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# ATMOSPHERIC NITRIC ACID AND CHLOROFLUOROMETHANE 11 FROM INTERFEROMETRIC SPECTRA OBTAINED AT THE OBSERVATOIRE DU PIC DU MIDI

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KEY WORDS :

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## Acide nitrique et chlorofluorométhane 11 atmosphériques à partir de spectres interférométriques obtenus à l'Observatoire du Pic du Midi

RÉSUMÉ : Des spectres d'absorption et d'émission obtenus à l'Observatoire du Pic du Midi dans les Pyrénées françaises permettent de déduire le contenu total d'acide nitrique et conduisent à une valeur de  $1,2 \times 10^{10}$  molécules/cm<sup>3</sup> à l'altitude de 22 km. CFCl<sub>3</sub> est observé en mélange dans la troposphère à la valeur de 148 ppt.

Aucune évidence de HNO<sub>4</sub>, HNO<sub>2</sub> ou NH<sub>3</sub> n'a pu être observée. Les difficultés présentées par l'observation de H<sub>2</sub>O<sub>2</sub> et de l'obtention de valeurs précises de O<sub>3</sub> et de CF<sub>2</sub>Cl<sub>2</sub> sont également discutées.

SUMMARY : Absorption and emission spectra obtained at the Observatoire du Pic du Midi in the French Pyrenees permit to deduce the nitric acid integrated column and lead to a value of  $1.2 \times 10^{10}$  mol./cm<sup>3</sup> at the altitude of 22 km. CFCl<sub>3</sub> is found to be mixed in the troposphere with a value of 148 ppt.

No evidence of HNO<sub>4</sub>, HNO<sub>2</sub> or NH<sub>3</sub> was observed. The difficulties in observing H<sub>2</sub>O<sub>2</sub> and in obtaining accurate values for O<sub>3</sub> and CF<sub>2</sub>Cl<sub>2</sub> are discussed.

## INTRODUCTION

Mountain observatories, situated far from industrial centers, are ideal stations for the monitoring of the global atmospheric content. The *Observatoire du Pic du Midi* is situated in the French Pyrenees, at an altitude of 2 887 m, at a latitude of 42° 56' N and a longitude of 0° 09' E. The reported observations were made on April 11 and 12, 1980 at sunrise and sunset for the first day and at sunrise only for the second one. The solar absorption and telluric emission spectra were recorded between 750 and 1 300 cm<sup>-1</sup>. Two constituents of interest for atmospheric chemistry : nitric acid and CFCl<sub>3</sub> can be determined with reasonable accuracy from the spectra using their bands at 879 cm<sup>-1</sup> and 847 cm<sup>-1</sup>. Important absorptions by ozone and CF<sub>2</sub>Cl<sub>2</sub> are also observed but no accurate values could be determined. The spectra were searched for other important species, sometime introduced in the theoretical models, like HNO<sub>4</sub>, HNO<sub>2</sub>, NH<sub>3</sub> but none of those could be observed. H<sub>2</sub>O<sub>2</sub> presents also some spectral features in the spectral interval

covered but these are probably too weak and too broad to be observable.

## INSTRUMENTATION

A modified Block Engineering model 700 interferometer was mounted on a platform to observe the rising and setting Sun at about 1 degree below the horizon. This condition is dependent on the season of observation due to the relative configuration of the mountains, observatory buildings and observation platform. A photograph of the instrument on its observation platform is shown on *figure 1*.

A manually operated pointing device directs the 2 degrees wide field of view to the Sun direction. A spectral resolution of 0.125 cm<sup>-1</sup> was programmed which is the highest possible for this instrument. The retardation rate being 5 cm/sec, a complete interferogram was generated in 1.6 sec. An associated Digilab data system, located inside the Observatory buildings, some 50 m away, commanded the instrument. Upon operation request, data were sampled, digitized and



FIG. 1. — Photograph of the instrument on its observation platform without its environmental protection.

transferred to disk files. In the case of calibration and emission spectra, the interferograms were coadded. The system uses a 32 K words memory and the maximum sampling rate is of 20 kHz. This undersampling necessitates to reduce the optical 3-14  $\mu\text{m}$  range of the instrument to 5.12-14  $\mu\text{m}$  by including a filter in the optical path.

#### DATA REDUCTION

During the observation period, the interferograms are acquired on disk files in the Digilab Data system and are transferred to a magnetic tape between the acquisition cycles. Each time, an absorption has been preceded or followed by an emission obtained at the same zenith angle; emission data are also obtained before sunrise and after sunset at an elevation of 5 degrees. Absorption spectra are calculated using a standard *Cooley-Tukey FFT* program by transforming the difference between an absorption interferogram and its associated background emission interferogram. This procedure has the advantage of giving pure absorption spectra and reproduces well the zero level as the common level of the saturating lines. Spectra of a cold temperature reference have also been taken from time to time in order to have a reference for emission spectra, these are obtained using a black aluminium tank filled with liquid nitrogen, the unisolated face gives the reference. The extremely low humidity observed at the *Pic du Midi* prevented the icing of the

plate. The emission spectra have been reduced by making the difference between the reference spectrum and the transformed emission data.

#### OBSERVATIONS

Interpretable spectra were obtained on April 11 and April 12 1980. Only the first day of observation permitted to record both sunset and sunrise. The meteorological situation on the morning of the 11 is shown on *figure 2*. The high pressure center on the European continent moved slowly to the East during the observations which led to unstable maritime currents, the air mass surrounding the *Pic du Midi* came, mainly from the Atlantic ocean and the industrial cities like Toulouse were down the wind.

A typical absorption spectrum is given in *figure 3* showing the data which will be used in the present quantitative analysis. *Table 1* lists the zenith angles and parameters of the spectra studied for  $\text{HNO}_3$  and  $\text{CFCl}_3$ . The region above 1 000  $\text{cm}^{-1}$ , which has not been quantitatively studied, is characterized by the very strong  $\nu_3$  band of ozone. Features of the weaker  $\nu_1$  band near 1 100  $\text{cm}^{-1}$  could be used for accurate interpretation but the difficulties in defining the continuum level of  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$  lines in this region and the overlapping of ozone lines themselves require a specific interpretation program.

Nitric acid is the main loss of stratospheric NO and  $\text{NO}_2$ , once formed, it is washed out by clouds

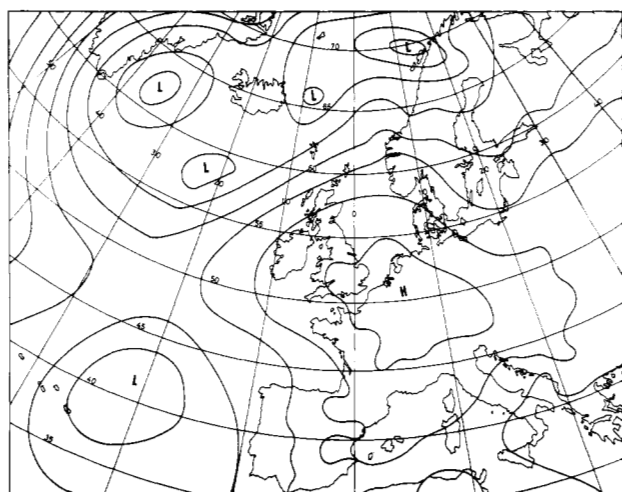


Fig. 2. — Synoptic map of the meteorological situation at 6 TU on April 11. Isobars are separated by 5 mb intervals, the line next to the high pressure center on continental Europe corresponding to 1 025 mb.

below the tropopause as outlined by Brasseur and Nicolet [1] in 1973. It has been first reported in absorption spectra by Murcra *et al.* [2] in 1968 and Murcra *et al.* [3] in 1973 were also able to deduce a vertical

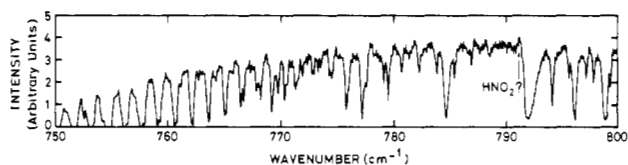


Fig. 3(a). — Absorption spectrum at 5.3° of solar elevation April 11, 1980, 750-800 cm<sup>-1</sup> region.

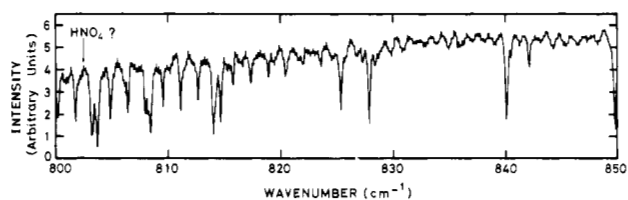


Fig. 3(b). — Absorption spectrum at 5.3° of solar elevation April 11-1980, 800-850 cm<sup>-1</sup>.

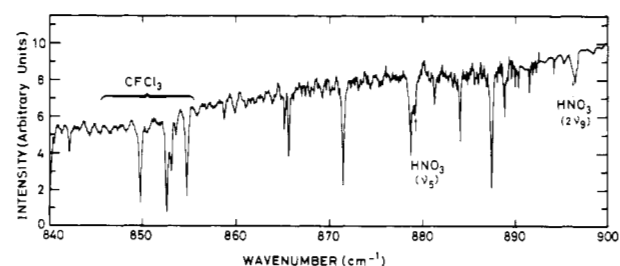


Fig. 3(c). — Absorption spectrum at 5.3° of solar elevation April 11, 1980, 840-900 cm<sup>-1</sup> region.

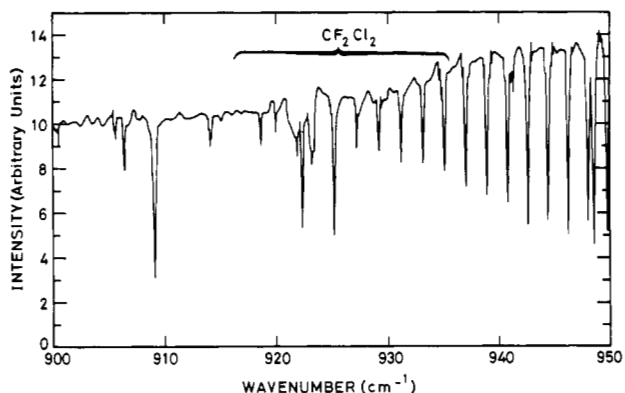


Fig. 3(d). — Absorption spectrum at 5.3° of solar elevation April 11, 1980, 900-950 cm<sup>-1</sup> region.

TABLE I

Observational data of the absorption spectra used for the determination of CFCl<sub>3</sub> and HNO<sub>3</sub> on April 11, 1980.

Time (TU)	Solar height (decimal degrees)	Swider [8] factor	Equivalent widths CFCl <sub>3</sub> (cm <sup>-1</sup> )	HNO <sub>3</sub> (cm <sup>-1</sup> )
5 : 31 : 30	0.6	28.9	3.56	
5 : 37 : 40	1.6	21.2	2.36	0.031
5 : 45 : 00	3.5	13.4	1.75	0.024
5 : 55 : 00	4.7	10.7	(*)	0.024
6 : 10 : 00	7.3	7.4	(*)	0.017
17 : 43 : 15	9.5	5.8	(*)	0.021
18 : 00 : 00	6.5	8.2	(*)	0.013

(\*) Absorption too weak to be measured with reasonable accuracy.

distribution from emission spectra obtained during a balloon ascent, later, sampling techniques by Lazrus and Gandrud [4] gave also HNO<sub>3</sub> values. Since then, several groups have published nitric acid distributions and these values will be compared with the ones be deduced from our spectra.

Nitric acid is observed in its overlapping ν<sub>5</sub> and 2 ν<sub>9</sub> bands. The main features are the two Q branches at 879 and 896 cm<sup>-1</sup>. However, the 896 cm<sup>-1</sup> feature is wider and less intense than the 879 cm<sup>-1</sup> line. The size of the contamination by CO<sub>2</sub> and H<sub>2</sub>O on the 896 cm<sup>-1</sup> branch is difficult to evaluate, on the opposite, the water vapor line beside the 879 cm<sup>-1</sup> feature is easier to separate. Qualitatively, no nitric acid was observed nor in the spectra below the horizon nor in the emission spectra. HNO<sub>3</sub> is thus negligible below the observation altitude and is situated at temperatures much lower than the ground level 260-270 K observed on April 11. This confirms that the bulk of nitric acid is in the stratosphere.

From a quantitative point of view, the 0.12 cm<sup>-1</sup> resolution is too good to use the band model parameters by Goldman *et al.* [5], a calibrated laboratory spectrum of nitric acid was obtained with the same instrument in conditions close to the atmospheric conditions, except for the temperature (figure 4).

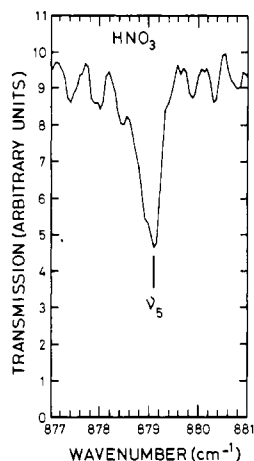


FIG. 4. — Laboratory nitric acid spectrum of the  $\nu_5$  Q branch for a 13 cm cell and a nitric acid pressure of 4.54 mbar.

The equivalent width measurement of the  $\nu_5$  Q branch leads to a line strength of  $1.15 \times 10^{-19} \text{ cm}^{-1}/\text{molecule}$ . This value is compatible with the integrated value given by Goldman *et al.* [5] for  $880 \text{ cm}^{-1}$ . The molecular line parameters of the  $\nu_5$  band have been determined by Dana [6]. These values were used by Lado-Bordowsky [7] and Dana and Lado-Bordowsky [8] to generate portions of synthetic spectra outside the Q branch.

The case of our observations, the absorption is in the linear part of the curve of growth which permit to obtain direct values of the column density. The  $\nu_5$  Q branch should present the supplementary advantage of being quite insensitive to temperature due to the overlapping of a large number of lines of different  $J$  numbers (\*). Table 1 gives the values of the observed  $\nu_5$  intensities as a function of the zenith angle and the air-mass from Swider [9]. No diurnal variation seems to be significant and the average value of the vertical column density is  $(1.8 \pm 0.4) \times 10^{16} \text{ molecule cm}^{-2}$ . This value is translated in a  $\text{HNO}_3$  vertical distribution by assuming a nitric profile compatible with the reviews of Ackerman [10] in 1975 and Hudson and Reed [11] in 1979. The maximum deduced value of the nitric acid concentration is  $1.2 \times 10^{10} \text{ molecule/cm}^3$  at 22 km (figure 5). These two values permit to compare with other results; Lado-Bordowsky [7], using a similar technique from Montlouis has obtained an average value of  $2.7 \times 10^{16}$  for the column density. The values obtained in [7] during several observation campaigns from Montlouis show significant day to day variations. If we use the stratospheric results, our value is lower by a factor of 6 from the upper limit of the Fontanella *et al.* [12] distribution, it is higher by a factor of 8 from the lowest value in the sampling results of Lazrus and Gandrud [4]. Other results are reviewed on figure 6.

Another interesting point of comparison are the latitudinal column density above 18 km obtained by

(\*) This hypothesis has to be checked by laboratory and theoretical studies taking into account the fact that lines of the  $2\nu_9$  band could overlap the  $\nu_5$  Q branch.

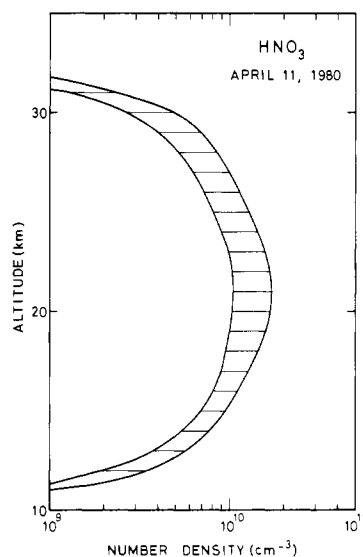


FIG. 5. — Vertical distribution of nitric acid, the shape has been deduced from the reviews [9] and [10].

Murcay *et al.* [13], our values agree with their  $60^\circ \text{ N}$  value but are twice higher than their average  $30^\circ \text{ N}$ . The data obtained by these authors present variations of a factor of 3 at the same location. In our own data, the two spectra obtained on April 12, yield values consistently 30% above the April 11 result. The latitudinal data obtained by Girard *et al.* [14] above the 12 km altitude is higher than the Murcay [13] data, showing a non negligible contribution of the stratosphere between 12 and 18 km to the nitric acid burden.

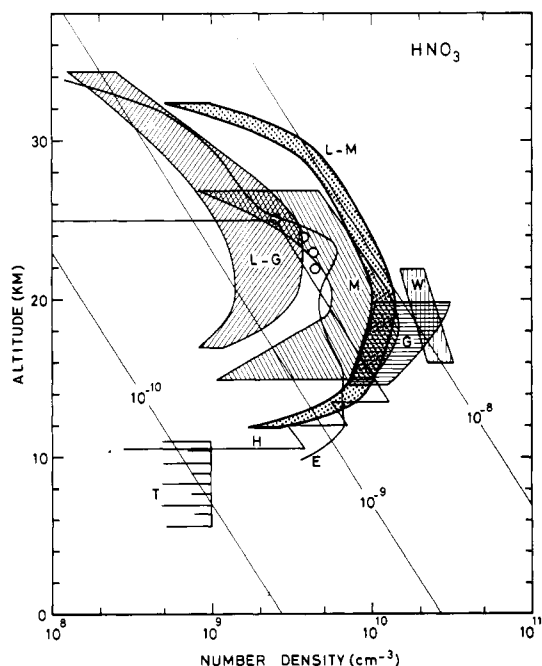


FIG. 6. — Observed nitric acid : L. M. : this work, E : Evans *et al.* [27], G : Fontanella *et al.* [12], L. G. : Lazrus and Gandrud [4], H : Harries *et al.* [28], W : Fried and Weinman [29], M : Murcay *et al.* [3], T and the circles o : Ackerman [9].

This natural variability of nitric acid is thus confirmed and has not yet received a satisfactory explanation from a theoretical point of view due, perhaps, to the difficulty of modelling the transport processes.

Chlorofluoromethane 11 ( $\text{CFCl}_3$ ) possesses very sharp absorption bands near  $850 \text{ cm}^{-1}$ , these appear well in our data, including the spectra at zenith angles higher than  $90^\circ$  and in emission spectra as well, confirming that  $\text{CFCl}_3$  is present in the troposphere. Figure 7 shows a typical portion of an emission spectrum in the  $850 \text{ cm}^{-1}$  region.

It was assumed, in agreement with the models, that  $\text{CFCl}_3$  is mixed in the troposphere and then rapidly decreasing in the stratosphere where it is photodissociated (Hudson and Reed) [11].

The  $\text{CFCl}_3$  equivalent width on each absorption spectrum has been measured, as for  $\text{HNO}_3$ , and the absorption being linear, the band model parameters of Goldman *et al.* [15] could directly be used to retrieve column densities. The question of molecular data for  $\text{CFCl}_3$  has been recently reviewed by Nanes *et al.* [16] and Silvaggio *et al.* [17]. There is a good agreement between all laboratory studies of  $\text{CFCl}_3$  and also, due to the extreme overlapping of lines, it will be difficult to perform a line by line study of the spectrum, even the isotopes being separated and with an infinite resolution instrument. Figure 8 shows the technique used to separate  $\text{CFCl}_3$  from its contaminants. Table 1 gives the  $\text{CFCl}_3$  results which, averaged, give a volume mixing ratio of  $1.48 \pm 0.12 \times 10^{-10}$ . This value

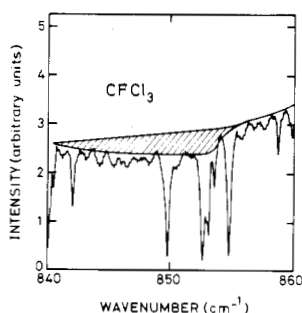


FIG. 7. — Emission spectrum obtained April 11, 1980 at an elevation of  $0.5^\circ$  and showing an intense  $\text{CFCl}_3$  emission.

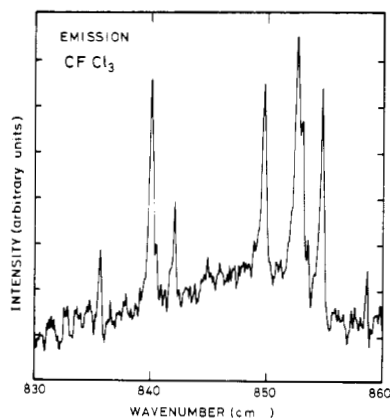


FIG. 8. — Absorption spectrum obtained April 11, 1980 at an elevation of  $1.6^\circ$  outlining the technique used to obtain the equivalent widths of  $\text{CFCl}_3$  in the  $850 \text{ cm}^{-1}$  region.

corresponds to the baseline value compiled by Hudson and Reed [11] mainly from sampling techniques (Rasmussen [18], Lovelock [19]). The only conclusion that could be drawn is that since 1976, there has neither been a spectacular increase of the  $\text{CFCl}_3$  concentration nor a measurable drop despite the decision of several countries to ban its use in consumer products.

Chlorofluoromethane 12 ( $\text{CF}_2\text{Cl}_2$ ) is also detectable on the spectra in conditions similar to  $\text{CFCl}_3$  but contamination by  $\text{CO}_2$  and  $\text{H}_2\text{O}$  occurs which, associated with the broadness of the overlapping bands do not permit an accurate interpretation of the spectra, the determination of the zero absorption line, in this case, leads to errors of a factor 2 which would lead to a meaningless determination compared to the very accurate sampling values.

$\text{HNO}_4$  could not be observed at its main absorption at  $802.7 \text{ cm}^{-1}$ ; using the cross sections measured by Graham *et al.* [20], an upper limit for  $\text{HNO}_4$  of 20 times less than  $\text{HNO}_3$  could be deduced. This contradicts the results of some theoretical models (for example, Jesson *et al.* [21]). The same authors [22], after new results in the photochemistry of  $\text{HNO}_3$ ,  $\text{OH}$  and  $\text{HNO}_4$  agree that the  $\text{HNO}_4$  concentrations should be lower than expected. Similarly, none of the strong  $\text{HNO}_2$   $Q$  branches at  $853$  and  $791 \text{ cm}^{-1}$  could be observed. Despite the fact that ammonia has been observed at the altitude of  $1600 \text{ m}$  by Murcray [23], it does not appear on our spectra, as it does not show up in other University of Denver spectra obtained at higher altitudes. At the present stage,  $\text{NH}_3$  might be interpreted as a local pollutant which is not a permanent constituent of the upper troposphere.

$\text{H}_2\text{O}_2$  may not be observed in our spectra because of the broadness of the spectrum and the lack of well distinct features, similar conclusions have been reached by Murcray *et al.* [24] in an extensive study of balloon spectra.

Ozone is observed in its  $\nu_1$  and  $\nu_3$  bands but, due to the overlapping and saturation of individual lines, no simple interpretation method exists. An automatic data fitting program, to be developed for this case, would be necessary to obtain quantitative values for ozone. It would be similar to techniques previously developed for analysis of  $\text{NO}_2$  spectra obtained from balloons (Ackerman and Muller [25], Ackerman *et al.* [26]). But due to the difficulties encountered in assigning the 100% transmission level, the final result would not be, in the present case, as accurate as the Dobson technique. However, it could be qualitatively useful to monitor the relative evolutions of  $\text{O}_3$  and  $\text{HNO}_3$ .

### CONCLUSION

A permanent mountain station would permit continuous monitoring of nitric acid which the presented observations prove to be highly variable. The variations of the main chlorofluoromethanes could also be measured using the same technique, giving a permanent record of their current values. The  $\text{CFCl}_3$  concentration observed here is consistent with the growth measured between 1972 and 1976. The total burden of  $\text{HNO}_4$ ,  $\text{HNO}_2$  and  $\text{NH}_3$  appears to be negligible at the time of the observations.

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