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

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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 μm window, in both absorption and emission, permit to determine that most of the nitric acid absorbs above the tropopause while on the contrary, CFCl_3 emits and absorbs in the troposphere. The trend of 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 μm , 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, CFCl_3 émet et absorbe dans la troposphère. L'observation de 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 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 $15\ \mu\text{m}$ CO_2 bands and from the saturating $9.6\ \mu\text{m}$ 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 O_3 and H_2O 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 ν_5 band, while a similar analysis [Lado-Bordowsky, 1980; Dana and Lado-Bordowsky, 1981] studied manifolds of the ν_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 ν_5 Q branch (fig. 1) was definitively well separated from the neighbouring H_2O line and could be unambiguously interpreted. In the Montlouis spectra, obtained at lower altitude, where the local H_2O lines are wider and with greater humidity, it is much more difficult to observe [Dionne, 1972]. The ν_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.

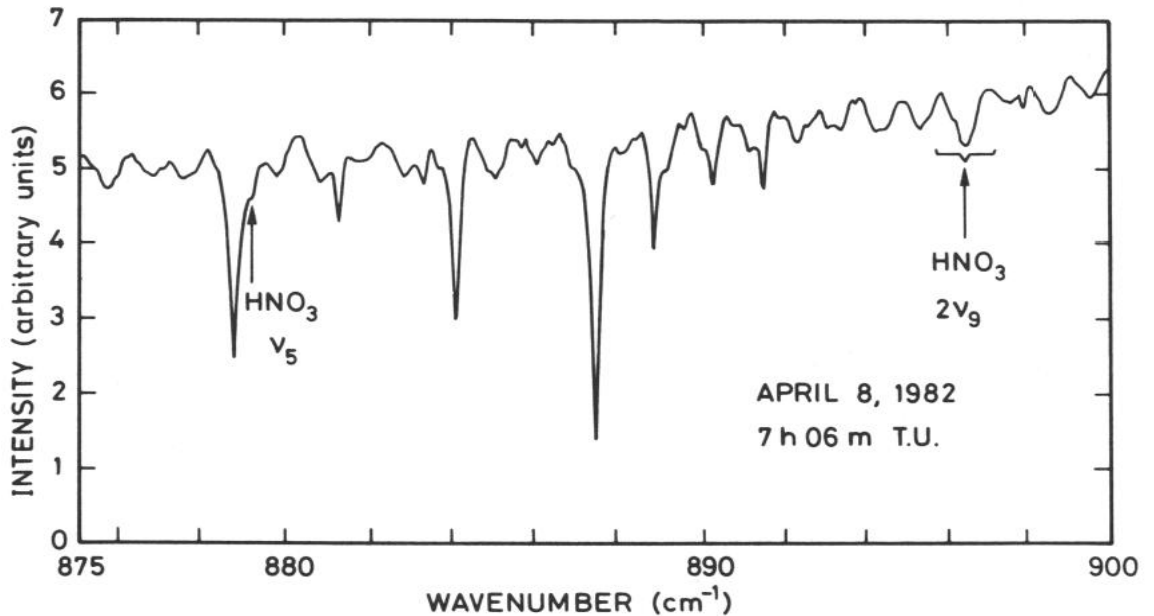


FIG. 1. — Absorption spectrum obtained on April 8, 1982 at 7h06 m T.U. and a solar elevation of 19.1 deg in the region of the ν_5 and $2\nu_9$ HNO₃ bands. The two features indicated are the nitric acid Q branches. On this spectrum, the weaker ν_5 band appears as a shoulder on a water vapor line from 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⁻¹. 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 ν_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 HNO₃ 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 HNO₃ 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 HNO₃ 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 2ν₉ Q branch in the observational conditions of the April 8, 1982, 7h06m TU spectrum. For this spectrum, the ν₅ Q branch gives a zenith HNO₃ value of 2.26 × 10¹⁶ HNO₃ molecules/cm² using the linear technique described by Lippens and Muller [1981]. A similar analysis of the 2ν₉ branch using the cumulated values of the measured line intensities leads to a zenith angle of 6.67 × 10¹⁶ molecules/cm².

This result is not only inconsistent with the ν₅ 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 2ν₉ 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 2ν₉ band, even saturation, bringing the final result to a value close of the one observed in the ν₅ band. Finally, the problems of the Fermi resonances between ν₅ and 2ν₉ is not yet resolved, leading to even greater difficulties in the interpretation of temperature effect. More theoretical and laboratory studies of HNO₃ are thus needed before its value and its variations could be

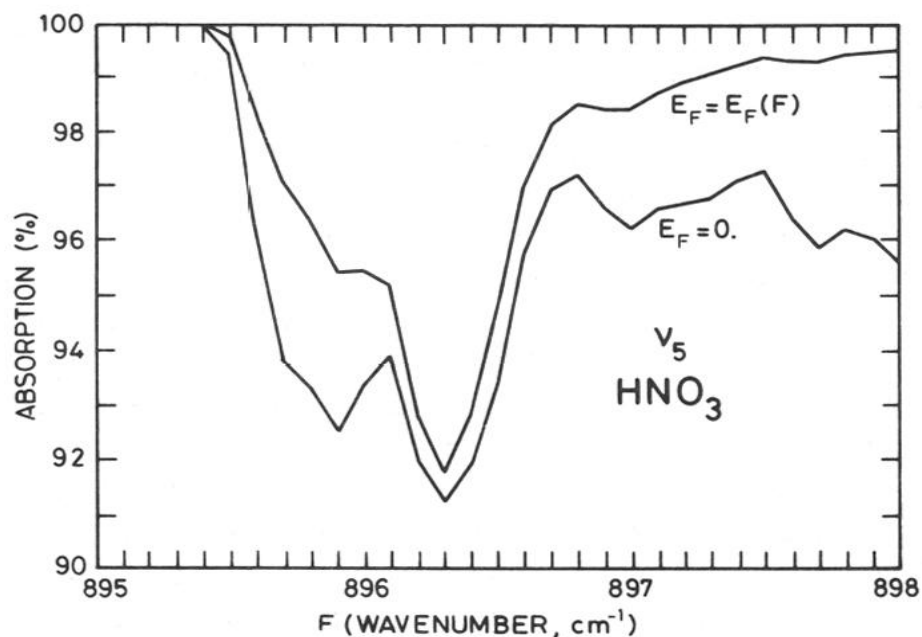


FIG. 2. — Synthetic nitric acid atmospheric spectra of the $2\nu_5$ Q branch computed for lines with identical ground state and lines with a ground state energy assumed to be a function of the distance to the band center. The upper spectrum is much closer in its aspect to the observed spectrum (fig.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

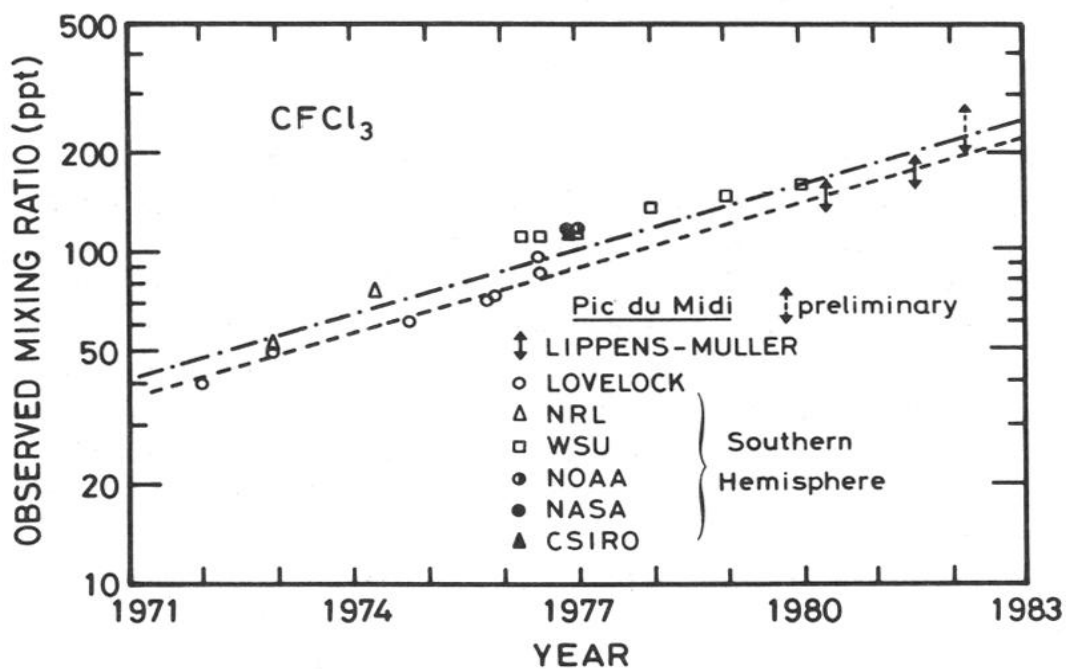


FIG. 3. — Growth of the CFM 11 mixing ratio since 1970, the data are from Hudson and Reed [1980] and Rasmussen, *et al* [1981]. The lower line corresponds to the Southern hemisphere trend while the upper one is extrapolated to the Northern hemisphere using the ratio of Singh, *et al* [1979].

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 cm^{-2} for April 1980, $2. \times 10^{16}$ for 1981 and 2.2×10^{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 (2.7×10^{16}) is however higher.

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

The spectra were again searched for HNO_4 and HNO_2 without finding any evidence which should lead to a column density larger than 1×10^{15} for both constituents.

CFCl_3

An analysis of CFCl_3 (freon 11) was made in the three sets of spectra, the 850 cm^{-1} feature, was very detectable on the 1980 low sun spectra, in both absorption and emission, it was thus used to deduce a 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 ± 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 ± 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, CFCl_3 and CF_2Cl_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 CFCl_3 increases still by a factor of two, which, if the present trend does not level off is within 4 years, 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.

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