AIRBORNE AND BALLOONBORNE SPECTROSCOPY FOR THE STUDY

OF ATMOSPHERIC GAS POLLUTANTS

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ABSTRACT

Infrared absorption spectrometry was recently used from aircraft and balloon for analyzing concentrations of minor constituents of the stratosphere, using the sun as a source, seen tangentially to the earth. Grille spectrometers with a resolution limit close to that of their gratings were used in connection with sun seekers. Experiments were performed on Concorde 001 prototype and on a 300 000 m^3 balloon at 40 km altitude. The vertical profile of NO between 20 and 40 km altitude was determined for the first time. Number density of NO_2 at 16 km was found to be $10 \pm 3\,10^8$ cm^{-3}. Other results obtained in the 1300 cm^{-1} absorption band of HNO_3 are presented.

INTRODUCTION

Eventuality of stratospheric pollution by SST aircraft is a subject of many discussions and controversies. It has been pointed out that active chemical processes take place throughout the stratosphere. They involve species of which the mixing ratio by volume are lower than 10^{-9}. So the accurate knowledge of the stratosphere is of major interest to define the possible role of these elements.

Two experiments were performed during 1973 to detect and measure the concentration profile of some species (NO, NO_2, HNO_3, HCHO, SO_2) within the stratosphere.

They consist in infrared absorption grille spectrometry from a high flying platform using the setting or rising sun as a source. Data are obtained by studying the variations with altitude of the solar spectrum in narrow wavelength intervals. When the spectra are observed at large solar zenith angles (> 90°) the air mass crossed by the solar energy is significantly increased and the method reaches its ultimate sensitivity.

The first spectrometer was flown at 40 km altitude in a 320 kg gondola carried by a 300,000 m^3 balloon from Aire sur l'Adour (S.W. France), May 14, 1973. The second spectrometer was flown on Concorde 001 at 16 km altitude and several experiments were achieved during June and July 1973. These two experiments are quite complementary. In the first one the altitude is high enough to minimize absorption by other constituents such as CO_2 or H_2O ; the different measurements versus solar angles make it possible to get a concentration profile

along altitudes lower than the balloon altitude. The second one allows an accurate measurement of the concentration around the flight altitude. They were not simultaneous but rather close in place and time.

Minimum Detectable Densities

The simplest method of analysis is based on the measurement of the equivalent width of a spectral line, W, which is the integrated absorption over the frequencies

$$W = \int_0^{\infty} A_{\nu}\, d\nu$$

were A_{ν} is the monochromatic absorption by the element.

Under the restriction that this line is suitably isolated, the equivalent width is independent from the slit function and if this slit function is much larger than the linewidth it is possible to write

$$W \simeq \int_{\nu - \Delta\nu}^{\nu + \Delta\nu} A_{\nu}\, d\nu$$

where $\Delta\nu$ is the slit function halfwidth.

Figure 1 indicates absorption line-growth for different total number of molecules and for two altitudes :
- 45 km (Doppler profile)
- 15 km (Lorentz profile).

In fact, the atmospheric infrared line shapes are given by the Voigt profile, which is a convolution of the Lorentz and Doppler shapes. It is possible to see that in the case of the stratosphere the linewidth is approximately 0.005 cm^{-1}, and one must remember that the best balloonborne spectrometer has a slit function width of only about 0.1 cm^{-1}.

So it is not easy to find a suitably isolated line. Many absorption lines from CO_2, N_2O, H_2O, CH_4, etc. may be inside the selected spectral interval and partially or totally mask the absorption to be measured. From this point of view the AFCRL atmospheric lines compilation[1] is of great help in the spectral interval of highest interest.

The equivalent width w for an isolated line is dependent of :

– N, the total number of absorbing molecules through the optical path,

– S(T), the integrated absorption cross-section at temperature T,

– α (p, T), the profile halfwidth at temperature T and pressure p.

In some cases the spectroscopic constants of the molecule have already been measured, and it is possible to compute S(T) and α (p, T).

The inverted profile of concentration versus altitude may then be deduced from the measured equivalent width versus solar zenith angle by computing, with an atmospheric model, the equivalent width versus grazing altitude of solar rays for different pollutant concentration profiles, and comparing it with the measurements.

A linear approximation may be accepted for w if $\dfrac{N\bar{S}}{\bar{\alpha}} < 0,1$, $\bar{S}$, $\bar{\alpha}$ being mean values over the optical path.

Then $\overline{W} = N\bar{S}$, and inside the stratosphere $\bar{S} \sim S_{220°K}$. So the minimum detectable total amount of molecules N_{min} is linearly dependent of the smallest detectable area A. This area is a simple function of two instrumental parameters :

– $\Delta\sigma$, the slit function width,

– R, the signal to noise ratio.

Finally :

$$N_{min} = \frac{1}{S}\frac{\Delta\sigma}{R}.$$

Table I lists the N_{min} values for NO and NO_2 molecules and the minimum detectable concentration in following conditions :

– grazing ray is 20 km altitude,
– the pollutant is uniformly mixed in the atmosphere,
– signal/noise ratio is 500 for NO and 100 for NO_2,
– $\Delta\sigma = 0.1$ cm^{-1} for both cases.

A more elaborate method of analysis consists in computing a synthetic spectrum inside the interval explored by the instrument. This method must be used if the resolution is not sufficient to suitably isolate a characteristic line.

Lastly, if the spectroscopic constants of the molecules are not known the spectra must be analysed only by comparison with laboratory spectra. This is an empirical, temporary method, and we used it only for HNO_3 and SO_2 molecules.

We have remarked on the importance of the instrumental parameters. In classical spectrometry it is well known that resolution and luminosity are absolutely related, while they are dependant upon separate parameters with Fourier spectroscopy and grille spectrometry.

Fourier transform spectrometry is generally the most attractive method. However when operated from flying platforms (aircraft and balloon) with severe requirements for resolution and reliability, many delicate problems have to be solved. On the other hand, a good stability is required for the phenomena under study during the whole interferogram recording time. This condition is difficult to fulfil since solar zenith angle is changing with time. Lastly, what is strictly required to detect each component is the record of only one or a few absorption lines, so the multiplex advantage of Fourier spectroscopy is not in this case of great interest. With a grille spectrometer it is possible to reach the theoretical resolution of the grating without serious instrumental problems.

Instrument Description

The two spectrometers used for airborne and balloonborne experiments are essentially a grille spectrometer associated with a sun tracker. In both cases the optical configuration of the monochromator is the same :

– Littrow mounting with an off-axis parabolic mirror, whose focal length is 600 mm ;

– Jobin-Yvon grating with 59,63 grooves/mm and 65 × 65 mm ruled area ; the incidence is around 65 to 70° ;

– the grille is deposited on a 15 × 15 mm calcium fluoride window and the minimum step is 0.2 mm ; so the resolution is very close to the theoretical limit and the half-width instrumental profile is about 0.1 cm^{-1} ;

– chopping is ensured by vibration of the collimating mirror ; the vibration frequency is 180 Hz, which is the resonance frequency of the mechanical mounting ; a servo system including this mechanical mounting keeps the vibration amplitude stabilized ; in this way the useful signal is 360 Hz-chopped ;

– the selected spectral range is scanned continuously ; the scanning speed is about one spectral element per second ;

– spectral calibration is performed with absorption lines of CO_2 and H_2O ; interpolation is made possible by simultaneous recording of the spectrum and position grating marks ;

– an optical auxiliary mounting is built to control any possible deformation of the mechanical system.

The other parts of the apparatus (sun tracker, amplifiers, optical photometric platforms) are different in the two experiments.

Concorde Instrumentation

The optical configuration is presented fig. 2. One of the aircraft scuttles is a 140 mm diameter calcium fluoride window. The image of the sun is obtained on the grille by means of lenses L_1 and L_2. The sun tracker P allows the mirror M to maintain the solar radiation on the spectrometer axis. At the output the image of the sun is focused on the detector area.

The detectors are :
– liquid nitrogen cooled SAT InSb photo-element for spectral range < 5,3 μm,

– for larger wavelengths, liquid nitrogen cooled Mullard HgTe-CdTe photoelement.

The total instrument is kept within a nitrogen atmosphere in order to avoid any parasitic absorption.

The flight trajectory is computed so as to maintain the sun direction approximately in the direction of the instrument.

The heliostat accuracy is 3' and the field of view is 3°. Measurements are made while the sun zenith angle is varying from 80° to 92°. Nine experiments have been performed on board the SST prototype Concorde 001, 6th June and during the 9-26 July period. The flight altitude was around 16 km. Seven spectra were obtained at sunset between the north-west of Spain and the west of Cornwall (fig. 3) ; two spectra were obtained at sunrise between the west of Cornwall and the Bay of Biscay.

Balloonborne Instrumentation (fig. 4)

The telescope is of Cassegrain type. Its diameter is 300 mm, the focal length is 4 meters. It conjugates the sun and the grille. The sun rays are reflected by the grille inside the monochromator.

To maintain the instrumental performance during the whole flight it is necessary to balance the mechanical deformations ; so the whole optical path inside the monochromator is servo controlled. Two annex grilles are used, alongside the main grille, to obtain this result. The first one is illuminated by an incandescence filament. The rays path is close to that of the sun rays. The flux is received by the second grille and focused on a germanium photodiode detector. The mirror vibrating at frequency f induces a photodiode signal with frequencies f and 2f. The f component is a characteristic of some irregularity : this component, called "error signal", constitutes the information to be sent to the servo system, which maintains the instrument properly tuned. Synoptic diagram of the total chain is shown figure 5.

The servo system consists in :

- a preamplifier,
- a synchronous demodulator (the reference signal comes from the excitation circuit oscillator of the parabolic mirror),
- a low frequency filter,
- a logical comparator which drives a motor bound to the mechanical mounting of the parabolic mirror.

The logical comparator turns the error signal into a logical information in order to act only in discontinuous mode :

- as long as the error is less than a fixed limit, the role of the servo system is null ;
- as soon as the error reaches the limit the servo system acts and the motor rotates.

Two different detectors can be used :

- photovoltaïc indium antimonide with a transformer,
- gold doped germanium with a bias of 48 volts.

The signal from the detector is amplified by a preamplifier Barnes DP7 with a gain of 5000. This preamplifier has a very good stability over a very wide temperature range ; it is mounted as close as possible to the detector.

Synoptic of the electronic chain is shown figure 6.

In the electronic box there is first a switch, disconnecting the signal of the preamplifier from the electronics during about 15 sec at one of the inversions of the grating drive motor. At that moment calibrating signals are fed to the electronic chain. There are signals at different levels coming from the excitation circuit oscillator of the parabolic mirror, and shifted in the correct phase by a phase shifter. There are consequently a zero and three signals calibrating the three channels of the electronics.

In the normal position of the switch the signal from the preamplifier is fed to a bandpass filter with a centerfrequency of 360 Hz (twice the oscillating frequency of the parabolic mirror). The bandwith is 30 Hz. It is an active filter with separate band and frequency controls.

First, there are three non inverting amplifiers with gains of 3, 9 and 27 respectively. The following circuit is the synchronous detection. The signal is rectified with a phase depending on the reference signal coming through a phase shift circuit. Before the flight, the phase relation between the reference signal and the incoming signal is matched in order to have a maximum positive d.c. output. This reference signal is provided from the vibration of the mirror, with a frequency doubler.

After the demodulator, a low frequency filter with a cutting frequency of 3 Hz and a voltage limiter to 2 volts delivers a low impedance signal to the telemetry. Other parameters are also measured during the flight. The outside pressure is measured with a CEC pressure gauge. This information is multiplexed with two temperature measurements (one on the spectrometer and one in the electronics box) in the low speed commutator and sent to the telemetry.

The sun pointing system used for this experiment is the "Astrolab" from former Compagnie des Compteurs, already used for other experiments and described before.

The principle of pointing can be summed up as follow. The gondola is uncoupled on the three axes. In a first mode, the gondola is oriented along a fixed axis referred to the earth. The sensors are a gyroscope and a magnetometer. The couples are provided by inertia wheels. At the end of the acquisition mode a rendez-vous is realized with the sun. At the moment of switching from acquisition to pointing mode by a timer, the sun has to be in the field of the sun sensors. From that moment the pointing information is given by the sun sensors.

RESULTS

Only nitric oxide was studied with both balloon (from 1900 to 1915 cm^{-1}) and Concorde spectrometers (from 1885 to 1915 cm^{-1}) ; absorption lines of CO_2 and H_2O were also identified ; so a profile can be deduced for these molecules from 15 km to 40 km by division of the atmosphere in successive layers of three kilometers thickness. Other molecules (nitrogen dioxide, sulfur dioxide, nitric acid, etc.) were only studied from aircraft ; for these species, only the number density at the flight altitude may be defined.

Nitric oxide

The analysis is made chiefly with the 1909.14 cm^{-1} and 1914.99 cm^{-1} lines (fig. 7). Although the first is partially mixed with CO_2 1909.21 cm^{-1} line, corrections were made and simultaneous results with the two

lines are correct, within the limit of accuracy. The integrated line absorption cross sections for 220°K are listed in Table II[2].

The number density of NO versus altitude was inferred from the equivalent width of the lines and are presented figure 8 with other experimental data. The limits of error correspond to the maximum scattering of the original data points.

These results are only obtained with the linear approximation.

Computed by the more elaborate method, these values will be probably slightly increased.

An example of spectra obtained on Concorde at 1890 cm^{-1} is presented figure 9. We can see that the spectral element width is 0.1 cm^{-1}. The signal/noise ratio is better than 100 with the Concorde spectrometer and 500 with the balloon spectrometer.

We see on figure 10 that the integrated amount of NO measured in balloon along the optical path for a grazing ray altitude of 16 km. is $8 \pm 2 \, 10^{16}$ moles cm^{-2}. The measured value from Concorde at solar zenith angle of 90° is 6 ± 2.10^{16}. This value is larger than expected from balloon measurements. This fact may be explained by the photochemistry of NO, the path from the sun to Concorde being more illuminated with UV than the path between the balloon and Concorde. Analysis of the 1909,512 and 1912,519 cm^{-1} lines of CO_2 yields to a constant mixing ratio of $3\pm1 \, 10^{-4}$ in agreement with the generally accepted value.

Nitrogen dioxide

The spectra were taken from 1603 cm^{-1} to 1617 cm^{-1}. The integrated line absorption cross sections for 220°K are listed in Table III[3]. Figure 11 is an example of result. The number density deduced at 16 km is $10 \pm 3 \, 10^{8}$ cm^{-3}.

Nitric acid

Spectra were taken in the 1300 cm^{-1} region. The empirical method was used, comparing the amplitude of lines with laboratory spectra. The analysis is made with the Q Branch. An exemple of result is presented figure 12. Number density is not still available at the state of the analysis.

CONCLUSION

Identification and measurements on gases need high resolution spectra on a few specific lines for each component. The results presented here clearly show the ability of the spectral method used to solve the specific problem of remote detection of minor gaseous components in the stratosphere :

– high reliability for airborne experiments ;

– high luminosity due to independence of parameters governing resolution and available energy ;

– each scanned spectral line gives an information by itself so that the phenomena under study have only to remain steady during a very short interval of time.

Many other spectra obtained with Concorde Instrumentation have yet to be analysed, and there remains a lot of work to do.

The results obtained with NO and NO_2 show that simultaneous measurements on these species are of great interest for the knowledge of photochemical processes.

Lastly any gain on spectral resolution will allow improvement on the minimum detectable concentration.

Further experiments are planned for next year with improved instrumentation.

REFERENCES

[1] Mac Clatchey et al. - Infrared Compilation (1973).

[2] S. Cieslik and C. Muller - Aeronomica Acta A nr 114 (1973).

[3] C.A. Barth - J. Geophys. Res. 69 3301 (1964).

[4] L.G. Meira Jr. - J. Geophys. Res. 76, 202 (1971).

[5] L.C. Hale in Mc Elroy - Proceedings of the survey. Conf. DOT- T SC OST 72-13. Cambridge, Ma, 1972.
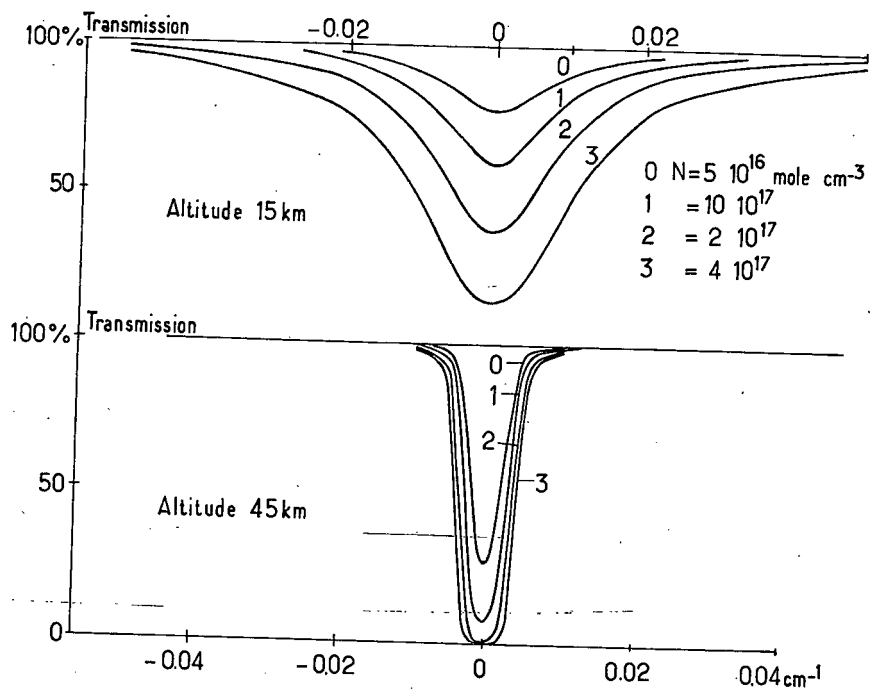
[6] C. Muller (private communication).

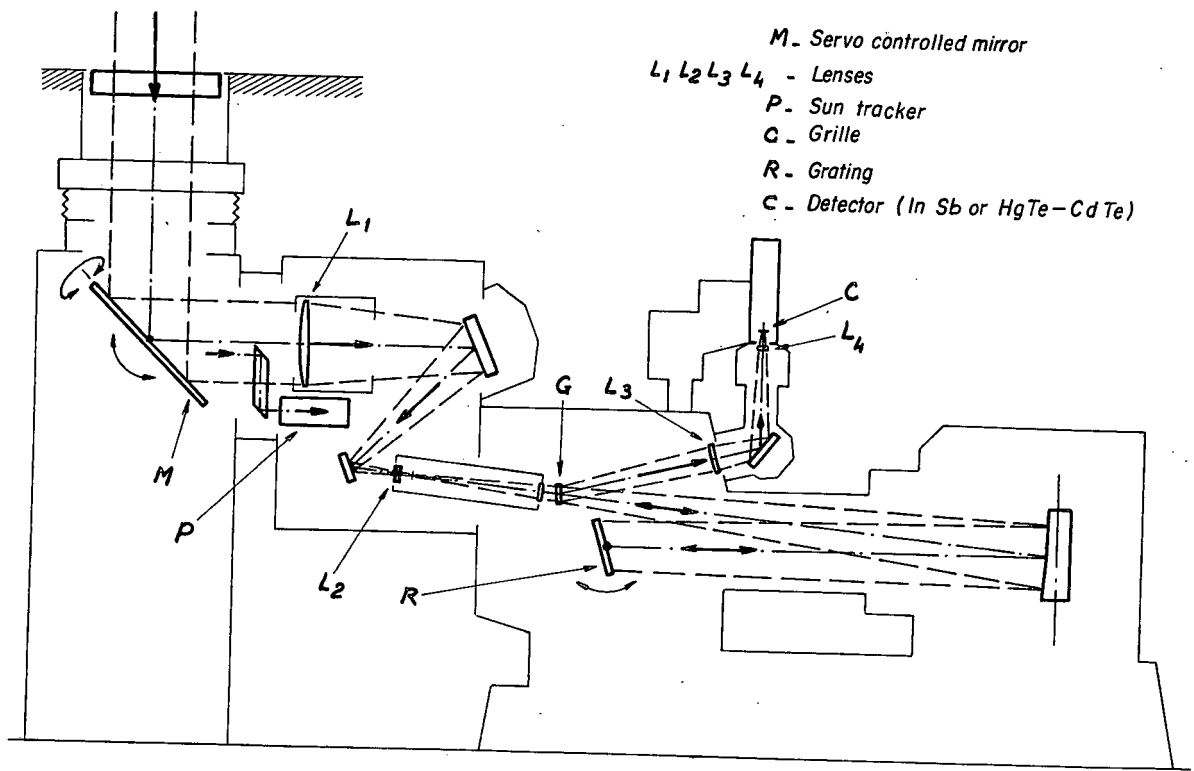Fig. 1 - *Absorption line growth with Doppler and Lorentz profiles for various optical thicknesses.*

M - Servo controlled mirror

L_1 L_2 L_3 L_4 - Lenses

P - Sun tracker

G - Grille

R - Grating

C - Detector (In Sb or HgTe−CdTe)

Fig. 2 - *Optical diagram for the Concorde spectrometer.*
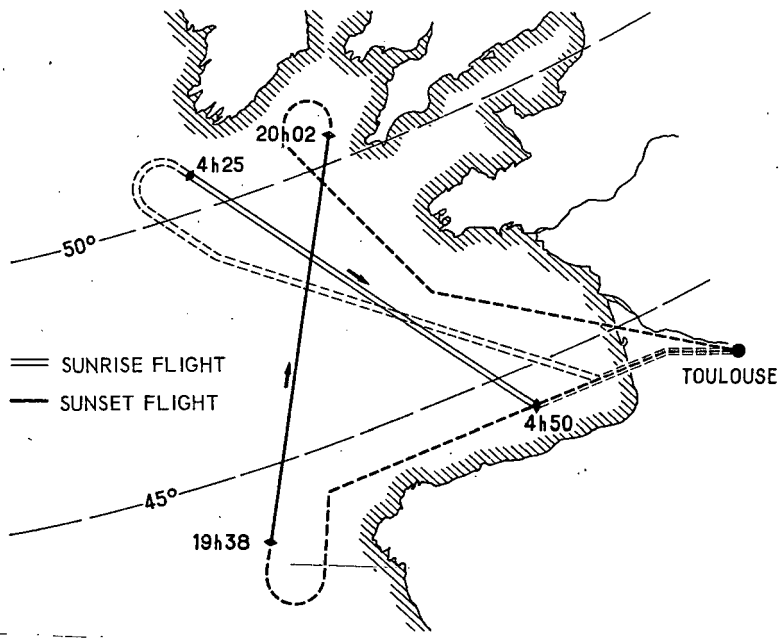
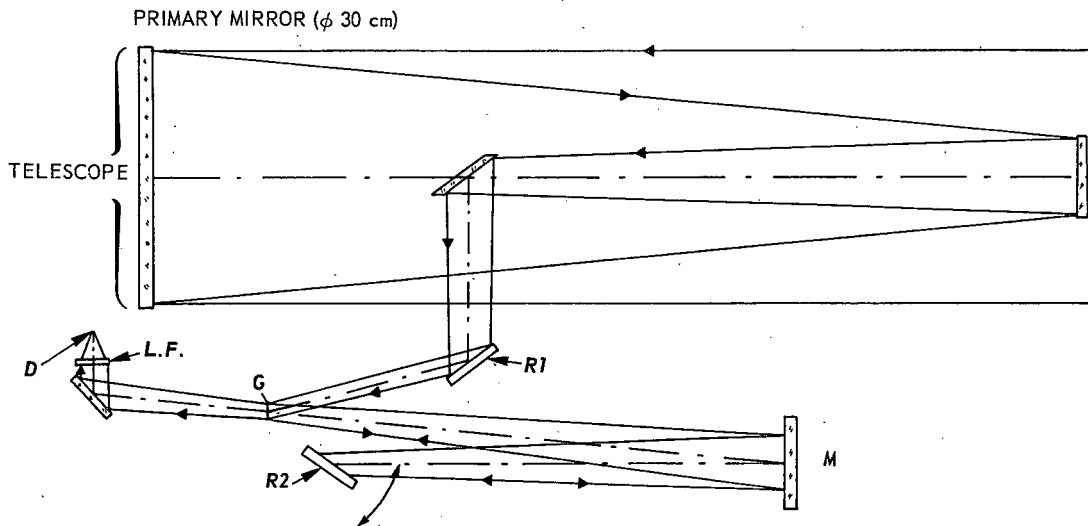Fig. 3 - Concorde 001 environmental flights. June-July 1973.

PRIMARY MIRROR (ϕ 30 cm)

TELESCOPE

D

L.F.

G

R1

R2

M

Fig. 4 - Optical diagram for the balloonborne spectrometer.

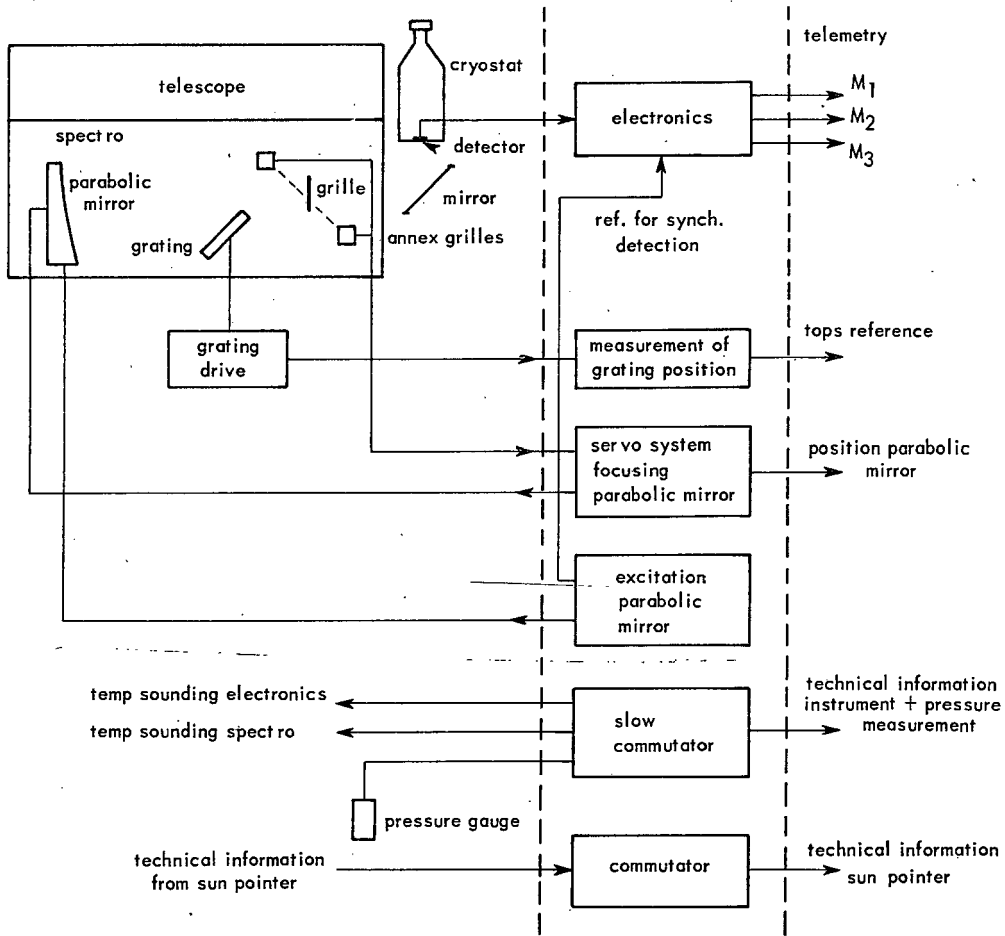| D - InSb detector	R1 - pre-dispersing grating
L.F. Lens + filter	R2 - Chief grating
G - Grille	M - Off axis mirror (F = 600 mm)

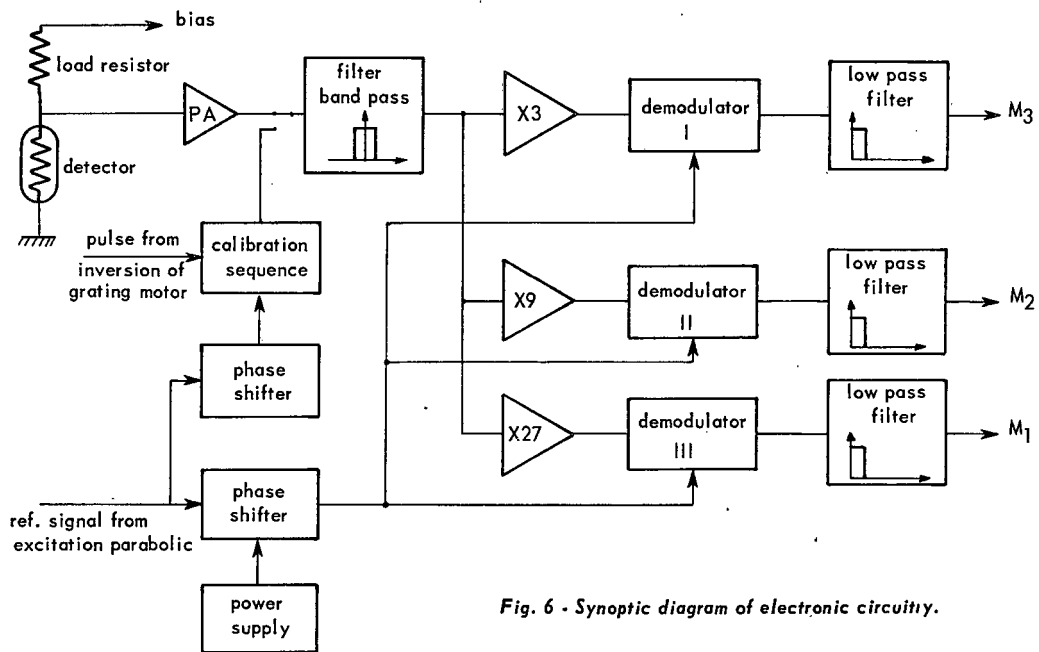**Fig. 5 - Synoptic diagram of the total chain.**

Fig. 6 - Synoptic diagram of electronic circuitry.

45

Fig. 7 - NO stratospheric absorption spectrum.
Balloonborne experiment (May 14, 1973).

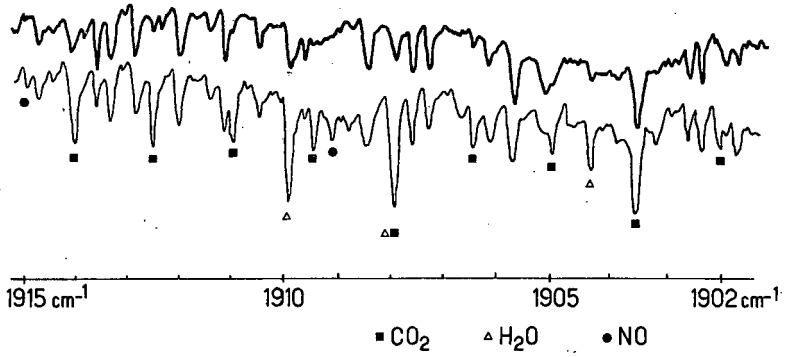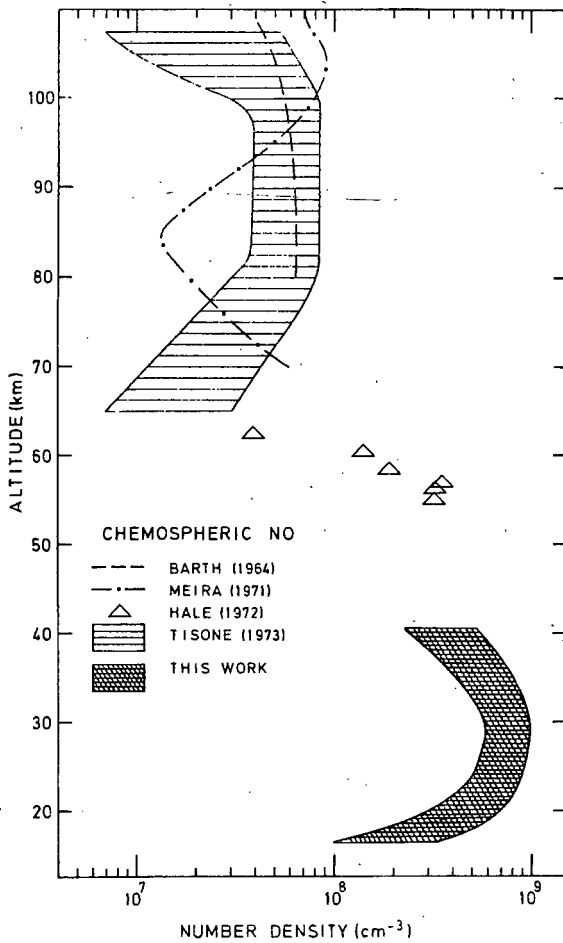Solar zenith angle $88°$ $93°$

Fig. 8 - NO number density versus altitude.
Experimental values of the number density
of nitric oxide versus altitude in the
chemosphere. The results published by
Barth[3], Meira[4], Hale and Tisone[5]
are shown, together with those presented
here for the stratosphere.

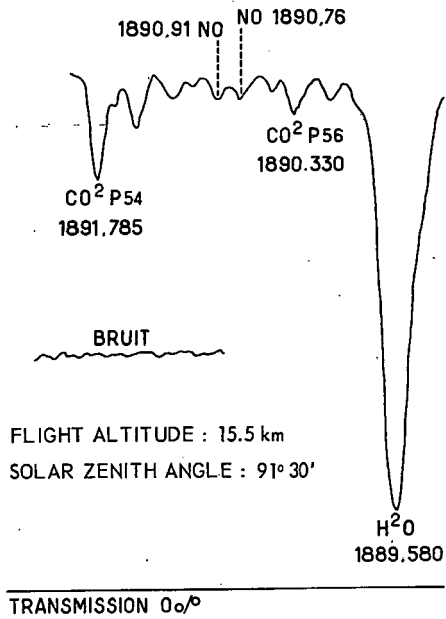1915 cm⁻¹   1910   1905   1902 cm⁻¹

■ CO_2 △ H_2O ● NO

0% Transmission

ALTITUDE (km)

100
90
80
70
60
50
40
30
20

CHEMOSPHERIC NO
--- BARTH (1964)
-·- MEIRA (1971)
△ HALE (1972)
▤ TISONE (1973)
▨ THIS WORK

10^7 10^8 10^9
NUMBER DENSITY (cm⁻³)

1890,91 NO   NO 1890,76

CO^2 P56
1890.330

CO^2 P54
1891,785

BRUIT

FLIGHT ALTITUDE : 15.5 km
SOLAR ZENITH ANGLE : 91° 30'

H^2O
1889,580

TRANSMISSION 0o/°

Fig. 9 - NO stratospheric absorption spectrum.
Concorde 001 experiments, July 13, 1973, sunrise.

$(8 \pm 2).10^{16}$ mol. cm⁻²

$(6 \pm 2) 10^{16}$ mol. cm⁻²

SUN

40 km
B

15,5 km
A

Fig. 10 - Integrated amount of NO
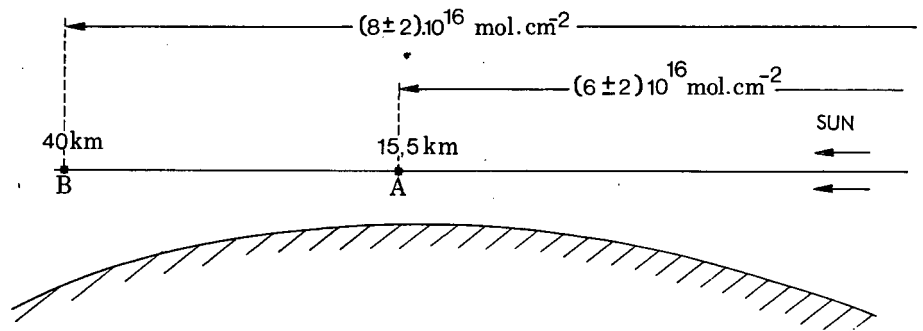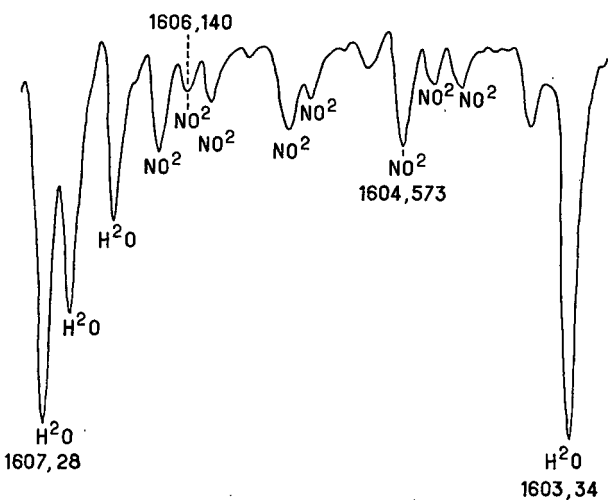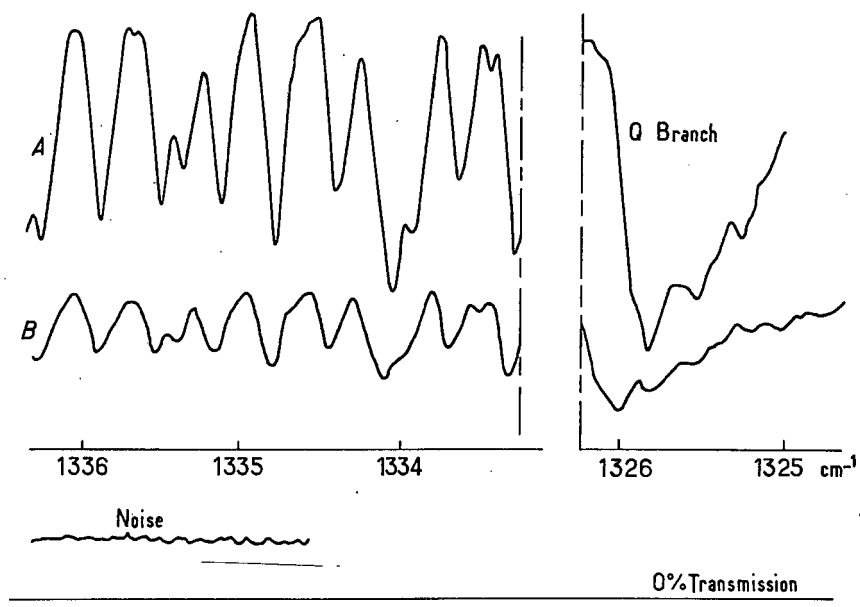measured along the optical
path from aircraft A and
from balloon B.

Fig. 12 - HNO₃ stratospheric absorption spectrum.
Concorde 001 experiments.
Flight altitude : 15.5 km
Solar zenith angle 90°20' (A)
and 86°50' (B)

Q Branch

1336   1335   1334   1326   1325 cm⁻¹

Noise

0% Transmission

1606,140

NO²
NO²   NO²
NO²   NO²
H²O
NO²   NO²
H²O
NO²
1604,573
H²O
1607,28
H²O
1603,34

FLIGHT ALTITUDE : 15.5 km
SOLAR ZENITH ANGLE : 84° 49'

TRANSMISSION 0₀/°

Fig. 11 - NO₂ stratospheric absorption spectrum.
Concorde 001 experiments,
July 17, 1973, sunset.

Table I

Molecule	Minimum detectable number of molecules	Minimum detectable concentration (constant mixing ratio)
NO	$2 \ 10^{15}$ mole cm⁻²	$2.5 \quad 10^{-11}$
NO₂	$1 \ 10^{15}$ mole cm⁻²	$1.3 \quad 10^{-11}$

Table II

σ cm⁻¹	S cm mole⁻¹ 220° K
1890,71	$1.31 \quad 10^{-19}$
1909,14	$1.23 \quad 10^{-19}$
1914.99	$9.09 \quad 10^{-20}$

Table III

σ cm⁻¹	S cm mole⁻¹ 220° K
1604.154	$0.544 \quad 10^{-18}$
1604.350	$0.344 \quad 10^{-18}$
1606.140	$0.316 \quad 10^{-18}$