Abstract. Four of the most prominent and sharpest infrared absorption features of chlorine nitrate at 780.2, 807.7, 809.4, 1292.6 cm\(^{-1}\) have been observed in a series of infrared solar spectra obtained at an unapodized spectral resolution of 0.01 cm\(^{-1}\), using the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument on board Spacelab 3.

A quantitative analysis of the \(v_4\) Q branch at 780.2 cm\(^{-1}\) has provided insight into the concentration of ClONO\(_2\) between 19 and 40 km altitude. While the mean profile deduced from 3 sunset occultations near 30\(^\circ\) N latitude exhibits a shape close to that predicted by model calculations, its concentrations in the 20 to 32 km altitude range are, however, about 30\% larger, reaching a peak concentration of \(9 \times 10^8\) molecules/cm\(^3\) at 25 km. The concentrations above 32 km, deduced from one sunrise occultation at 47\(^\circ\) S, are even larger than the corresponding sunset values at 30\(^\circ\) N latitude. Some of these discrepancies may be caused by the rather large uncertainty in the assumed Q branch strength.

The results reported here constitute a significant input towards understanding the chemistry prevailing in the stratosphere as well as for model calculations predicting the secular evolution of our atmosphere.

Introduction

The importance of the existence of chlorine nitrate in the stratosphere, first raised by Rowland et al. [1976], has been extensively and repeatedly stressed during the last decade. It is mainly based on the role which ClONO\(_2\) plays as a temporary reservoir for stratospheric chlorine, through the set of reactions:

\[
\text{ClO + NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \quad \text{(nighttime reaction)} \\
\text{ClONO}_2 + \hbar \rightarrow \text{Cl} + \text{NO}_3 \quad \text{(daytime reaction)}
\]

which involve strong coupling between the ClO\(_x\) and NO\(_x\) catalytic cycles and control the diurnal variation of ClO\(_x\).

While laboratory investigations have progressed in evaluating the rates of these reactions [JPL Publication 85-37, 1985], a milestone for a better understanding of the ClO\(_x\) catalytic cycle prevailing in the stratosphere is undoubtedly the unambiguous detection of ClONO\(_2\) above 20 km and the accurate determination of its concentration with altitude.

Graham et al. [1977] were the first to report laboratory results on the infrared absorptivity characteristics of the \(v_1\) to \(v_4\) bands of gaseous chlorine nitrate, while Murnray and Goldman [1981] and Murnray et al. [1984] have published a set of high-resolution laboratory runs at ambient temperature, showing relatively strong ClONO\(_2\) absorptions at 1735.4, 1292.6, 807.7, 780.2 cm\(^{-1}\) and between 778 and 779 cm\(^{-1}\).

Over the past several years, some of these characteristic absorptions have been searched for in solar spectra recorded during sunset occultations from balloon altitudes [Murnray et al., 1977 and 1979; Rinsland et al., 1985]. Even the last and most convincing of these attempts could only be realistically quantified as a tentative identification of the \(v_4\) Q branch of ClONO\(_2\) at 780.2 cm\(^{-1}\), as only the feature was observed in the set of balloon spectra available.

In the present article we report on the simultaneous observation of 4 of the strongest IR-absorption features of chlorine nitrate, and on the retrieval of its concentration profile between 19 and 40 km altitude using the \(v_4\) Q branch observed at 780.2 cm\(^{-1}\).

Experimental

The prime objective of the ATMOS (Atmospheric Trace Molecule Spectroscopy) experiment during its first mission (on Spacelab 3 in April-May 1985) was to provide series of high-resolution mid-infrared solar spectra recorded in the sunrise and sunset occultation mode by a fast Fourier Transform Spectrometer (FFTS). That FFTS is a double-passed Michelson interferometer yielding an unapodized spectral resolution of 0.01 cm\(^{-1}\). Using a HgCdTe detector cooled to 77\(^\circ\) K, the 600 to 4800 cm\(^{-1}\) region can be recorded in one of 4 overlapping sets of high-resolution laboratory runs at ambient temperature, showing relatively strong ClONO\(_2\) absorptions at 1735.4, 1292.6, 807.7, 780.2 cm\(^{-1}\) and between 778 and 779 cm\(^{-1}\).

The spectra from three sunset transitions (SS02, SS05 and SS08 in Table 1) obtained near 30\(^\circ\) N latitude are however, about 30\% larger, reaching a peak concentration of \(9 \times 10^8\) molecules/cm\(^3\) at 25 km.
TABLE 1

<table>
<thead>
<tr>
<th>Occultation</th>
<th>Geographical Location</th>
<th>Date</th>
<th>U. Time</th>
</tr>
</thead>
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<tr>
<td></td>
<td>LAT. Deg. LONG. Deg. Hrs.Min.</td>
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<td>Sunsets</td>
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<td></td>
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<tr>
<td>SS02</td>
<td>32N 115E</td>
<td>4/30/85</td>
<td>10.54</td>
</tr>
<tr>
<td>SS05</td>
<td>31N 0.5E</td>
<td>4/30/85</td>
<td>18.33</td>
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<tr>
<td>SS08</td>
<td>30N 115W</td>
<td>5/01/85</td>
<td>02.11</td>
</tr>
<tr>
<td>Sunrise</td>
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<td>SR06</td>
<td>47S 50W</td>
<td>5/01/85</td>
<td>10.24</td>
</tr>
</tbody>
</table>

Data Analysis

All synthetic spectra shown in the following figures have been calculated with the dedicated ATMS computer system, whose line parameters are basically those of the last versions of the AFGL-1982 [Rothman et al., 1983a, 1983b] and the GEISA [Husson et al., 1982] compilations with extensive additions or modifications from recent laboratory work compiled by one of us (L.R. Brown). The calculation of the refracted slant path transmission is based on an atmosphere in hydrostatic equilibrium, extending from 0 to 150 km altitude in 1-km thick layers homogeneous in pressure, temperature and density. Pressure and temperature values used here were directly retrieved from series of CO2 lines observed by ATMS. The fitting of the successive observed spectra is achieved by adjusting the concentrations in the various layers encountered along the corresponding slant paths; high TH runs were used to determine the background envelope while low TH sections were used to check the zero transmission level.

On the basis of laboratory spectra of atmospheric interest [Murcray et al., 1984], four ClONO2 IR-absorption features have been unambiguously identified in the ATMS occultation spectra. Of these, the $\nu_4$ Q branch near 780.2 cm$^{-1}$ is the most prominent, being the sharpest and moderately strong and relatively free of interferences from other atmospheric species; it is therefore best suited for a quantitative investigation. Figure 1 shows excerpts from seven zonal average spectra recorded at THs between 41 and 19 km and covering the 779.63 to 780.67 cm$^{-1}$ region. The vertical scaling is the same for all traces, which have been displaced for clarity. The observed discrete absorptions are mainly produced by O3, CO2 and NO2; they have been identified by the use of the existing line parameters compilations. The broad and asymmetric $\nu_4$ Q branch of ClONO2 is clearly noticeable on the tracings below 37 km TH; it extends from 780.0 to 780.3 cm$^{-1}$ with its maximum absorption occurring at 780.21 cm$^{-1}$ (position indicated by an arrow in Figures 1 and 2). A feature at 780.18 cm$^{-1}$, observed on all spectra of Figure 1, is marked with a (?) as no satisfactory identification has yet been found. Figure 2, trace A, is an enlargement of the central section of the spectrum shown in Figure 1 for the TH of 25 km. As no line parameters are available in the compilations for any of the bands of ClONO2, we have used the set of data derived by Rinsland et al. [1985] from the analysis of laboratory spectra to synthetically reproduce the observations; over 300 lines (total strength of 1.9E-19 cm/mol) were adjusted to best fit the $\nu_4$ Q branch. Also taken into account were the revised positions and intensities of those O3 and CO2 lines appearing in or near the spectral region analyzed here. Trace B of Figure 2 corresponds to the fitting of the observed spectrum, with no ClONO2 in the atmosphere; the fit is quite good except between 780.1 and 780.3 cm$^{-1}$. Adding an appropriate amount of chlorine nitrate in the

![Fig. 1. Excerpts from seven zonal average solar spectra showing the region near the 780.2 cm$^{-1}$ $\nu_4$ Q branch of ClONO2. The THs are given for each tracing. Most discrete absorptions have been identified on the basis of existing line parameters compilations. An unassigned line appearing on all spectra is noted with a (?). The arrow indicates the position where the strongest absorption of ClONO2 occurs.](image)

![Fig. 2. Example of fitting the average spectrum corresponding to 25 km TH (Trace A) in the vicinity of the $\nu_4$ Q branch of ClONO2. The 3 upper traces are the individual absorptions by ClONO2, CO2, and O3. Traces B and C show the fits achieved, respectively without and with ClONO2 in the stratosphere. The bottom part reproduces the residuals between traces A and C.](image)
layers above the corresponding TH significantly improves the fit (trace C) over the whole spectral interval. The individual absorptions produced by the three strongest absorbing gases, O$_3$, CO$_2$, and ClONO$_2$, are shown in the upper part of Figure 2; their vertical scaling is the same as that of the observed spectrum A. The bottom part of Fig. 2 indicates the residuals remaining after fitting trace A; the RMS residual over the whole interval is 0.61%; this is about twice as high as the noise level, indicating that some spectral features remain imperfectly computed. Fitting as outlined above has been applied to all spectra of Figure 1, starting at 41 km and proceeding down to 19 km; the ClONO$_2$ profile retrieved from this "onion peel" method is reproduced in Figure 5.

Figures 3 and 4 show two other ClONO$_2$ absorption features (shaded areas) observed by ATMOS and identified on the basis of comparisons with laboratory spectra of "exotic" molecules of atmospheric interest [Murcray and Goldman, 1981; Murcray et al., 1984]. The 807.7 cm$^{-1}$ absorption (which has not been assigned in terms of its vibration-rotation quantum transition) and the $v_3$ Q branch at 809.4 cm$^{-1}$ have been observed here for the first time in atmospheric transmission spectra; their shapes, relative intensities, and the altitude range over which the absorption occurs support their association with ClONO$_2$. The $v_2$ O branch of chlorine nitrate at 1292.6 cm$^{-1}$ has also been identified in spectra recorded by ATMOS during three sunsets and one sunrise. Its wide absorption extending from 1291.6 to 1293.3 cm$^{-1}$ is heavily masked by strong, interfering N$_2$O, CH$_4$, and HNO$_3$ lines. While the absorptions by N$_2$O and CH$_4$ can be computed quite accurately [Toth, 1984, 1986], the HNO$_3$ absorption cannot because of unreliable line parameters; therefore, a quantitative measurement of the concentration of ClONO$_2$, based on its $v_2$ O branch, will remain less reliable until better HNO$_3$ spectral parameters become available. Additional weaker ClONO$_2$ absorptions have also been observed (e.g. between 778 and 779 cm$^{-1}$ and at 803.4 cm$^{-1}$); the latter was identified while evaluating the absorption by the Q branch of the 802.7 cm$^{-1}$ band of NO$_2$ [Rinsland et al., 1986].

Results and Discussions

Figure 5 summarizes the results obtained so far concerning the concentration of chlorine nitrate in the stratosphere, expressed in terms of its volume mixing ratio as a function of altitude. The thick line corresponds to the profile deduced here from the average 30$^\circ$ N sunset spectra. The profile represented by the dotted line was derived from the sunrise occultation SR06 (see Table 1); this 47$^\circ$ S profile indicates larger amounts of ClONO$_2$ above 32 km (about 3 times higher in terms of the integrated column between 32 and 38 km) than found at 30$^\circ$ N. This difference may reflect both latitude and seasonal variations as predicted by Solomon and Garcia [1984], but mainly represents diurnal changes [Ko and Sze, 1984].

Both the Rinsland et al. [1985] and the present results have been derived from the $v_2$ Q branch at 780.2 cm$^{-1}$, using closely similar sets of spectroscopic line parameters. The main difference lies in the strength used for the interfering R29 line of CO$_2$ at 780.227 cm$^{-1}$, which was set 20% lower in the present analysis (as suggested by recent laboratory work carried out by L.R. Brown); that
was partly supported by the Ministère de l’Education Nationale, Belgium. We thank J. Bosseloirs for their help in various preparatory phases of this manuscript. 

At the lower Teds, the fit between observed and computed spectra deteriorates somewhat over the ClONO₂ ν₄ Q branch (especially in the central part where the observations appear deeper), indicating that either the set of ClONO₂ line parameters has not been sufficiently adjusted to the contours observed in the laboratory or that the ClONO₂ absorption is indeed temperature dependent. No such temperature dependence can be inferred from the laboratory data published until now. Earlier balloon results obtained by Murcray et al. [1979] have been included in Figure 5 for completeness; as they were derived from evidence for absorption by the ν₂ O branch of ClONO₂ at 1292.6 cm⁻¹, they should be considered with caution for the reasons mentioned earlier.

The main sources of uncertainty in the values retrieved here are of instrumental, geometric, atmospheric and spectroscopic origin. Instrumental effects (smearing, limited S/N ratio, zero transmission level shifts, etc.) may amount to as much as 20% uncertainty in the results above 25 km and 10% below. Relative errors in line intensity uncertainties have been evaluated as 10% above 25 km and 20% below. Uncertainties originating from spectroscopic corrections for interferences by other species range from 30% above 30 km to 20% below. Pressure and temperature inaccuracies introduce an error of perhaps 10% over the whole altitude range. The resulting 2σ errors are 45% at 37 km, 30% at 30 km and 33% at 20 km.

The absolute uncertainty in the integrated intensity of the ν₄ Q branch of ClONO₂ may be as high as ± 50% (Rinsland et al., 1985); this parameter, which has not been included in the above error estimates, along with the temperature dependence of the integrated intensity and the shape of the O branch, is the principal source of systematic uncertainty which limits severely the absolute accuracy for ClONO₂ profile determinations. This prohibits speculating about the difference between the present results and the model predictions also shown in Figure 5 (N.D. Sze, private communication, 1986). It should be noticed, however, that all the results displayed in Figure 5 are equally and similarly hampered by this factor, as they are all derived with reference to the same laboratory samples of ClONO₂. Further laboratory research is needed to establish a reliable set of line parameters for all of the ClONO₂ absorption features which can now be clearly observed in the spectra. The data reported here represent the first time infrared atmospheric chlorine nitrate bands have been observed simultaneously; the four features observed in the ATMOS spectra provide an unambiguous identification of the presence of ClONO₂ in the stratosphere.

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