

RESEARCH NOTE

STRATOSPHERIC WATER VAPOR FROM HIGH RESOLUTION INFRARED SPECTRA

(Received 15 February 1974)

Abstract—A volume of mixing ratio equal to $(3.4 \pm 0.7) \times 10^{-6}$ is deduced for the stratospheric water vapour from 20 to 37 km. The results have been obtained by absorptiometry from a balloon platform at 40 km.

INTRODUCTION

The dominant role of water vapour in determining many of the properties of the stratosphere was recognized a long time ago, even before its concentration was measured in the lower stratosphere for the first time by Dobson, Brewer and Cwiling in 1945. Since that time many measurements have been made of the stratospheric water vapour concentration. They are based on *in situ* measuring techniques and on remote soundings in the infrared by the absorption or by the emission method. There are great discrepancies in the various data available and many of them must now be rejected on the basis of the most recent values obtained which indicate that the stratosphere is essentially dry (Mastenbrook, 1968). This conclusion has been generally accepted following the radiometric measurements of emission from stratospheric water vapour made by Williamson and Houghton (1964). The difficulty of the measurements consists mostly in avoiding the contamination of the instrumentation by water carried aloft. The accuracy reached at present is such that the problem of small irregularities in the vertical distribution of the mixing ratio can be tackled as shown by the recent work of Goldman *et al.* (1973).

Little information seems to have been obtained at altitudes higher than 30 km. The purpose of this article is to present CO_2 and H_2O volume mixing ratios for the altitude range between 20 and 37 km measured at mid-latitude in spring. Carbon dioxide is considered as being uniformly mixed at these heights so that its simultaneous measurement with the same technique—absorption spectrophotometry—yields a useful comparison. Eventually this is a way of testing in some respects the method used by Ackerman *et al.* (1973), to derive the vertical distribution of the mixing ratio of nitric oxide in the stratosphere.

DATA REDUCTION

The data have been obtained by means of an instrumentation the description of which has been outlined elsewhere (Ackerman *et al.*, 1973). The method is based on the absorptiometry of the stratosphere using the setting Sun as a source. This offers several advantages. Changes in absorption can be correlated with the rather fast change in zenith angle leading to the increase of the optical path through the atmosphere and to the increase of absorption as the radiation traverses denser and denser layers. This possibility of correlation allows one to discriminate between atmospheric absorption and spurious effects due to contamination by the instrumentation. The absorption takes place in a narrow altitude range so that the data can be treated under the assumption of absorption taking place at constant pressure and temperature at least for uniformly distributed constituents.

In the experiment under consideration, the spectrometer was recording the solar spectrum from an altitude of 40 km between 1902 and 1915 cm^{-1} . Some rotation-vibration absorption lines due to the $3\nu_2$ CO_2 and the ν_2 H_2O bands occur in this range. They appear in the spectra shortly after the solar zenith angle is equal to 90° . Due to the instrumental resolution (0.1 cm^{-1}) and to the narrowness of the lines the absorption is small and increases slowly for solar grazing rays having a minimum altitude down to about 30 km. Below this altitude pressure broadening adds its contribution to the Doppler width and makes the absorption increase more quickly. Since the integrated absorption of the CO_2 and H_2O lines is known (McClatchey *et al.*, 1973) it is possible to assign to the measurements a number of molecules on the optical path. To give a better idea of the systematic and random uncertainties it has been preferred to compute the line absorption that should be observed versus the altitude of the solar grazing rays for various values of constant volume mixing ratios of H_2O and CO_2 in the stratosphere. The tables of the equivalent width of isolated lines with combined Doppler and collision broadened profiles of Jansson and Korb (1968) have been used for this purpose. A single atmospheric layer has been considered, the pressure of which has been chosen equal to the pressure two km above the minimum altitude of the solar grazing rays. The volume mixing ratios have been computed on the basis of a standard model (Nicolet, 1972) for the total atmospheric number density. The Earth geometry factors have been taken from Swider (1964).

The results for the CO_2 line at 1906.521 cm^{-1} and for the H_2O lines at 1909.95 cm^{-1} and at 1904.35 cm^{-1} are respectively shown in Figs. 1 and 2. The measured percentage absorption at the line centre has also been plotted.

DISCUSSION AND CONCLUSION

There has never been, up to now, any experimental evidence for seriously thinking that the stratospheric volume mixing ratio of CO_2 differs much from 3×10^{-4} . The fact that the data points of Fig. 1 are, on the average, closer to the curve computed for 2×10^{-4} than for 4×10^{-4} cannot be taken as evidence for changing the above-mentioned opinion. It should rather be taken as an indication of a systematic error since the value that one would deduce would be $(2.6 \pm 0.7) \times 10^{-4}$. The error could, for instance, be mostly taken care of by an altitude shift of only one km. Even if the scatter of the data points is relatively small, corresponding to a few percent of absorption, it leaves a rather large uncertainty. However, the observations follow remarkably well the predicted curve of growth. This result supports the validity of the assumption on which the computation of the curve has been based and justifies a high degree of confidence in the results obtained for H_2O .

These results, for which two lines could be treated unambiguously, are shown in Fig. 2. Here the data points can be included within the limits $(3.4 \pm 0.7) \times 10^{-6}$ which do not take into account systematic errors. This indicates the dryness of the stratosphere up to 37 km. A slight and broad maximum between

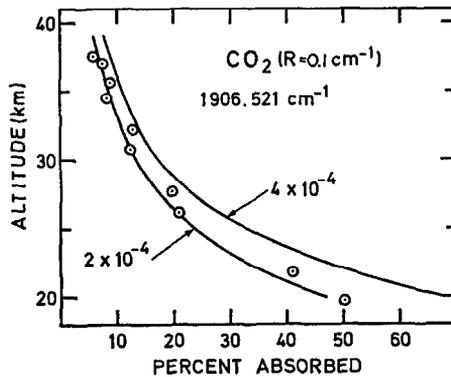


FIG. 1. COMPUTED PERCENTAGE OF ABSORPTION AT THE CENTRE OF THE CO_2 LINE AT 1906.521 cm^{-1} FOR AN INSTRUMENTAL HALF WIDTH (R) EQUAL TO 0.1 cm^{-1} AND FOR TWO ASSUMED VALUES OF CO_2 CONSTANT VOLUME MIXING RATIO: 2×10^{-4} AND 4×10^{-4} VS SOLAR GRAZING RAY ALTITUDES. THE CIRCLES REPRESENT THE OBSERVATIONS.

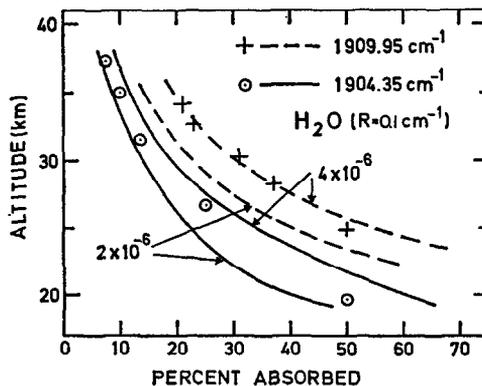


FIG. 2. COMPUTED PERCENTAGE OF ABSORPTION AT THE CENTRE OF THE H_2O LINES AT 1909.95 cm^{-1} AND 1904.35 cm^{-1} FOR AN INSTRUMENTAL HALF WIDTH (R) EQUAL TO 0.1 cm^{-1} AND FOR TWO ASSUMED VALUES OF H_2O CONSTANT VOLUME MIXING RATIO: 2×10^{-6} AND 4×10^{-6} VS SOLAR GRAZING RAYS ALTITUDES. THE CIRCLES AND THE CROSSES REPRESENT THE OBSERVATIONS.

20 and 30 km can not be excluded on the basis of the results. However, in the circumstances of the experiment considered, the increase in this altitude range can not be larger than 30 per cent relative to the values observed at 20 km.

The accuracy of the results can probably still be improved by the line by line computation in progress that is primarily designed to improve the results obtained on nitric oxide. The limitations due to the resolution achieved will, however, remain.

Acknowledgements—This work has been sponsored in part by the C.I.A.P. Office of the U.S. Department of Transportation through the Office of Naval Research under contract N0014-73-C-0076, by the Centre National d'Etudes Spatiales and by the Comité sur les conséquences des vols stratosphériques.

*Institut d'Aéronomie Spatiale de Belgique,
B-1180 Brussels,
Belgium*

M. ACKERMAN

REFERENCES

- ACKERMAN, M., FRIMOUT, D., MULLER, C., NEVEJANS, D., FONTANELLA, J. C., GIRARD, A. and LOUISNARD, N. (1973). *Nature, Lond.* **245**, 205.
- DOBSON, G. M. B., BREWER, A. W. and CWILONG, B. M. (1945). *Proc. R. Soc.* **185A**, 144.
- GOLDMAN, A., MURCRAY, D. G., MURCRAY, F. H., WILLIAMS, W. J. and BROOKS, J. N. (1973). *Appl. Optics* **12**, 1045.
- JANSSON, P. A. and KORB, C. L. (1968). *J. Quant. Spectrosc. Radiat. Transfer* **8**, 1399.
- MASTENBROOK, H. J. (1968). *J. atmos. Sci.* **25**, 299.
- MCCLATCHEY, R. A., BENEDICT, W. S., CLOUGH, S. A., BURCH, D. E., CALFEE, R. F., FOX, K., ROTHMAN, L. S. and GARING, J. S. (1973). AFCRL atmospheric absorption line parameters compilation, AFCRL TR-73-0096, 26 Jan. 1973. Environmental Research Papers, Nr 434, L. G. Hanscom Field, Bedford, Mass. 01730.
- NICOLET, M. (1972). *Planet. Space Sci.* **20**, 1671.
- SWIDER, W. (1964). *Planet. Space Sci.* **12**, 761.
- WILLIAMSON, E. J. and HOUGHTON, J. (1965). *Q. Jl R. met. Soc.* **91**, 330.