

OBSERVATION OF SEVERAL CHLORINE NITRATE (ClONO<sub>2</sub>) BANDS IN STRATOSPHERIC INFRARED SPECTRAR. Zander<sup>1</sup>, C. P. Rinsland<sup>2</sup>, C. B. Farmer<sup>3</sup>, L. R. Brown<sup>3</sup>, and R. H. Norton<sup>3</sup><sup>1</sup>Institute of Astrophysics, University of Liege, Belgium<sup>2</sup>Atmospheric Sciences Division, NASA Langley Research Center<sup>3</sup>Jet Propulsion Laboratory, California Institute of Technology

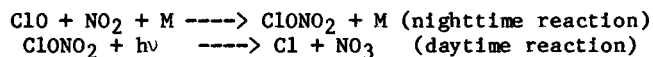
**Abstract.** Four of the most prominent and sharpest infrared absorption features of chlorine nitrate at 780.2, 807.7, 809.4 and 1292.6 cm<sup>-1</sup> have been observed in a series of infrared solar spectra obtained at an unapodized spectral resolution of 0.01 cm<sup>-1</sup>, using the Atmospheric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

A quantitative analysis of the  $\nu_4$  Q branch at 780.2 cm<sup>-1</sup> has provided insight into the concentration of ClONO<sub>2</sub> between 19 and 40 km altitude. While the mean profile deduced from 3 sunset occultations near 30° 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<sup>3</sup> at 25 km. The concentrations above 32 km, deduced from one sunrise occultation at 47° S, are even larger than the corresponding sunset values at 30° 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<sub>2</sub> plays as a temporary reservoir for stratospheric chlorine, through the set of reactions:



which involve strong coupling between the ClO<sub>x</sub> and NO<sub>x</sub> catalytic cycles and control the diurnal variation of ClO.

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<sub>x</sub> catalytic cycle prevailing in the stratosphere is undoubtedly the unambiguous detection of ClONO<sub>2</sub> 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

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Paper number 6L6171.  
0094-8276/86/006L-6171\$03.00

characteristics of the  $\nu_1$  to  $\nu_4$  bands of gaseous chlorine nitrate, while Murcray and Goldman [1981] and Murcray et al. [1984] have published a set of high-resolution laboratory runs at ambient temperature, showing relatively strong ClONO<sub>2</sub> absorptions at 1735.4, 1292.6, 809.4, 807.7, 780.2 cm<sup>-1</sup> and between 778 and 779 cm<sup>-1</sup>.

Over the past several years, some of these characteristic absorptions have been searched for in solar spectra recorded during sunset occultations from balloon altitudes [Murcray 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  $\nu_4$  Q branch of ClONO<sub>2</sub> at 780.2 cm<sup>-1</sup>, as only that 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  $\nu_4$  Q branch observed at 780.2 cm<sup>-1</sup>.

## 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<sup>-1</sup>. Using a HgCdTe detector cooled to 77° K, the 600 to 4800 cm<sup>-1</sup> region can be recorded in one of 4 overlapping intervals delineated by interference filters. Details of the instrument and its peripherals as well as the rationale for the experiment can be found in Farmer and Raper [1986].

For the purpose of the research described here, pairs of spectra Fourier transformed from single-sided interferograms measured between successive zero path difference positions, were averaged and apodized to 0.015 cm<sup>-1</sup> spectral resolution; they yield atmospheric transmission characteristics at about 4 km vertical separation. Furthermore, the spectra from three sunset transitions (SS02, SS05 and SS08 in Table 1) obtained near 30° N latitude and at approximately equal tangent heights (THs) were averaged to provide a set of "zonal average" sunset spectra, achieving in that way a signal-to-noise ratio in excess of 400 over the 600 to 1200 cm<sup>-1</sup> region. The individual occultations considered in this paper, covering the 150 to 10 km TH range, are detailed in Table 1.

The zonal average sunset spectra are designated hereafter as "Z.1.3SS.xx", where the two last digits give the corresponding THs.

TABLE 1

Occultation	Geographical Location		Date	U. Time
	LAT.	LONG.		
	Deg.	Deg.		
<u>Sunsets</u>				
SS02	32N	115E	4/30/85	10.54
SS05	31N	0.5E	4/30/85	18.33
SS08	30N	115W	5/01/85	02.11
<u>Sunrise</u>				
SRO6	47S	50W	5/01/85	10.24

## Data Analysis

All synthetic spectra shown in the following figures have been calculated with the dedicated ATMOS 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 CO<sub>2</sub> lines observed by ATMOS. 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 ClONO<sub>2</sub> IR-absorption features have been unambiguously identified in the ATMOS occultation spectra. Of

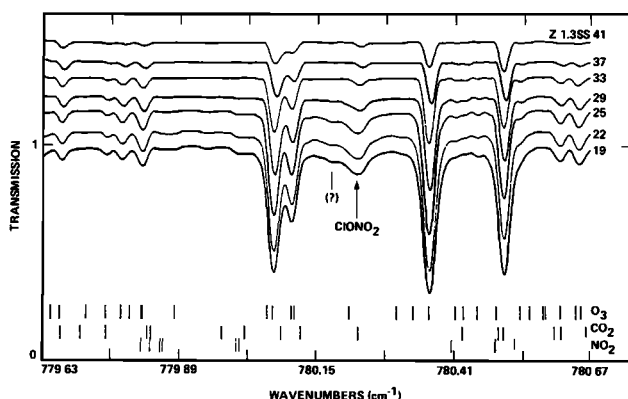


Fig. 1. Excerpts from seven zonal average solar spectra showing the region near the 780.2 cm<sup>-1</sup>  $\nu_4$  Q branch of ClONO<sub>2</sub>. The THs are given for each tracing. Most discrete absorptions have been identified on the basis of existing line parameters compilations. An unassigned line appearing on all spectra is noted with a (?). The arrow indicates the position where the strongest absorption of ClONO<sub>2</sub> occurs.

these, the  $\nu_4$  Q branch near 780.2 cm<sup>-1</sup> 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<sup>-1</sup> region. The vertical scaling is the same for all traces, which have been displaced for clarity. The observed discrete absorptions are mainly produced by O<sub>3</sub>, CO<sub>2</sub> and NO<sub>2</sub>; they have been identified by the use of the existing line parameters compilations. The broad and asymmetric  $\nu_4$  Q branch of ClONO<sub>2</sub> is clearly noticeable on the tracings below 37 km TH; it extends from 780.0 to 780.3 cm<sup>-1</sup> with its maximum absorption occurring at 780.21 cm<sup>-1</sup> (position indicated by an arrow in Figures 1 and 2). A feature at 780.18 cm<sup>-1</sup>, 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 ClONO<sub>2</sub>, 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 O<sub>3</sub> and CO<sub>2</sub> 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 ClONO<sub>2</sub> in the atmosphere; the fit is quite good except between 780.1 and 780.3 cm<sup>-1</sup>. Adding an appropriate amount of chlorine nitrate in the

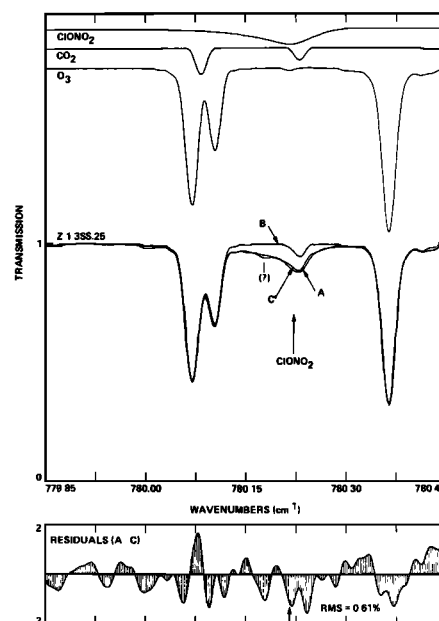


Fig. 2. Example of fitting the average spectrum corresponding to 25 km TH (Trace A) in the vicinity of the  $\nu_4$  Q branch of ClONO<sub>2</sub>. The 3 upper traces are the individual absorptions by ClONO<sub>2</sub>, CO<sub>2</sub>, and O<sub>3</sub>. Traces B and C show the fits achieved, respectively without and with ClONO<sub>2</sub> in the stratosphere. The bottom part reproduces the residuals between traces A and C.

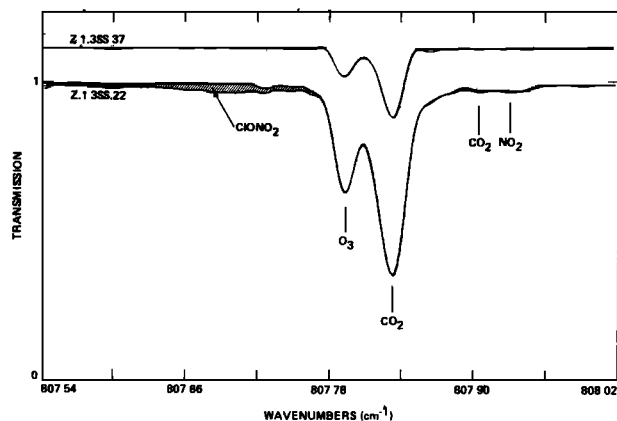


Fig. 3. Two excerpts from the average zonal spectra corresponding to THs of 37 and 22 km. The  $\text{ClONO}_2$  absorption at  $807.65 \text{ cm}^{-1}$  (shaded area) is clearly observed in the 22 km-TH run.

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,  $\text{O}_3$ ,  $\text{CO}_2$ , and  $\text{ClONO}_2$ , 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  $\text{ClONO}_2$  profile retrieved from this "onion peel" method is reproduced in Figure 5.

Figures 3 and 4 show two other  $\text{ClONO}_2$  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  $807.7 \text{ cm}^{-1}$  absorption (which has not been assigned in terms of its vibration-rotation quantum transition) and the  $\nu_3$  Q branch at  $809.4 \text{ cm}^{-1}$  have been observed here for the

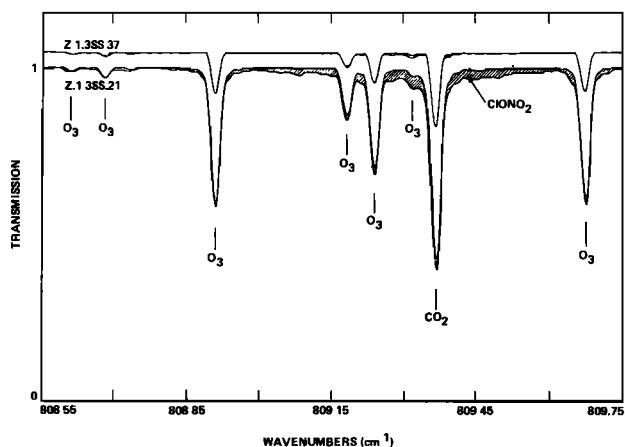


Fig. 4. Two additional excerpts from the average zonal spectra used for Fig. 3. The  $\text{ClONO}_2$  absorption at  $809.4 \text{ cm}^{-1}$  (shaded area) is clearly observed in the lower trace.

first time in atmospheric transmission spectra; their shapes, relative intensities, and the altitude range over which the absorption occurs support their association with  $\text{ClONO}_2$ . The  $\nu_2$  Q branch of chlorine nitrate at  $1292.6 \text{ cm}^{-1}$  has also been identified in spectra recorded by ATMOS during three sunsets and one sunrise. Its wide absorption extending from  $1291.6$  to  $1293.3 \text{ cm}^{-1}$  is heavily masked by strong, interfering  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{HNO}_3$  lines. While the absorptions by  $\text{N}_2\text{O}$  and  $\text{CH}_4$  can be computed quite accurately [Toth, 1984, 1986], the  $\text{HNO}_3$  absorption cannot because of unreliable line parameters; therefore, a quantitative measurement of the concentration of  $\text{ClONO}_2$ , based on its  $\nu_2$  Q branch, will remain less reliable until better  $\text{HNO}_3$  spectral parameters become available. Additional weaker  $\text{ClONO}_2$  absorptions have also been observed (e.g. between  $778$  and  $779 \text{ cm}^{-1}$  and at  $803.4 \text{ cm}^{-1}$ ); the latter was identified while evaluating the absorption by the Q branch of the  $802.7 \text{ cm}^{-1}$  band of  $\text{HO}_2\text{NO}_2$  [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  $30^\circ \text{ N}$  sunset spectra. The profile represented by the dotted line was derived from the sunrise occultation SRO6 (see Table 1); this  $47^\circ \text{ S}$  profile indicates larger amounts of  $\text{ClONO}_2$  above 32 km (about 3 times higher in terms of the integrated column between 32 and 38 km) than found at  $30^\circ \text{ N}$ . 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  $\nu_4$  Q branch at  $780.2 \text{ cm}^{-1}$ , using closely similar sets of spectroscopic line parameters. The main difference lies in the strength used for the interfering R29 line of  $\text{CO}_2$  at  $780.227 \text{ cm}^{-1}$ , which was set 20% lower in the present analysis (as suggested by recent laboratory work carried out by L.R. Brown); that

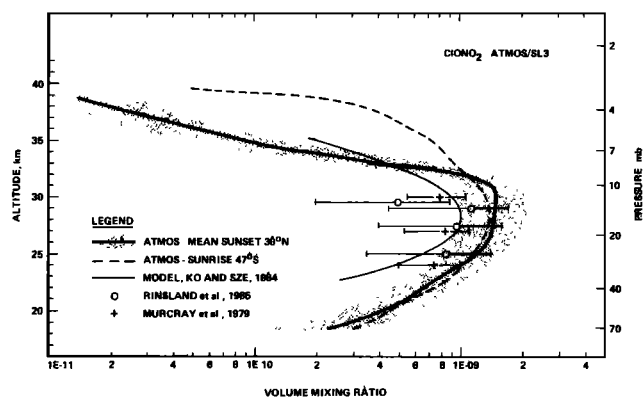


Fig. 5. Comparison of the concentration profiles of  $\text{ClONO}_2$  retrieved here from ATMOS observations and earlier evaluations from balloon data. The model results for  $30^\circ \text{ N}$  sunset are from Sze (private communication, 1986). The shaded area corresponds to the  $2\sigma$  uncertainty in the results.

difference can at most explain 15% of the factor of 1.4 between the integrated vertical columns above 25 km derived by Rinsland et al. ( $3.8E14$  mol/cm<sup>2</sup>) and the present mean zonal value ( $5.2E14$  mol/cm<sup>2</sup>), both corresponding to 30° N but 4 years apart. At the lower THs, the fit between observed and computed spectra deteriorates somewhat over the ClONO<sub>2</sub>  $\nu_4$  Q branch (especially in the central part where the observations appear deeper), indicating that either the set of ClONO<sub>2</sub> line parameters has not been sufficiently adjusted to the contours observed in the laboratory or that the ClONO<sub>2</sub> 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  $\nu_2$  Q branch of ClONO<sub>2</sub>, at  $1292.6$  cm<sup>-1</sup>, 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 due to geometric 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  $2\sigma$  errors are 45% at 37 km, 30% at 30 km and 35% at 20 km.

The absolute uncertainty in the integrated intensity of the  $\nu_4$  Q branch of ClONO<sub>2</sub> 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 Q branch, is the principal source of systematic uncertainty which limits severely the absolute accuracy for ClONO<sub>2</sub> 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 ClONO<sub>2</sub>. Further laboratory research is needed to establish a reliable set of line parameters for all of the ClONO<sub>2</sub> absorption features which can now be clearly observed in the spectra. The data reported here represent the first time that several infrared chlorine nitrate bands have been observed simultaneously; the four features observed in the ATMOS spectra provide an unambiguous identification of the presence of ClONO<sub>2</sub> in the stratosphere.

**Acknowledgments.** The research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA. One of us (R. Zander) was partly supported by the Ministère de l'Éducation Nationale, Belgium. We thank L. Lowes, S. Paradise, M. Dietrich and J. Bosseloirs for their help in various preparatory phases of this manuscript.

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(Received April 25, 1986;  
accepted May 16, 1986.)