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Stratospheric Nitric Oxide from Infrared Spectra

AERONOMERS have generally admitted that the abundance of nitric oxide is small in the chemosphere. Its detection and even more its measurement have been regarded as a difficult task. The importance of this species in atmospheric chemistry, however, makes the effort to measure it worthwhile. Data have been obtained up to now by using the resonant scattering of solar ultraviolet radiation[1] and the ionizing blunt probe technique[2] in the mesosphere and lower thermosphere. Here we report the first determination of the vertical distribution of the abundance of nitric oxide in the stratosphere. The method involves absorption spectrometry in the 5.2 μm band of NO using the setting Sun as a light source.

Because the postulated amount of absorber in the optical path is small and relatively fast wavelength scanning is necessary, the spectrometer used had to have the double advantage of large light input and high resolving power. The instrument, one of the grid spectrometers developed by Girard[3], had a focal length of 60 cm and was equipped with a 6 cm × 6 cm Yvon et Jobin grating ruled at 60 grooves mm^{-1} 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} halfwidth 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 11.6×10^6 foot^3 'Winzen' balloon.

Recording of the solar spectrum from an altitude of 40 km started when the solar zenith angle was 86°. The spectra then showed little structure partly on account of solar CO absorption lines[4]. As shown in Fig. 1, telluric absorptions become more and more pronounced for solar zenith angles larger than 90° because of the increase in the optical path, reaching lower and lower altitudes in the stratosphere. Absorption lines of NO, CO_2 and H_2O were predominant. CO_2 and H_2O lines were identified on the basis of the AFCRL infrared compilation[5] and for NO other laboratory data were used[6]. The amount of NO in the optical path was deduced from the integrated line absorption cross sections computed[7] from the band intensity[8]. The number density of NO against altitude was inferred from the total amounts measured by division of the atmosphere into successive layers, each 3 km thick.

Table 1 Data on NO

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	$(2 \pm 1) \times 10^8$	$(6.7 \pm 3.5) \times 10^{-11}$

The values are given in Table 1 with the corresponding mixing ratios. The limits of error indicated correspond to the maximum scatter of the original thirty data points taken for grazing ray altitudes from 38 to 15 km. The results are represented in Fig. 1 with other experimental data. On June 6, 1973, a similar spectrometer, previously flown on a Caravelle aircraft[9], was used on Concorde 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 $(3 \pm 1) \times 10^{16}$ and $(5.5 \pm 1) \times 10^{16}$ moles cm^{-2} at solar zenith angles of 88° and 90°, respectively. The results are, within experimental error, in agreement with the data presented in Fig. 2.

Several conclusions can be drawn from the new appearance of the chemospheric NO distribution resulting from the addition of the new data reported here. As suggested by Nicolet[10], a stratospheric source of NO must exist. The photodissociation of NO is a sufficiently large sink in the low mesosphere to compensate for the downward mesospheric and upward stratospheric NO fluxes[11]. The sum of the measured amounts of NO and NO_2 (ref. 12) indicates a large sink of NO_x below 25 km at mid-latitudes.

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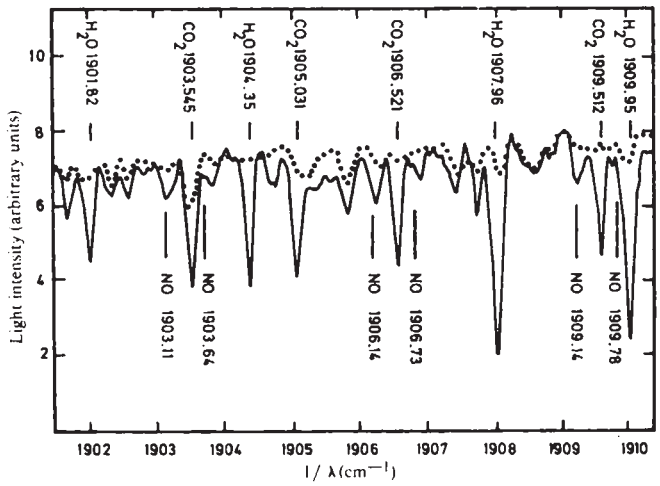

Fig. 1 Intensity of solar radiation recorded at an altitude of 40 km against wavenumber in cm^{-1}. . . . , Spectrum at a solar zenith angle of 86°; ——, spectrum at a zenith angle of 94°. The absorption lines due to stratospheric NO, CO_2 and H_2O are indicated.

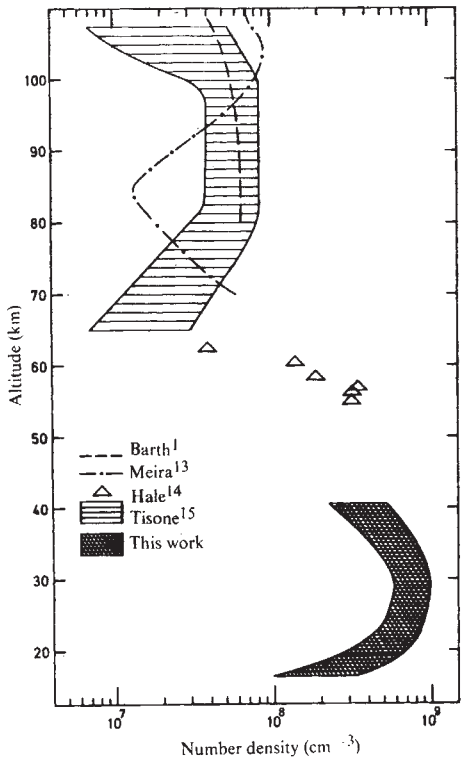

Fig. 2 Experimental values of the number density of nitric oxide against altitude in the chemosphere.

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Radio Detection of Low Energy Electrostatic Sparks

WE have carried out laboratory and outdoor studies to see whether radio observations with a tuned loop aerial can be used to monitor low energy electrostatic sparks and to separate spark discharges from corona-type discharges. Since corona is in general non-incendive in inflammable hydrocarbon air mixtures—but sparks may be incendive if sufficiently energetic—the observation of electromagnetic radiation from a discharge could form a simple technique for monitoring potential ignition hazards.

The types of discharge in which we have been interested are those which could provide a mechanism for the ignition of explosions in large oil tankers. Electrostatically charged mists can be generated in cargo holds by tank cleaning operations with high pressure water jets and by sloshing of water in part ballasted tanks due to ship motion. It is thought that electrostatic sparks may occur when conducting bodies such as slugs of water approach projections into the tank space where there is a concentration of electric field, or when such bodies leave these projections and move to the tank wall[1]. We have simulated this type of localized electrostatic discharge by discharges between a variety of isolated smooth metal electrodes and a plane metal electrode (see Fig. 1).

These bodies were connected to a high voltage supply by a very high impedance lead—around 10^{11} Ω. The large *RC* time constant of this lead, compared with radio frequencies, ensured that only the electrostatic charge on

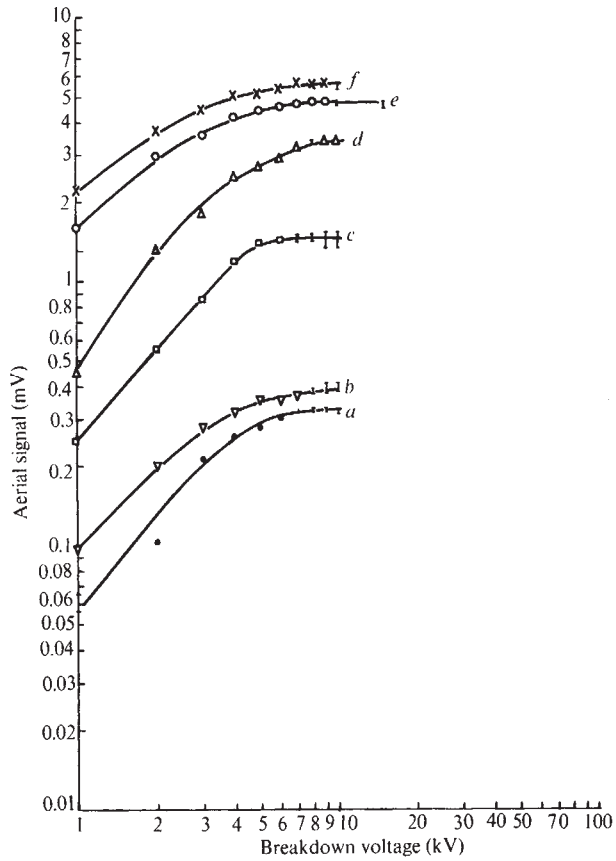

Fig. 1 Variation of 38 MHz aerial signal with breakdown voltage for various isolated bodies. Discharges were between a plane metal electrode and *a*, sphere 19 mm in diameter; *b*, sphere 25 mm in diameter; *c*, sphere 50 mm in diameter; *d*, spherically ended cylinder, 25 mm in diameter, 125 mm long; *e*, sphere 125 mm in diameter; *f*, spherically ended cylinder, 25 mm in diameter, 250 mm long. Spark gap at ground level. Aerial at 10 m range and 2.4 m elevation. Aerial bandwidth about 2 MHz.