

Recent Stratospheric Spectra of NO and NO₂

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NO and NO₂ spectra obtained by means of a grid spectrometer from a balloon gondola and from a Concorde are presented. The corresponding stratospheric abundance of these species is deduced.

On présente les spectres de NO et NO₂ obtenus au moyen d'un spectromètre à grille placé dans une nacelle de ballon et un Concorde. On en déduit l'importance de chacune de ces espèces dans la stratosphère. [Traduit par le journal]

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Introduction

Interest in stratospheric chemistry has grown during the past few years. The lowest stratosphere had been particularly neglected from this point of view and was considered to be a region where photochemistry was unimportant. This conclusion was based on the fact that ozone has a long lifetime in the low stratosphere even if most of the ozone molecules have a relatively short lifetime in the whole atmosphere. It is now recognized that active chemical processes take place throughout the stratosphere. They involve species for which the mixing ratios by volume are lower than 1 p.p.m. 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 been recognized for a long time by many authors, and have been exploited by means of ground based instruments. Infrared spectrometers acquire even more versatility when operated from space platforms.

Determinations of NO and NO₂ 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 has 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. Since the postulated amount of absorber on the optical path is small and a relatively fast wavelength scanning is necessary, the spectrometer used had to have the double advantage of large light input combined with high resolving power. Girard (3) developed this type of grid spectrometer. The instrument of 60 cm focal length was equipped with a 6 cm × 6 cm "Yvon et Jobin" grating ruled at 60 grooves/mm and used in the sixth 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 × 18 mm having a step of 0.2 mm. The instrument was mounted on a sun-seeker equipped 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 × 10⁶ ft³ "Winzen" balloon.

The instrument used on Concorde 001 was similar. Due to the limited dimension of the CaF₂ 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

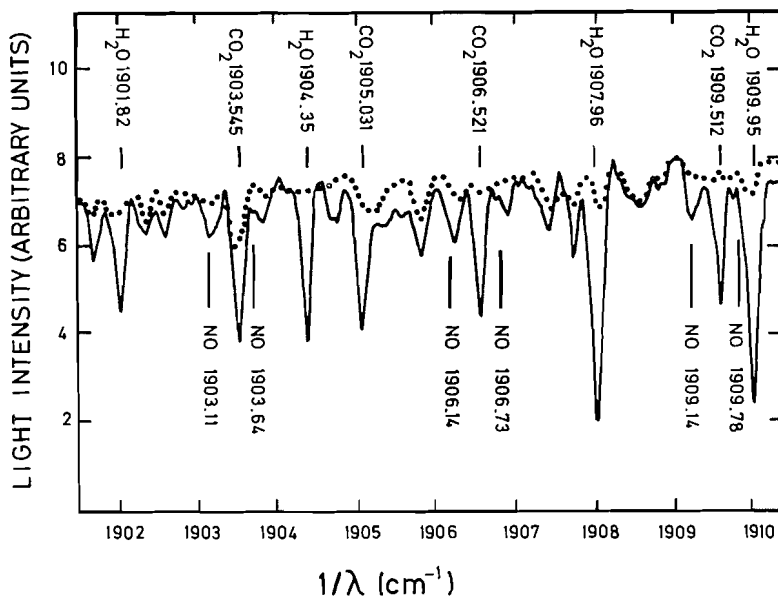


FIG. 1. Intensity of solar radiation recorded at 40 km altitude *vs.* wavenumber in cm^{-1} . The dotted line represents the spectrum at a solar zenith angle of 86° . The continuous line represents the spectrum at a zenith angle of 94° . The absorption lines due to stratospheric NO, CO₂, and H₂O are indicated.

instrument was flushed with dry nitrogen. A sun seeker was mounted to bend the solar radiation at a right angle and to track the sun over amplitudes of azimuth and elevation angles of about 10° . The spectra discussed here were obtained on constant heading trajectories travelled over at Mach 2 between the northwest of Spain and the west of Cornwall.

Results

Nitric Oxide

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 Fig. 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, CO₂, and H₂O were mostly present. CO₂ and H₂O 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 *vs.* altitude was inferred from the total amounts measured and represented in Fig. 2 by division

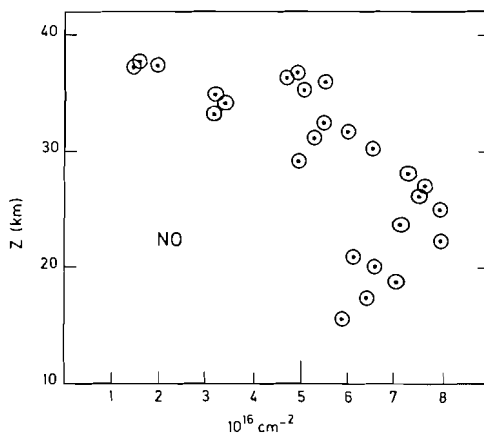


FIG. 2. Total number of NO molecules observed from the balloon gondola on the optical path *vs.* grazing altitude of solar rays.

of the atmosphere in successive layers of 3 km thickness. The deduced values are given in Table 2 with 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 km. The results are represented in Fig. 3 with other experimental data. On June 6, 1973, the aircraft spectrometer previously flown on board a Cara-

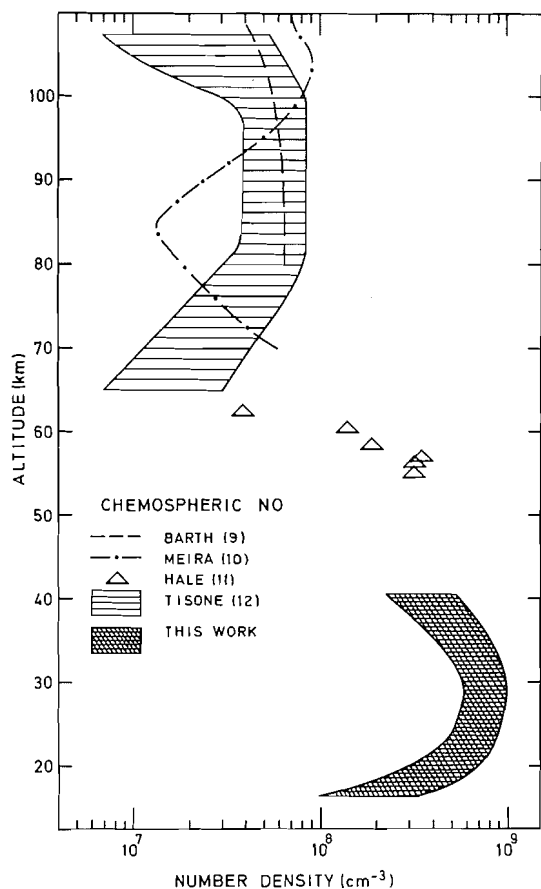


FIG. 3. Experimental values of the number density of nitric oxide *vs.* altitude in the chemosphere. The results published by Barth (9), Meira (10), Hale (11), and Tisonne (12) are shown with those presented here for the stratosphere.

velle airplane (8) was used on board 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/cm². The results are within experimental uncertainties in agreement with the data presented in Fig. 2.

Nitrogen Dioxide

Spectra of NO₂ 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 Fig. 4. The NO₂ lines have been identified according to recent data (13) based on molecular constants that are

TABLE 1. Wavenumbers and integrated absorption cross sections (220°K.) of the observed NO lines

| $1/\lambda$ (cm ⁻¹) | s (cm ² cm ⁻¹) |
|---------------------------------|---|
| 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 2. Nitric oxide 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 | $(2 \pm 1) \times 10^8$ | $(6.7 \pm 3.5) \times 10^{-11}$ |

in close agreement with those used by Ackerman and Muller (1, 14) to determine a vertical distribution of NO₂ from stratospheric spectra. The computed total number of molecules in the optical path has been obtained by using the line strengths applied previously (1, 14) that agree within 20% 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 uncertainties in agreement with the lowest values of the vertical profile published previously by Ackerman and Muller.

Conclusion

The results presented here indicate without ambiguity the presence of NO and NO₂ 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 90° is particularly useful. It indicates that the transformation of NO into NO₂ in sunset conditions probably cannot

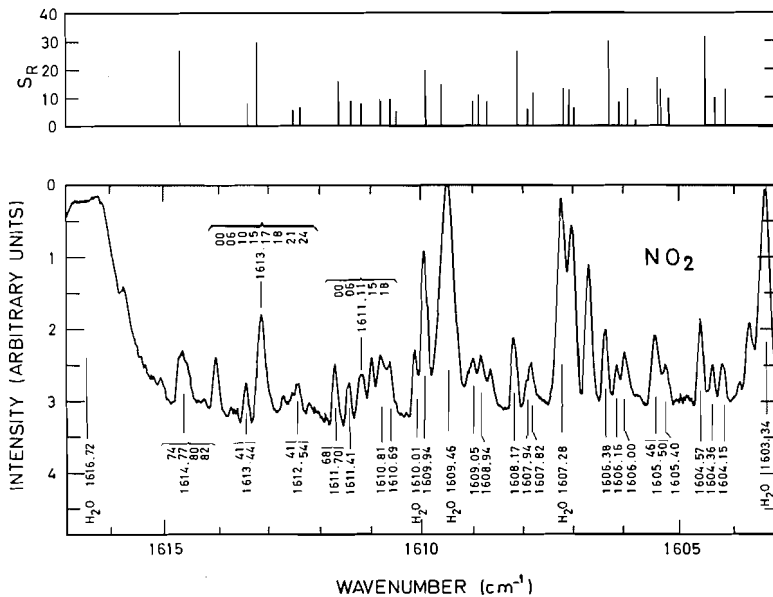


FIG. 4. Solar spectrum recorded from Concorde 001 at an altitude of 16 km and a zenith angle of 91° between 1603 and 1617 cm^{-1} . Telluric water vapor (5) and nitrogen dioxide (13) lines are indicated. The computed relative intensities (1, 14) are represented for NO₂ in the upper part of the figure.

be neglected and that simultaneous measurements of both species have to be performed, especially because changes of NO_x with time cannot be excluded. Such measurements present 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 uncertainty. The method of Limb measurement that one is forced to use to observe constituents in very small concentrations also presents inherent uncertainty factors. Values of concentrations of H₂O and CO₂ deduced from the spectra obtained by means of the balloon-borne spectrometer, however, give confidence in the results that can be obtained. Using the Jansson and Korb tables (15) the analysis of the H₂O absorption at 1904.35 cm^{-1} and at 1909.95 cm^{-1} and of CO₂ at 1906.521 cm^{-1} yields respective mixing ratios by volume of these two constituents between 25 and 35 km equal to $(3.4 \pm 0.7) \times 10^{-6}$ and $(2.6 \pm 0.7) \times 10^{-4}$, in agreement with the generally accepted values.

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