Stratospheric nitrogen dioxide from infrared absorption spectra

by M. ACKERMAN and C. MULLER
FOREWORD

This article has been accepted from publication in NATURE.

AVANT-PROPOS

Cet article a été accepté pour publication dans NATURE.

VOORWOORD

Deze tekst zal in NATURE gepubliceerd worden.

VORWORT

Dieser Text wird in NATURE herausgegeben werden.
STRATOSPHERIC NITROGEN DIOXIDE FROM INFRARED ABSORPTION SPECTRA

by

M. ACKERMAN and C. MULLER

Abstract

Stratospheric absorption spectra of nitrogen dioxide have been interpreted quantitatively NO₂ 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 NO₂ de 12 à 28 km d'altitude sont présentées.

Samenvatting

De stratosferische absorptiespectra van stikstofdioxyde werden kwantitatief verklaard. De mengverhoudingen van NO₂ tussen 12 en 28 km worden vermeld.

Zusammenfassung

Stratosphärische Absorptionsspektren von Stickdioxyde werden analysiert. Die Mischungsverhältnisse von NO₂ 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, constituent 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 $\nu_3$ 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 $\nu_3$ 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 $\nu_3$ 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 °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 NO₂ mixing ratio by volume.
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, equal to NO$_x$. 

<table>
<thead>
<tr>
<th>Balloon altitude (km)</th>
<th>Solar zenith angle</th>
<th>Grazing solar rays altitude</th>
<th>NO$_2$ Mixing ratio by volume (by volume)</th>
<th>Observed band</th>
<th>Reference to spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>94.1</td>
<td>12.5</td>
<td>(3.4 ± 1) × 10$^{-9}$</td>
<td>$\nu_1 + \nu_3$</td>
<td>(1, 2)</td>
</tr>
<tr>
<td>34</td>
<td>94.3</td>
<td>16.1</td>
<td>&lt; 2.3 × 10$^{-9}$</td>
<td>$\nu_1 + \nu_3$</td>
<td>(1, 2)</td>
</tr>
<tr>
<td>29.7</td>
<td>92.8</td>
<td>21.9</td>
<td>(8.3 ± 1.5) × 10$^{-10}$</td>
<td>$\nu_3$</td>
<td>(3)</td>
</tr>
<tr>
<td>29.7</td>
<td>92.4</td>
<td>23.9</td>
<td>(1.7 ± .5) × 10$^{-9}$</td>
<td>$\nu_3$</td>
<td>(3)</td>
</tr>
<tr>
<td>29.7</td>
<td>92.0</td>
<td>25.7</td>
<td>(3.8 ± 1.3) × 10$^{-9}$</td>
<td>$\nu_3$</td>
<td>(3)</td>
</tr>
<tr>
<td>29.7</td>
<td>91.5</td>
<td>27.5</td>
<td>(7.8 ± 1.5) × 10$^{-9}$</td>
<td>$\nu_3$</td>
<td>(3)</td>
</tr>
<tr>
<td>29.7</td>
<td>91.2</td>
<td>28.3</td>
<td>(4.0 ± 1.5) × 10$^{-9}$</td>
<td>$\nu_3$</td>
<td>(3)</td>
</tr>
</tbody>
</table>
REFERENCES