

## COMMUNICATION

### AÉRONOMIE SPATIALE

#### **Inversion of infrared spectra obtained at the « Observatoire du Pic du Midi »**

C. LIPPENS and C. MULLER

Belgian Institute for Space Aeronomy  
Avenue Circulaire, 3 - B-1180 Brussels (Belgium)

*Abstract.* — Three campaigns of observations performed at the « Observatoire du Pic du Midi » are analysed from the point of view of nitric acid and chlorofluorocarbon 11. The spectra, obtained in the 10  $\mu\text{m}$  window, in both absorption and emission, permit to determine that most of the nitric acid absorbs above the tropopause while on the contrary,  $\text{CFCl}_3$  emits and absorbs in the troposphere. The trend of  $\text{CFCl}_3$  is observed between 1980 and 1982; an increase rate equal to the one measured between 1972 and 1980 is determined.

*Résumé.* — Trois campagnes d'observations effectuées à « l'Observatoire du Pic du Midi » sont analysées du point de vue de l'acide nitrique et du chlorofluorocarbène 11. Les spectres, obtenus dans la fenêtre de 10  $\mu\text{m}$ , à la fois en émission et en absorption, permettent de déterminer que la plus grande partie de l'acide nitrique absorbe au-dessus de la tropopause tandis qu'au contraire,  $\text{CFCl}_3$  émet et absorbe dans la troposphère. L'observation de  $\text{CFCl}_3$  entre 1980 et 1982 donne un taux de croissance égal à celui mesuré entre 1972 et 1980.

#### INTRODUCTION

The present knowledge of the minor atmospheric constituents began with the study of the solar spectrum one hundred years ago, from the ultraviolet limit which led to the discovery of upper atmospheric ozone to the infrared where numerous telluric bands revealed methane and nitrous oxide [see Goody, 1954 for review]. Later carbon monoxide and many other constituents were also observed from the ground and attempts were made to deduce the total column and even

the vertical distribution of these gases. However, the development of balloonborne and airborne platforms permitting direct limb sounding in the stratosphere offered a complete new set of vertical distributions in the last ten years [Ackerman, 1979 ; Hudson, *et al.* 1981]. These results present the disadvantage of being punctual and lack both time and space coverage. The best solution would reside in a permanent scientific space station where several instruments would monitor the Earth's atmosphere and of which a first approach consists in the Nimbus satellites and the European Spacelab. This approach, is by now, still very limited, because of its technological complexity and very high price. It would be thus tempting to revert to much more manageable ground based observations using improved technology.

Interferometers, heterodyne spectrometers permit to achieve high resolution spectra in scans much faster than the apparent motion of the sun and permit to give the atmospheric absorption of the solar radiation. The inversion technique will consist in determining the total content of atmospheric gases and even better, in inferring the vertical distribution. In the case that will be studied here, spectra are obtained with a  $0.1 \text{ cm}^{-1}$  resolution in the  $10 \mu\text{m}$  window in both absorption and emission at various zenith angles.

#### OBSERVATION

Three observation campaigns have been conducted at the « Observatoire du Pic du Midi » in April 1980, August 1981 and April 1982. The experimental aspects and the results of the first campaign have already been described in a previous paper [Lippens and Muller, 1981]. Absorption observations are made at both Sunset, Sunrise and smaller zenith angles. Nighttime absorption observations have been attempted using the full moon as a source. Emission spectra are also obtained in the same conditions. The altitude of the observatory (2987 m) and its geographic situation where the main winds come from the Atlantic ocean makes it one of the less polluted sites of Europe, its low winter temperature leads also to remarkably dry conditions.

The absorption spectra are obtained by making the « Fast Fourier Transform » of the difference between the absorption interferogram and an emission interferogram obtained at the same zenith angle. For

the emission spectra, a cold black body is used as the reference. These procedures eliminate the instrumental effects and, in the case of the absorption spectra reproduce well the O level expected from the  $15\ \mu\text{m}$   $\text{CO}_2$  bands and from the saturating  $9.6\ \mu\text{m}$   $\text{O}_3$  lines. The careful study of the spectra of 1980 has revealed a high frequency component in some regions of the spectra, which was found to be related to internal reflections in the beamsplitter, this component was later identified in the interferogram and systematically suppressed in the 1981 and 1982 spectra.

The operational procedure consisted in first collecting the interferograms on disk files in the data system, then saving them on tape files, making the transforms, saving them and finally plotting the spectra for analysis. In 1982, the data system failed to function after plotting only a few spectra, this led to a revision of the procedure for future operations which will consist of collecting the data on a cassette system and making the interpretations at the Brussels laboratory where the tasks of maintenance are much easier performed. However, for the 1982 campaign, a complete plot of an absorption spectrum on April 8, in the morning at an elevation of  $19.1\ \text{deg}$  was obtained and permitted to make a full interpretation. The spectral region studied range from  $750$  to  $1000\ \text{cm}^{-1}$ , spectra up to  $1250\ \text{cm}^{-1}$  could be also used but the number of strongly absorbing  $\text{O}_3$  and  $\text{H}_2\text{O}$  lines demands a further step of interpretation if an accuracy similar to the one presented here is desired.

#### NITRIC ACID

The previous interpretation [Lippens and Muller, 1981] relied mainly on the Q branch of the  $\nu_5$  band, while a similar analysis [Lado-Bordowsky, 1980; Dana and Lado-Bordowsky, 1981] studied manifolds of the  $\nu_5$  P branch from spectra obtained at a 1800 m altitude from the Pyrenean station of Montlouis. In 1980, where mostly high zenith angle spectra were interpreted, the  $\nu_5$  Q branch (fig. 1) was definitively well separated from the neighbouring  $\text{H}_2\text{O}$  line and could be unambiguously interpreted. In the Montlouis spectra, obtained at lower altitude, where the local  $\text{H}_2\text{O}$  lines are wider and with greater humidity, it is much more difficult to observe [Dionne, 1972]. The  $\nu_5$  Q branch, being a tight manifold of hundreds of lines of different energy level, has a weak dependance in temperature its weakness

makes it also linear and permits to infer the total nitric acid column by direct comparison with laboratory measurements.

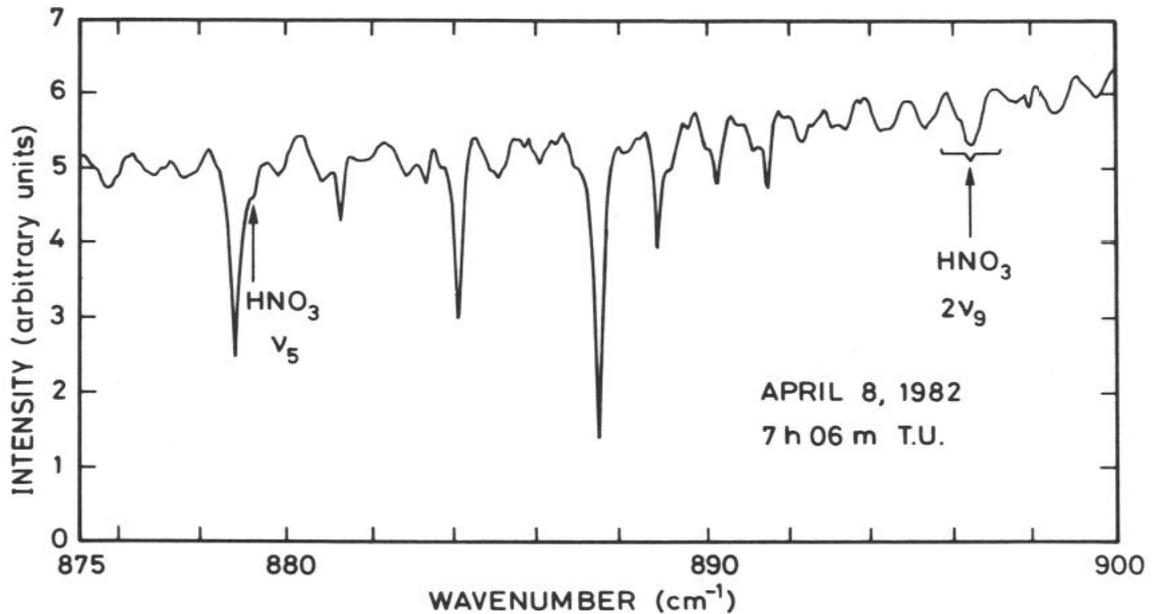


FIG. 1. — Absorption spectrum obtained on April 8, 1982 at 7h06 m T.U. and a solar elevation of 19.1 deg in the region of the  $\nu_5$  and  $2\nu_9$  HNO<sub>3</sub> bands. The two features indicated are the nitric acid Q branches. On this spectrum, the weaker  $\nu_5$  band appears as a shoulder on a water vapor line from which, it cannot be separated at a lower altitude.

The manifolds used by Lado-Bordowsky [1980] present the problem of being temperature dependant in a still to be determined way. Temperature corrections, computed after a parametrization of laboratory and observed spectra have been used by Lado-Bordowsky and Dana [1981]. The only table of positions and line strengths available by now has been published by Brockman, *et al* [1978] using a laser diode study of the  $2_9$  band including its Q branch near 896 cm<sup>-1</sup>. The lines are not yet assigned and thus, the temperature dependance is still unknown. From the ground, the  $2\nu_9$  Q branch is wider and more intense than the  $\nu_5$ , it is also completely free of contamination by other atmospheric lines. A careful examination of the emission spectra in the regions of the two HNO<sub>3</sub> Q branches could not yield any signal distinct from the instrumental noise while the  $2_9$  Q branch is observable on all absorption spectra. It could be then assumed that HNO<sub>3</sub> is mainly in much colder regions of the atmosphere than the ones

where the other emission lines are created and in the cold and dry observational conditions used, it excludes the influence of tropospheric HNO<sub>3</sub> on the observations.

The data of Brockman, *et al* [1978], as compiled in the AFGL trace gas file, were used to compute synthetic spectra of the  $2\nu_9$  Q branch in the observational conditions of the April 8, 1982, 7h06m TU spectrum. For this spectrum, the  $\nu_5$  Q branch gives a zenith HNO<sub>3</sub> value of  $2.26 \times 10^{16}$  HNO<sub>3</sub> molecules/cm<sup>2</sup> using the linear technique described by Lippens and Muller [1981]. A similar analysis of the  $2\nu_9$  branch using the cumulated values of the measured line intensities leads to a zenith angle of  $6.67 \times 10^{16}$  molecules/cm<sup>2</sup>.

This result is not only inconsistent with the  $\nu_5$  value but also above the range of previous in situ nitric acid observations [Hudson, *et al*, 1981]. A synthetic spectrum computation was performed using the nitric acid vertical distribution used by Lippens and Muller [1981] and found a similar high value proving that the saturation of individual lines in the  $2\nu_9$  Q branch was not the dominant factor in the overevaluation. An interpretation attempt was made by building a temperature dependence of the lines, a spectrum was calculated assuming an energy of the fundamental level of

$$E'' = |F - 896.2| \times 1000.\text{cm}^{-1}$$

where  $F$  is the wavenumber of the line. The spectrum obtained this way is shown on figure 2 as well as a spectrum without any temperature dependence. The spectrum is computed in 10 layers and incorporate 500 nitric acid lines. One sees that the transformed spectrum resembles much more to the observed one and absorbs less for the same nitric acid quantity. For the case of a real temperature variation, the integrated intensities for the two spectra of the Q branches should be the same because they range on all kind of levels and while the high  $J$  lines have their intensity decrease with temperature, the low  $J$  lines increase. This would lead to a strong enhancement of the central absorption and in the case of  $2\nu_9$  band, even saturation, bringing the final result to a value close of the one observed in the  $\nu_5$  band. Finally, the problems of the Fermi resonances between  $\nu_5$  and  $2\nu_9$  is not yet resolved, leading to even greater difficulties in the interpretation of temperature effect. More theoretical and laboratory studies of HNO<sub>3</sub> are thus needed before its value and its variations could be

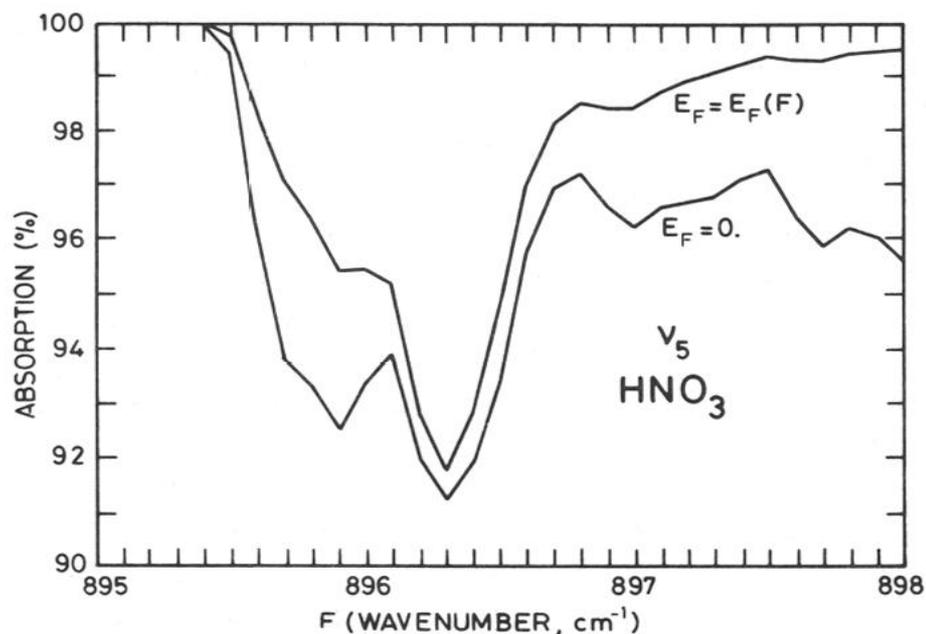


FIG. 2. — Synthetic nitric acid atmospheric spectra of the  $2\nu_5$  Q branch computed for lines with identical ground state and lines with a ground state energy assumed to be a function of the distance to the band center. The upper spectrum is much closer in its aspect to the observed spectrum (fig. 1).

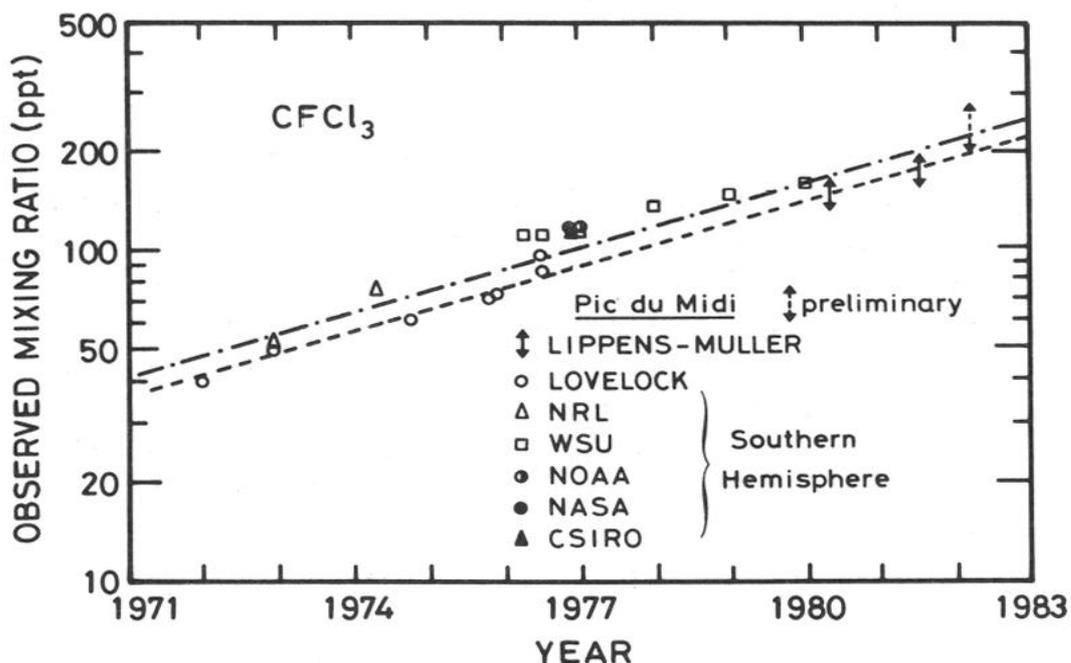


FIG. 3. — Growth of the CFM 11 mixing ratio since 1970, the data are from Hudson and Reed [1980] and Rasmussen, *et al* [1981]. The lower line corresponds to the Southern hemisphere trend while the upper one is extrapolated to the Northern hemisphere using the ratio of Singh, *et al* [1979].

inferred from the comparison of works in different regions of the spectrum.

The results obtained are  $1.8 \pm 0.4 \times 10^{16}$  molecules  $\text{cm}^{-2}$  for April 1980,  $2. \times 10^{16}$  for 1981 and  $2.2 \times 10^{16}$  for August 1982. All three results are in agreement within experimental errors and are consistent with the lower limit of Lado-Bordowsky [1980], whose average value ( $2.7 \times 10^{16}$ ) is however higher.

The analysis of a lunar absorption spectrum obtained in August 1981 at a  $9^\circ$  zenith angle yields a value of  $2.3 \times 10^{16}$  not discernable from the daytime value and thus shows no evidence of a diurnal cycle.

The spectra were again searched for  $\text{HNO}_4$  and  $\text{HNO}_2$  without finding any evidence which should lead to a column density larger than  $1 \times 10^{15}$  for both constituents.

### $\text{CFCl}_3$

An analysis of  $\text{CFCl}_3$  (freon 11) was made in the three sets of spectra, the  $850 \text{ cm}^{-1}$  feature, was very detectable on the 1980 low sun spectra, in both absorption and emission, it was thus used to deduce a  $\text{CFCl}_3$  volume mixing ratio (Lippens and Muller, 1981). This feature was even more visible in the 1981 and 1982 spectra, appearing at all zenith angles and leading to values of  $180 \pm 15$  ppt in August 1981 and a value of 260 ppt for a spectrum of April 1982. For this last value, the error bar is still preliminary because only one spectrum could be analysed. Combined with the  $148 \pm 12$  ppt 1980 result, these results compare well with observations shown on figure 4 [Hudson and Reed, 1979] and Rasmussen, *et al* [1981]. This proves a global increase of the concentrations of fluorocarbons despite the recent decrease of their use related to concerns about the effect of chlorine on the stratospheric ozone layer [Chemical Manufacturers Association, 1981]. The absence of an observed atmospheric decrease may be traced either to the long atmospheric lifetime of these constituents [Owens, *et al*, 1982] or either to a differed release or even [Rowland *et al*, 1982] to an unaccounted production. Independantly of its cause, if this increase persists,  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$ , already clearly visible at all zenith angles in our spectra, will become important to the radiative transfer in the  $10 \mu\text{m}$  atmospheric « window » and will contribute to the warming of the troposphere [Ramanathan, 1975 ; Lacis, *et al*, 1981].

## CONCLUSION

Despite 15 years of observations of stratospheric nitric acid in the infrared, its spectrum is not yet known enough to provide the necessary parameters for the computation of line-by-line spectra. This casts a doubt on all the interpretations made up to now and it is suggested that all observers carefully file their raw spectra for future reinterpretation. From our data, and those of other authors, no significant diurnal, seasonal or day to night predictable variation could be observed.

For chlorofluoromethane 11, a significant increase is visible on the spectra; if  $\text{CFCl}_3$  increases still by a factor of two, which, if the present trend does not level off is within 4 years,  $\text{CFCl}_3$  will saturate in the low sun spectra and only spectra near noon will be interpretable without using a line by line computation which is by now impossible due to the extreme complexity of the spectrum.

## ACKNOWLEDGMENTS

The authors are happy to thank Professor Zahn, director of the « Observatoire du Pic du Midi » and all the personnel of the observatory for the warm welcome and generous help that they always received at the observatory. These campaigns would not have been possible without individual grants from the NFWO-FNRS (Belgian National Science Foundation) to which we express our gratitude.

## REFERENCES

- ACKERMAN, M., 1979. In situ measurements of middle atmosphere composition, *J. Atm. Terr. Phys.*, **41**, 117-126.
- BROCKMAN, P., BAIR, C. H. and ALLARIO, F., 1978. High resolution spectral measurement of the  $\text{HNO}_3$  11.3  $\mu\text{m}$  band using tunable diode lasers, *Appl. Opt.*, **17**, 91-100.
- CALLIS, L. B. and NATARAJAN, N., 1981. Atmospheric carbon dioxide and chlorofluoromethanes: combined effects on stratospheric ozone, temperature, and surface temperature, *Geophys. Res. Lett.*, **8**, 587-590 (1981).
- CHEMICAL MANUFACTURES ASSOCIATION, 1981. 1980 world production and sales of fluorocarbon FC-11 and FC-12, *C.M.A. Fluorocarbon Research*, Washington DC 20037.

- DANA, V. and LADO-BORDOWSKY, O., 1981. Spectres synthétiques de  $\text{HNO}_3$  dans la région de  $11,5 \mu\text{m}$ . Application au dosage de l'acide nitrique atmosphérique, *J. Opt.*, **12**, 377-394.
- DIONNE, J., 1972. *spectres d'absorption atmosphérique de 9,1 à 11,6  $\mu$* , thèse de doctorat de troisième cycle, Université de Paris VI.
- GOODY, R. M., 1954. *The physics of the stratosphere*, Cambridge University Press.
- HUDSON, R. D., 1981. editor in chief, *The stratosphere, 1981*, Theory and measurements, WMO, NASA, FAA, NOAA, WMO ozone research project 11, Geneva.
- HUDSON, R. D. and REED, E. I., 1979. *The stratosphere, present and future*, NASA reference publication n° 1049.
- LACIS, A., HANSEN, J., LEE, P., MITCHELL, T. and LEBEDEFF, S., 1981. Greenhouse effect of trace gases, 1970-1980, *Geophys. Res. Let.*, **8**, 1035-1038.
- LADO-BORDOWSKY, O., 1980. *Détermination de la quantité totale d'acide nitrique atmosphérique par spectrométrie d'absorption infrarouge dans la région de 11,4  $\mu\text{m}$* . Thèse de doctorat d'état, Université Pierre et Marie Curie, Paris.
- LIPPENS, C. and MULLER, C., 1981. Atmospheric nitric acid and chlorofluoromethane 11 from interferometric spectra obtained at the « Observatoire du Pic du Midi », *J. Optics*, **12**, 331-336.
- OWENS, A. J., STEED, J. M., MILLER, C., FILKIN, D. L. and JESSON, J. P., 1982. The atmospheric lifetimes of CFC 11 and CFC 12, *Geophys. Res. Let.*, **9**, 700-703.
- RASMUSSEN, R. A., KHALIL, M. A. K., DALLUGE, R. W., 1981. Atmospheric trace gases in Antarctica, *Science*, **211**, 285-287.
- RAMANATHAN, V., 1975. Greenhouse effect due to chlorofluorocarbons : climatic implications, *Science*, **190**, 50-55.
- ROWLAND, F. S., TYLER, S. C., MONTAGUE, D. C. and MAKIDE, Y., 1982. Dichlorofluoromethane,  $\text{CF}_2\text{Cl}_2$ , in the Earth's atmosphere, *Geophys. Res. Let.*, **9**, 481-484.