2 from stratospheric spectra. The computed total number of molecules on the optical path has been obtained by using the line strengths applied previously [1, 14] that agree within 20 percent with the more recent values [13]. The total number of molecules observed from 16 km at zenith angles of 88° and 90° are respectively $(3.2 \pm 1) \times 10^{16}$ cm^{-2} and $(4.2 \pm 1.5) \times 10^{16}$ cm^{-2}. These numbers are within experimental uncertainities in agreement with the lowest values of the vertical profile previously published by Ackerman and Muller.

CONCLUSION

The results presented here indicate without any ambiguity the presence of NO and NO_2 in the stratosphere. The measurements from balloon and aircraft are complementary since in this particular case the molecules are photochemically linked. The comparison of the aircraft data obtained at low altitude and solar zenith angle smaller than 90° with the vertical profiles deduced from balloon measurements taken at solar zenith angle larger than

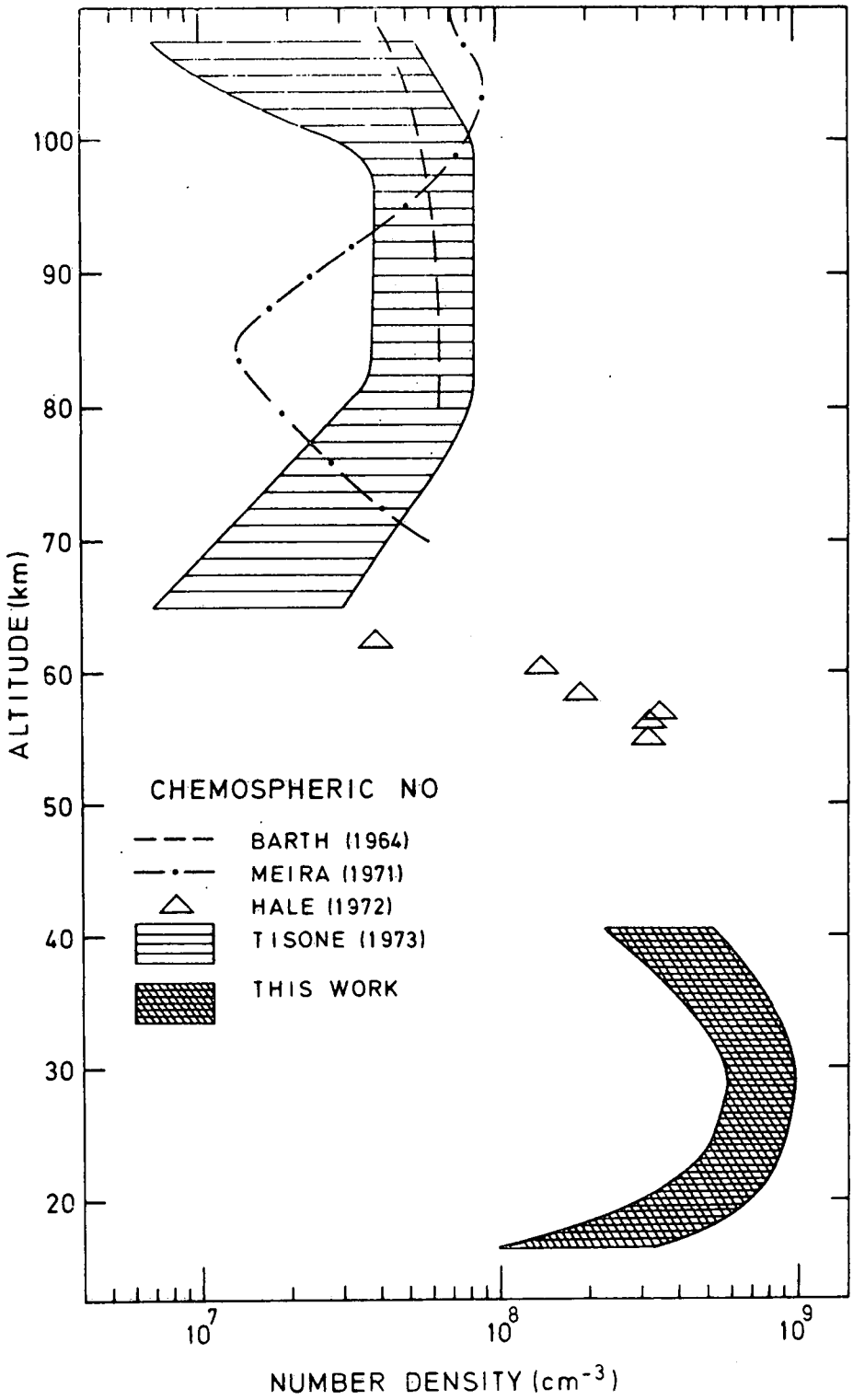

Fig. 3.- Experimental values of the number density of nitric oxide versus altitude in the chemosphere. The results published by Barth [9], Meira [10], Hale [11] and by Tisone [12] are shown with those presented here for the stratosphere.

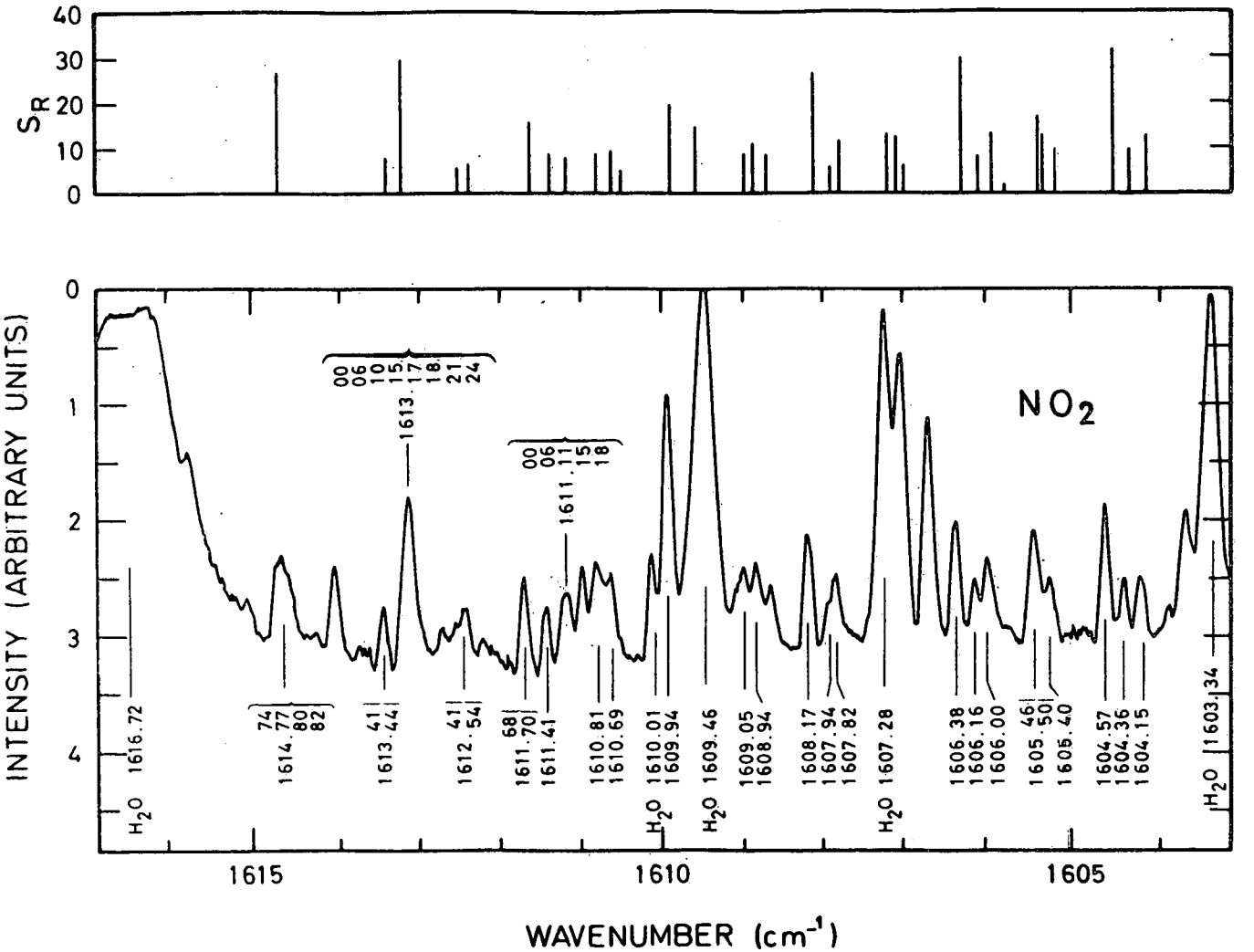

Fig. 4.- Solar spectrum recorded from Concorde 001 at an altitude of 16 km and a zenith angle of 91^0 between 1603 and 1617 cm^{-1}. Telluric water vapor [5] and nitrogen dioxyde [13] lines are indicated. The computed relative intensities [1, 14] are represented for NO_2 in the upper part of the figure.

90^0 is particularly usefull. It indicates that the transformation of NO into NO_2 in sunset conditions can probably not be neglected and that simultaneous measurement of both species have to be performed especially because changes of NO_x with time has not to be excluded. Such measurement presents some technical difficulties that will soon be overcome in future flights. The limited number of measurements performed separately leaves at present a relatively large range of uncertainity. The method of limb measurement that one is forced to use to observe constituents in very small concentrations presents also inherent uncertainity factors. Values of concentration of H_2O and CO_2 deduced from the spectra obtained by means of the balloon borne spectrometer give however confidence in the results that can be obtained. Using the Ladenberg and Reiche function [15] the analysis of the H_2O absorption at 1904.35 cm^{-1} and of CO_2 at 1906.521 cm^{-1} yields respective mixing ratios by volume of these two constituents between 25 and 35 km equal to $(5 \pm 2) \times 10^{-6}$ and $(3 \pm 1) \times 10^{-4}$ in agreement with the generally accepted values.

ACKNOWLEDGEMENT

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TABLE I : Wavenumbers and integrated absorption cross sections (220 ^{o}K) of the observed NO lines.

$1/\lambda(cm^{-1})$	$S(cm^{-1}/molecule\ cm^{-2})$
1903.112	14.8×10^{-20}
1903.643	6.45
1906.142	13.7
1906.729	5.99
1909.139	12.3
1909.79	5.37
1912.076	10.7
1912.787	4.66

TABLE II : Nitric oxyde results.

Altitude (km)	NO number density (cm^{-3})	NO mixing ratio by volume
37.5	$(5 \pm 2) \times 10^{8}$	$(4.4 \pm 1.8) \times 10^{-9}$
34.5	$(6 \pm 2) \times 10^{8}$	$(3.4 \pm 1.2) \times 10^{-9}$
31.5	$(8 \pm 2) \times 10^{8}$	$(2.8 \pm 0.7) \times 10^{-9}$
28.5	$(8 \pm 2) \times 10^{8}$	$(1.8 \pm 0.5) \times 10^{-9}$
25.5	$(7.4 \pm 2) \times 10^{8}$	$(9.7 \pm 2.2) \times 10^{-10}$
22.5	$(6.5 \pm 2) \times 10^{8}$	$(5.7 \pm 1.8) \times 10^{-10}$
19.5	$(4.6 \pm 2) \times 10^{8}$	$(2.5 \pm 1.1) \times 10^{-10}$
16.5	$(2 \pm 1) \times 10^{8}$	$(6.7 \pm 3.5) \times 10^{-11}$

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