AERONOMICA ACTA

A - N° 106 - 1972

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from infrared absorption spectra

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FOREWORD

This article has been accepted from publication in NATURE.

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Cet article a été accepté pour publication dans NATURE.

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STRATOSPHERIC NITROGEN DIOXIDE FROM INFRARED ABSORPTION SPECTRA

by

M. ACKERMAN and C. MULLER

Abstract

Stratospheric absorption spectra of nitrogen dioxide have been interpreted quantitatively NO_2 mixing ratios from 12 to 28 km are presented.

Résumé

Des spectres d'absorption du rayonnement infrarouge solaire par le peroxyde d'azote stratosphérique ont été interprétés quantitativement. Les valeurs obtenues pour le rapport de mélange de NO_2 de 12 à 28 km d'altitude sont présentées.

Samenvatting

De stratosferische absorptiespectra van stikstofdioxyde werden kwantitatief verklaard. De mengverhoudingen van NO_2 tussen 12 en 28 km worden vermeld.

Zusamenfassung

Stratosphärische Absorptionsspektren von Stickdioxyde werden analysiert. Die Mischungsverhältnisse von NO_2 werden zwischen 12 und 28 Km vorgestellt.

Stratospheric absorption due to NO_2 has been identified [1, 2, 3] in infrared spectra of the solar radiation recorded from balloon borne gondolas floating at mid-latitudes in the altitude range of 30 km when the solar zenith angle was larger than 91°. In this particular geometric situation most of the absorption by the atmosphere takes place at altitudes smaller than float altitude over very long optical paths. This offers two great advantages : the sensitivity of the absorption method is maximum and the quantitative interpretation is easier since absorption takes place mostly at constant total pressure, constituant concentration and temperature where the solar radiation passes closest to the earth surface.

A quantitative interpretation of the available data leading to stratospheric mixing ratios of NO_2 from the edge of the tropopause at 12 km up to 28 km is reported here. Synthetic spectra have been computed on the basis of the spectroscopic constants given for NO_2 by Olman and Hause [4] using a Lorentz line full half width of 0.16 cm^{-1} in S.T.P. conditions. The choice of this value is based on the work of Yamamoto and Aoki [5]. The line intensity was determined by comparing the integrated synthetic spectra with the integrated absorption measured in the laboratory by Guttman [6]. Fig. 1 shows the transmission versus wavenumber of a portion of the ν_3 band computed for the laboratory conditions used by Guttman [6]. The positions of water vapor lines are shown at the wavenumbers given by Benedict and Calfee [7]. One of these overlaps the NO_2 absorption feature numbered O on the figure. Absorptions numbered 1 and 2 are very well isolated. This part of the spectrum particularly well marked in the atmospheric recordings [3] has mainly been used for the quantitative interpretation. The $\nu_1 + \nu_3$ band [1, 2] underlies very clearly the P branch of the ν_3 CH_4 band. The mixing ratios by volume shown in the table and in Fig. 2 refer to the altitudes of the solar grazing rays and have been deduced from the NO_2 concentrations determined from the spectra and from the total concentration given in the Mid-Latitude, Spring-Fall model of U.S. Standard Atmosphere Supplements, 1966. The quoted errors correspond to lower and upper values of the amount of absorber in the optical path leading to computer generated spectra that could be distinguished from the observed atmospheric spectra.
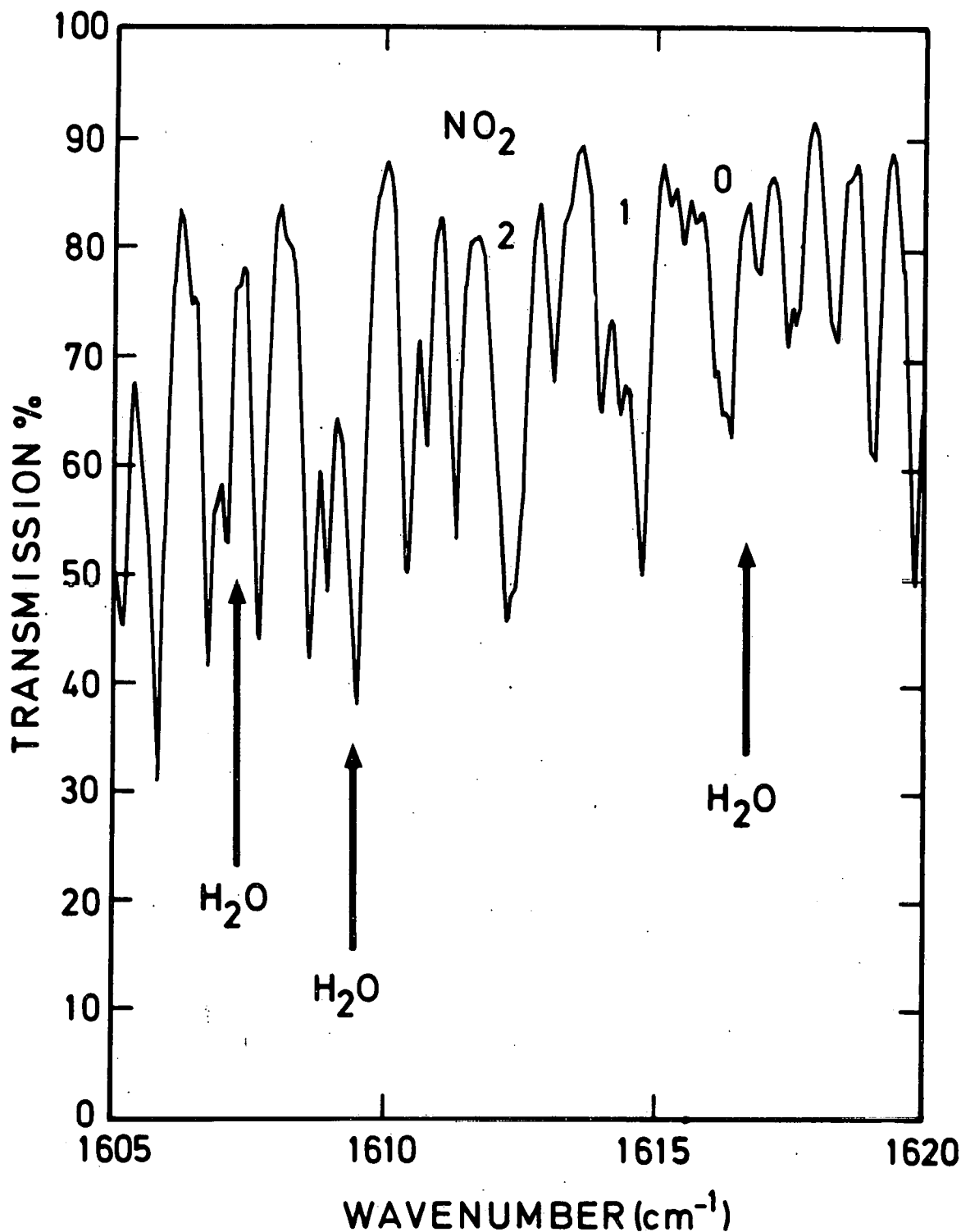
Fig. 1.- Synthetic absorption spectrum of a portion of the ν_3 band of NO_2 computed on the basis of the available spectroscopic data [4] and calibrated in absolute value by means of the laboratory measurements of Guttman [6] ; optical thickness : 0.014 atm.cm, total pressure : 1.18 atm, temperature : 298 $^\circ$K. The position of water vapor lines is indicated, one of them overlapping the NO_2 absorption marked 0. Absorptions 1 and 2 are unaffected by water vapor and appear clearly in the atmospheric spectra.
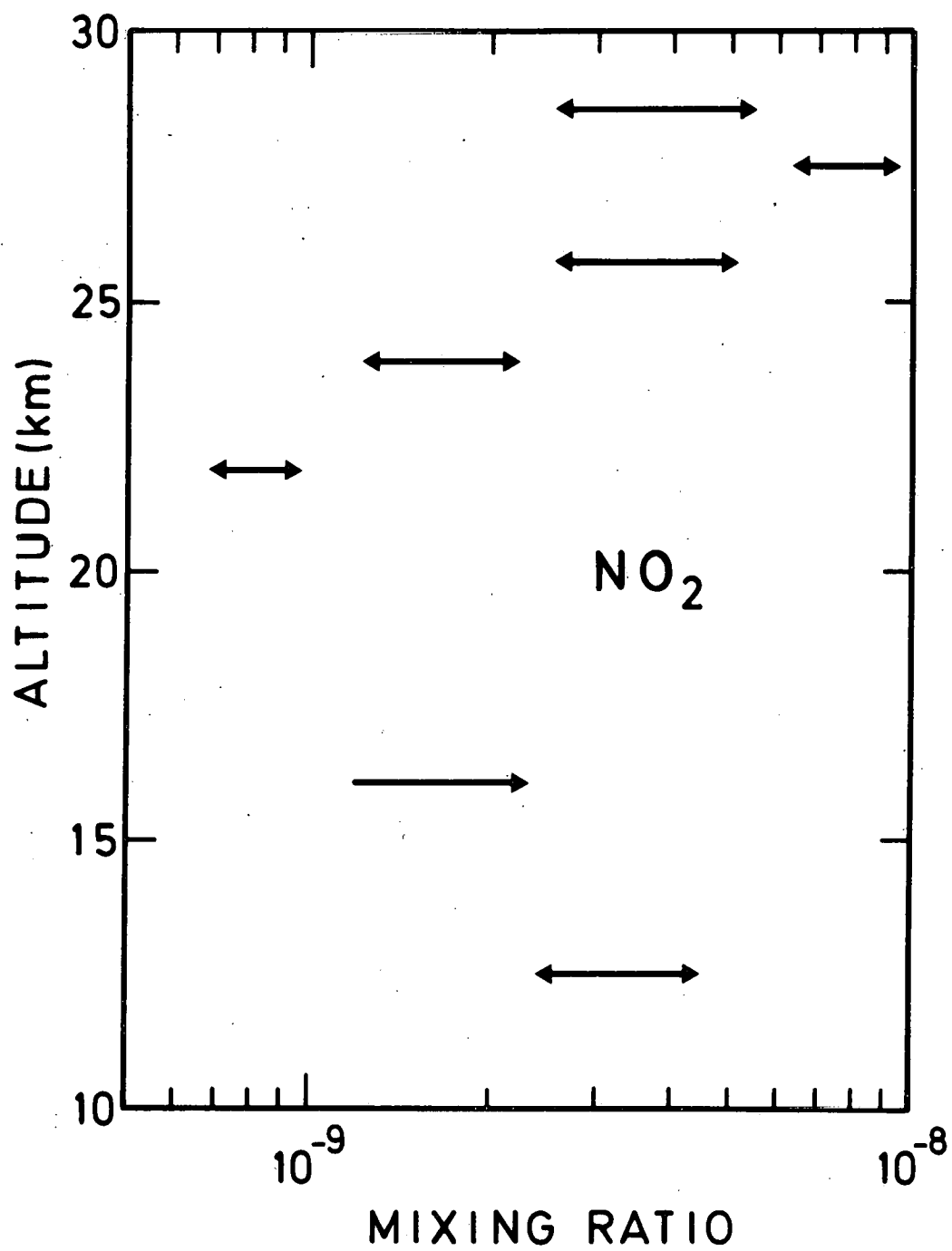
Fig. 2. Stratospheric NO_2 mixing ratio by volume.

Balloon altitude (km)	Solar zenith angle	Grazing solar rays altitude	NO_2 Mixing ratio by volume (km)	Observed band	Reference to spectra
29	94.1	12.5	$(3.4 \pm 1) \times 10^{-9}$	$\nu_1 + \nu_3$	(1, 2)
34	94.3	16.1	$< 2.3 \times 10^{-9}$	$\nu_1 + \nu_3$	(1, 2)
29.7	92.8	21.9	$(8.3 \pm 1.5) \times 10^{-10}$	ν_3	(3)
29.7	92.4	23.9	$(1.7 \pm .5) \times 10^{-9}$	ν_3	(3)
29.7	92.0	25.7	$(3.8 \pm 1.3) \times 10^{-9}$	ν_3	(3)
29.7	91.5	27.5	$(7.8 \pm 1.5) \times 10^{-9}$	ν_3	(3)
29.7	91.2	28.3	$(4.0 \pm 1.5) \times 10^{-9}$	ν_3	(3)

The relatively high value observed at the lowest altitude is thought to be due to a tropospheric influence. The mixing ratio appears to increase from 20 to 28 km showing the presence of a stratospheric layer of NO_2. This particularity might be a reason why no evidence for NO_2 has been found up to now in submillimetre stratospheric emission spectra [8] taken from an altitude of 12 km at a zenith angle of 75°.

Following the theoretical investigation made by Nicolet [9] on the role of NO_2 on the stratospheric ozone, the values listed in the table indicate an influence of natural nitrogen dioxide on O_3. In sunset conditions as it is the case for these determinations, NO_2 mixing ratios can be taken, within experimental errors, equel to NO_x.

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