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Abstract

Stratospheric volume mixing ratio profiles of chlorine nitrate (ClONO$_2$) have been retrieved from 0.01 cm$^{-1}$ resolution infrared solar occultation spectra recorded at latitudes between 34$^\circ$N and 54$^\circ$S by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer during the ATLAS 1 shuttle mission (March 24 to April 2, 1992). The results were obtained from nonlinear least-squares fittings of the ClONO$_2$ $\nu_4$ band Q branch at 780.21 cm$^{-1}$ with improved spectroscopic parameters generated on the basis of recent laboratory work. The individual profiles, which have an accuracy of about 120%, are compared with previous observations and model calculations.
1. Introduction

The second flight of the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer as part of the Atmospheric Laboratory for Applications and Science (ATLAS)-1 shuttle mission (March 24-April 2, 1992) [Gunson, 1992] provided the opportunity to obtain sets of nearly simultaneous concentration measurements of over two dozen stratospheric molecules about 9 1/2 months after the massive eruption of the Mt. Pinatubo volcano in the Philippine Islands and 6 years and 11 months after the first ATMOS flight onboard Spacelab 3 [Farrer, 1987; Farmer et al., 1987]. Of prime scientific interest are the measurements of trace gases involved in stratospheric ozone chemistry. In this paper, we report ATMOS/ATLAS-1 stratospheric volume mixing ratio (VMR) profiles of chlorine nitrate (ClONO$_2$), an important diurnally varying chlorine reservoir inhibiting ozone destruction by the ClO$_3$ catalytic cycle. Comparisons of these results with previous measurements and model calculations are also reported.

2. Observations

During the ATLAS-1 shuttle mission, the ATMOS Fourier transform spectrometer recorded ~10,000 two-sided solar interferograms with a maximum path difference of 67.5 cm. The spectra derived from processing these interferograms have an unapodized resolution of ~0.01 cm$^{-1}$. The measurements were obtained from an orbital altitude of ~300 km during 53 sunrises occurring between 30°N and 32°S latitude and 41 sunsets observed between 22°S and 54°S latitude. The 2.2-s intervals between successive observations corresponded to tangent height separations of ~7.5 km in the mid-stratosphere. The intensities in the atmospheric spectra were divided at each wavelength by the corresponding values in an exoatmospheric spectrum obtained by averaging all the high sun spectra.
and by normalizing the intensities on the basis of laboratory

and spectroscopic parameters.

In. the atmosphere was very thick, it could not account for the sun at least the regions where the attenuation by the

is obstructed covered of the forested (planted) areas and is limited to

parameters for the J8 ocean action even studied in this work. Here the key

feature of the plant species is detectable, probably, one of the key

in the 780 cm$^{-1}$ region where the most important C-O, C=O, and C-N

spectra obtained with J8 etc to have the best species. O-18 is not

C-O, C=O, and C-N

and C-O, C=O, and C-N
data. First, a terrestrial $^{35}\text{Cl}/^{37}\text{Cl}$ isotope ratio of 3.086 was assumed in
computing the relative intensities of the $\nu_4$ bands of $^{35}\text{ClONO}_2$ and $^{37}\text{ClONO}_2$. Next, the relative intensity of the $^{35}\text{ClONO}_2$ hot band with respect to the other two bands was adjusted to match the relative band strengths in a 0.002-cm$^{-1}$ resolution laboratory spectrum recorded at room temperature [Goldman et al., 1989, Fig. 8, spectrum C]. The $\text{ClONO}_2$ volume mixing ratio in the laboratory sample was then determined by comparing the integrated intensity in the 750-830-cm$^{-1}$ region with values reported in the literature [Davidson et al., 1987; Ballard et al., 1988; Tuszon and Wallington, 1989] and by fitting the $^{35}\text{ClONO}_2$ Q branch in the laboratory spectrum with the empirical line parameters of Ballard et al. [1988]. The standard deviation of these four VMR determinations is 16%. Finally, assuming the mean VMR as the correct value for the laboratory sample, a factor to scale the relative intensities in the line list to absolute values was derived by least-squares fitting the laboratory spectrum in the $^{35}\text{ClONO}_2$ $\nu_4$ Q branch region with the new line parameters. The derived intensity scaling factor is estimated to be accurate to about 12%. The sum of the intensities in units of cm$^{-1}$/molecule-cm$^2$) at 296 K and the number of lines in the list are $1.439 \times 10^{-16}$ and 11495 for the $\nu_4$ band of $^{35}\text{ClONO}_2$, $4.656 \times 10^{-19}$ and 10211 for the $\nu_4$ band of $^{37}\text{ClONO}_2$, and $9.191 \times 10^{-19}$ and 10493 for the $\nu_4 + \nu_9 - \nu_9$ hot band of $^{35}\text{ClONO}_2$, respectively.

The average room temperature $N_2$-broadening coefficient of 0.14 cm$^{-1}$ atm$^{-1}$ measured in the $\nu_4$ band $^{35}\text{ClONO}_2$ Q branch [Belli et al., 1992] has been adopted at 296 K for the atmospheric retrievals along with a $T^{0.75}$ temperature dependence for the line widths. Simulations with the new line list do not reproduce the rotational fine structure observed near 780.15 cm$^{-1}$ in the low pressure laboratory spectra [e.g., Goldman et al., 1989, Fig. 8], but published plots of
The pressure-temperature trajectories are projected as lines in the ensemble were developed directly from the spectra using a procedure developed by C. P. Smith.

Calculations (e.g., 1990; Kornilov and Khrizman, 1997). The selection algorithms include corrections for various partition functions. Some physical models and spectroscopic parameters are adopted, both in the temperature and pressure-dependent results in the CRONOZ volume mixing ratios in agreement to about 30 km. Above 35 km, the temperature dependence is the main focus of a set of microturbulences in [C] spectra. These results are [C] and [C] (Guenther et al., 1999) and based on a “togethers” approach with another [C] reported in independently developed a [C] Nasa Langley Research Center (1998). The CRONOZ results have been compared to other results performed in the [C] atmospheric development of the [C] photometry (1997). Not on and below 80 km, the CRONOZ profiles reported here were retrieved with the CRONOZ (Korth et al., 1992) and the Coriolis (Browne et al., 1977) for the AMOS. The [C] in the CRONOZ and the AMOS were taken from an updated version of the Coriolis, except for (K. Browne, private communication, 1999) of the AMOS parameters. The spectroscopic parameters for other molecules were taken from the Coriolis (Korth et al., 1992). In similar the CRONOZ, a branch the structure are retrieved for stratospheric complete geophysical and 30 km. [Korth et al., 1992, Fig. 4]. Therefore, the CRONOZ, a branch is barely noticeable above a total pressure of 10 mb and amplitudes above a spectra broadened by N2 show that this structure within the
(manuscript in preparation, 1994). Briefly, the ODS algorithm is used to perform independent, onion-peeling, CO$_2$ VMR retrievals from 100 narrow intervals, each centered on an isolated CO$_2$ line. The tangent-layer CO$_2$ VMRs retrieved from each spectrum are then least-squares fitted as a function of the CO$_2$ line lower state energy to determine corrections to initial guesses for the rotational temperature (which is assumed to equal the kinetic temperature) and the atmospheric pressure in the layer. A CO$_2$ profile equal to a constant VMR of $3.47 \times 10^{-6}$ in the lower stratosphere increasing to $3.54 \times 10^{-6}$ in the troposphere has been assumed for the 1992 ATMOS/ATM mission. This iterative procedure converges rapidly and results in pressures with estimated precisions of 5% below 35 km and 3% up to 70 km and temperatures with precisions of 1 to 2 K.

The ClONO$_2$ profiles were derived from fittings over a 0.6-cm$^{-1}$ wide microwindow centered on the $3^5$ClONO$_2$ $\nu_4$ band Q branch at 780.21 cm$^{-1}$. The primary interferences in this interval are O$_3$ and CO$_2$ lines with weaker absorptions from $\nu_6$ band of HNO$_3$ [Goldman et al., 1989; Zander et al., 1990]. In the ODS retrievals, the O$_3$ profile was first retrieved and then held fixed during the analysis for ClONO$_2$ while simultaneous fittings for the profiles of both molecules were performed with the large algorithm. Sensitivity tests indicate that realistic differences in the assumed HNO$_3$ profile have a negligible (<2%) effect on the retrieved ClONO$_2$ profile.

Figure 1 shows a comparison of least-squares fits obtained with the new ClONO$_2$ line parameters and the empirical ClONO$_2$ line parameters [Balard et al., 1988] used in the ATMOS 1SpaceLab 3 retrievals [Zander et al., 1990, 1992]. The new list produces slightly better fittings to the ATMOS spectra than the old list, both near the peak of the ClONO$_2$ Q branch where more absorption is now predicted and in the low wavenumber wing of the Q branch where less absorption
is now predicted (the same improvements have been noted from least-squares fits to the University of Denver ClONO₂ laboratory spectra).

No obvious differences were found among the six tropical sunrise profiles between 15.7° N and 16.7° S latitude or among the seven sunset profiles recorded between 44.5° S and 55.4° S latitude. Therefore, in Table 2 we report mean profiles for these two latitude bands along with a separate entry for the sunrise (SR) occultation SR03 at 78.2° S latitude.

The sources of random (R) and systematic (S) error and the 1-sigma uncertainty in the ClONO₂ VMR resulting from each error source are (1) instrumental effects (R), primarily due to the finite signal-to-noise ratio, ±8% at 20 to 30 km increasing to ±20% at 35 km; (2) the tangent pressure (R), ±15%; (3) the temperature profile (R), ±11%; (4) the assumed ClONO₂ line parameters (S), ±12%; (5) the CO₂ parameters assumed in the pressure-temperature retrieval (S), ±13%; (6) the assumed CO₂ volume mixing ratio profile (S), ±12%; and (7) the simulation of interfering spectral absorptions (R), ±4% at 20 to 30 km increasing to ±10% at 35 km. A total-1-sigma error of ±16% at 20 to 30 km increasing to ±26% at 35 km and a 1-sigma precision of ±11% at 20 to 30 km increasing to ±23% at 35 km for a single profile have been computed from the square root of the sum of the squares of the individual errors. The errors in Table 2 assume that the magnitude of the random errors is reduced by the square root of the number of averaged retrievals.

5. Discussion

Tropical ClONO₂ profile measurements have been reported prior to the present work. However, the southern hemisphere ATLAS I zonal mean sunset profile can be compared with the May 1985 Spacelab 3 sunrise profile at 47° S
latitude. For consistency, we reanalyzed the Spacelab 3 data with the new \textit{ClONO}_2 line list and a pressure-temperature profile retrieved with the algorithm described earlier. The upper panel of Figure 2 shows these two measured profiles.

The lower panel of Figure 2 presents three sets of \textit{ClONO}_2 profiles calculated for 47°S latitude with the Atmospheric and Environmental Research Inc. (AER) two-dimensional chemistry-transport model (NASA, 1993, Chap. 4). The solid curves are model-sunset profiles for day 90 of 1992 (appropriate for the ATLAS 1 mission observations), the long-dashed curves are model-sunrise profiles for day 170 of 1992, and the short-dashed curves are model-sunrise profiles for day 170 of 1985 (appropriate for the Spacelab 3 mission observations). Stratospheric total inorganic chlorine abundances at 5.25, 14.3, 38.8, and 63.9 mb were 3.28, 3.05, 3.00, and 1.28 ppbv (parts per billion, 10^{-9} by volume) for the 1992 calculations and 4.45, 3.30, 1.51, and 0.94 ppbv for the 1985 calculations, respectively. The three curves for each 1992 set represent calculations for gas-phase chemistry only, heterogeneous chemistry with background aerosol levels [World Meteorological Organization (WMO), 1992, Table 8.8], and heterogeneous chemistry with the volcanic aerosol surface as a profiles derived from Stratospheric Aerosol and Gas Experiment (SAGE I) measurements ([L. K. Yue, private communication, 1993]). The two curves for 1985 show calculations with gas-phase chemistry only and heterogeneous chemistry at background aerosol levels.

The heterogeneous chemistry calculations include two reactions:

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_3 \]  
\[ \text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCI} \]
The parameterization for reaction 1 is described by Rodríguez et al. [1991] with an assumed reaction probability per reaction of 0.1. The parameterization for reaction 2 is given in NASA [1993]. Aljol-story studies [Tolbert et al., 1988; Hanson and Ravi Shankar, 1991] indicate low probabilities for reaction (2) in the nonpolar stratosphere. The effect of this reaction on the AER model results shown in Figures 2 and 3 is small.

Three conclusions can be drawn from the results in Figure 2. First, comparison of the solid curves in the lower panel shows that the inclusion of heterogeneous chemistry with the volcanic aerosol levels occurring during the ATLAS 1 mission changes the calculated ClONO$_2$ volume mixing ratios by less than 10% at 47° S latitude for 5 to 40 mb. Second, comparison of the solid and long-dashed model curves in the lower panel shows that changes in the ClONO$_2$ volume mixing ratio due to the combined diurnal and seasonal differences between the S$^2$ ace$^2$ and ATLAS 1 missions are small for altitudes below 30 km. The small diurnal change in ClONO$_2$ below 30 km agrees with previous model calculations [Ko and Sze, 1984, Fig. 6]. Third, the measured ClONO$_2$ profiles for both 1985 and 1992 are significantly lower than the corresponding model profiles with the largest relative differences occurring near the VMR peak. The measured ATLAS 1 profile has a peak ClONO$_2$ mixing ratio of 0.94 ± 0.16 ppbv at 16 mb whereas the corresponding AER model sunset profile computed with heterogeneous chemistry and the ATLAS 1 volcanic aerosol levels reaches a maximum of 1.56 ppbv at 14.3 mb.

Although the absolute values are significantly different, the measured 1992-to-1985 ClONO$_2$ ratios at 47° S latitude are in better agreement with the corresponding model predictions. Adopting the 1992 clay 90 sunset calculations with the volcanic aerosol levels for the ATLAS 1 mission and the 1985 day 1
sunrise background heterogeneous chemistry calculations for the Spacelab 3 mission, we derive model 1997 sunset to 1985 sunrise ClONO₂ ratios of 1.18, 1.31, 1.30, and 1.39 at 0, 16, 30, and 50 mb, respectively, whereas the measured ratios (and 1-sigma uncertainties) at the same pressure levels are 1.36, 1.0±0.15, 1.49±0.17, and 1.12±0.13, respectively.

Figure 3 shows the mean tropical sunrise profile from the ATLAS 1 mission and the corresponding AER model predictions with heterogeneous chemistry and the March 1997 aerosol levels. Again, the measurements are systematically lower than the model calculations with the largest discrepancies occurring near the VMR peak. The May 1985 ATMOS/Spacelab 3 ClONO₂ 30° N sunset profile [Zander et al., 1990; 1997] is uniformly lower by about a factor of 1.5 than profiles calculated by five modeling groups for the same conditions [NASA, 1993, Chap. 5, section M]. A revised retrieval obtained with the new ClONO₂ 1 inferred and an improved temperature profile slightly increases the discrepancies. These model-measurement differences are significant given the important role of ClONO₂ in buffering O₃ destruction. Natarajan and Cal 1 is [1991] found that a secondary path for the reaction OOH + ClO, leading to the product ion of HCl, would improve the agreement between their model calculations and the Spacelab 3 measurements of ClONO₂ and HCl.

Recently, Webster et al. [1993] estimated ClONO₂ volume mixing ratios in the northern hemisphere mid- to high-latitude lower stratosphere based on N₂O and HCl measurements obtained during December 1991 and March 1992 aircraft flights outside of polar stratospheric cloud (PSC)-processed regions. Their inferred ClONO₂ VMRs are about a factor of 2 higher than the ATMOS/ATLAS 1 values corresponding to the same N₂O volume mixing ratio. A detailed analysis of stratospheric chlorine partitioning based on ATMOS/ATLAS 1 measurements including.
additional chlorine-bearing species, particularly HCl, and important chemically-linked species (e.g., CH₁, which affects the HCl distribution) will be reported in the near future (M. R. Gunisori, manuscript in preparation, 1994).

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References


Table 1. ATMOS/ATLAS 1 Occultations Analyzed in this Study

<table>
<thead>
<tr>
<th>Occultation Name*</th>
<th>Date, UT</th>
<th>Latitude,‡</th>
<th>Longitude,‡</th>
<th>Minimum Tangent Height (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S325</td>
<td>March 29, 1992</td>
<td>44.5°S</td>
<td>251.7°E</td>
<td>21.1</td>
</tr>
<tr>
<td>S326</td>
<td>March 29, 1992</td>
<td>46.2°S</td>
<td>293.9°E</td>
<td>19.9</td>
</tr>
<tr>
<td>S331</td>
<td>March 29, 1992</td>
<td>47.7°S</td>
<td>336.5°E</td>
<td>10.5</td>
</tr>
<tr>
<td>S337</td>
<td>March 30, 1992</td>
<td>50.6°S</td>
<td>245.9°E</td>
<td>18.8</td>
</tr>
<tr>
<td>S341</td>
<td>March 31, 1992</td>
<td>51.0°S</td>
<td>130.3°E</td>
<td>19.7</td>
</tr>
<tr>
<td>S343</td>
<td>April 1, 1992</td>
<td>53.6°S</td>
<td>241.0°E</td>
<td>21.9</td>
</tr>
<tr>
<td>S348</td>
<td>April 2, 1992</td>
<td>55.4°S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S35</td>
<td>March 25, 1992</td>
<td>28.2°S</td>
<td>300.8°E</td>
<td>5</td>
</tr>
<tr>
<td>S36</td>
<td>March 26, 1992</td>
<td>16.7°S</td>
<td>184.9°E</td>
<td>29.2</td>
</tr>
<tr>
<td>S37</td>
<td>March 28, 1992</td>
<td>0.6°S</td>
<td>202.3°E</td>
<td>28.4</td>
</tr>
<tr>
<td>S38</td>
<td>March 29, 1992</td>
<td>3.2°N</td>
<td>89.0°E</td>
<td>27.3</td>
</tr>
<tr>
<td>S39</td>
<td>March 29, 1992</td>
<td>8.2°N</td>
<td>222.3°E</td>
<td>27.1</td>
</tr>
<tr>
<td>S40</td>
<td>March 29, 1992</td>
<td>9.2°N</td>
<td>177.0°E</td>
<td>26.9</td>
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<tr>
<td>S41</td>
<td>March 30, 1992</td>
<td>15.7°N</td>
<td>219.8°E</td>
<td>27.1</td>
</tr>
</tbody>
</table>

*SS denotes sunset; SR, sunrise. The data were recorded with a 2.8-mrad diameter field of view corresponding to a 5.5-km vertical altitude range at the tangent point.

‡Tangent point location at a tangent altitude of 30 km.

#A few additional Spec et ra were recorded in the troposphere.
Table 2. ATMOS/ATLAS 1 ClONO₂ Retrieval Results

<table>
<thead>
<tr>
<th>Pressure (mb)</th>
<th>Approximate Altitude (km)</th>
<th>ClONO₂ Volume Mixing Ratio, $10^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15.7°N-16.7°S†</td>
</tr>
<tr>
<td>4</td>
<td>37.8</td>
<td>0.30(8)</td>
</tr>
<tr>
<td>5</td>
<td>36.2</td>
<td>0.46(10)</td>
</tr>
<tr>
<td>7</td>
<td>33.8</td>
<td>0.63(13)</td>
</tr>
<tr>
<td>10</td>
<td>31.4</td>
<td>0.78(15)</td>
</tr>
<tr>
<td>16</td>
<td>28.2</td>
<td>0.69(17)</td>
</tr>
<tr>
<td>30</td>
<td>24.0</td>
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<tr>
<td>50</td>
<td>20.8</td>
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</tr>
<tr>
<td>70</td>
<td>18.7</td>
<td></td>
</tr>
</tbody>
</table>

§Values in parenthesis are 1-sigma uncertainties in units of the last digit.
†Average of the profiles from 6 sunrise occultations.
*refile from sunrise occultation SR03.
‡Average of the profiles from 7 sunset occultations.
Figure Captions

Figure 1. Comparison of spectral fitting results obtained with the new ClONO$_2$ line parameters described in section 3 (labeled RNL) and the empirical ClONO$_2$ line parameters derived from laboratory measurements at the Rutherford Appleton laboratory by Ballard et al. [1988] (labeled RAL). The observed spectrum was recorded on March 25, 1992, at a tangent pressure of 30.6 mb during occultation SRO3 (28.2° S latitude). The arrow marks the approximate location of the maximum absorption by the $^{35}$ClONO$_2$ $\nu_4$ band Q branch. The measured spectrum has been apodized with Norton and Beer [1976, 1977] function number 2.

Figure 2. Upper frame: Comparison of ATMOS ClONO$_2$ profiles retrieved near 47° S latitude from the 1985 Spacelab 3 and the 1992 ATLAS I spectra. The Spacelab 3 profile is a revised retrieval obtained from the single sunrise occultation recorded on May 1, 1985. The ATLAS I profile is the mean of the individual profiles retrieved for the 7 sunset occultations listed in Table 1. Error bars are estimated 1-sigma precision. Lower frame: AER 47° S latitude model calculations for day 90 of 1992, sunset (solid curves), clay 120 of 1992, sunrise (long dashed curves), and day 170 of 1985 (short dashed curves). See text for details.

Figure 3. Comparison of the mean ATMOS/ATLAS I ClONO$_2$ tropical sunrise profile and AER model profiles calculated for day 90 of 1992 with heterogeneous chemistry and an aerosol surface area density profile from SAGE II for the same time period. Because of the high aerosol
loading in the tropics from the Mt. Pinatubo volcanic eruption of June 1991, no stratospheric observations were obtained below ~27 km altitude.
Figure 1

Obs. - Calc. (%) vs. Wavenumber (cm$^{-1}$)

- Atmos
- Bell
- Ral
Figure 2

Sunrise SL3 47°S
5/1/85
Sunset ATLAS 1
45°S- 55°S Mean
3/29- 4/2/92

AER Model 47°S
- Day 90 1992 SS
- Day 120 1992 SI
- Day 120 1985 SI
Figure 3

Pressure (mb)

Approximate Altitude (km)

C10N02 Volume Mixing Ratio (ppbv)

- ATOMS

AER MODEL

- 9°N
- 0°
- 90s
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