Measurement of chlorine nitrate in the stratosphere using the ν_4 and ν_5 bands

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Abstract

We present laboratory measurements of the absorption cross sections of the ν_5 band (540–580 cm^{-1}) of chlorine nitrate made under stratospheric conditions of temperature and pressure. We use the measured cross sections and observed mid-infrared stratospheric emission spectra to retrieve mid-latitude vertical mixing ratio profiles for both day and night in the altitude range 20–34 km, and compare the results with a sunset profile obtained simultaneously from solar absorption measurements of the ν_4 Q branch at 780 cm^{-1}. The profiles obtained using these two methods are shown to be in excellent agreement, validating retrievals using the ν_4 band. We also find good agreement in this altitude range between the observed day/night ratio and the results of a 1-D photochemical model

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Introduction

Chlorine nitrate ($ClONO_2$) is an important temporary reservoir of chlorine and nitrogen radicals, both of which act as catalysts to destroy ozone in the stratosphere. For example, at mid-northern latitudes $ClONO_2$ accounts for approximately 10% of the total odd nitrogen (NO_y = NO + NO_2 + HNO_3 + HNO_4 + $2N_2O_5$ + $ClONO_2$) and up to 50% of the total inorganic chlorine (Cl_y = HCl + ClO + HOCl + $ClONO_2$) [*McElroy and Salawitch*, 1989]. The ability to produce realistic estimates of the abundance of $ClONO_2$ is thus an important requirement for any model which is to be used to predict the stratospheric response to changing concentrations of NO_y and Cl_y.

Recent analyses of mid-latitude measurements made by the atmospheric trace molecule spectroscopy (ATMOS) spectrometer in 1985 [*Minschwaner et al.*, 1993] and 1992 [*Rinsland et al.*, 1994] indicate that standard photochemical models overestimate the abundance of $ClONO_2$ at the mixing ratio peak at 30 km by 30–50%. There are now several instruments besides ATMOS measuring $ClONO_2$, and the results are in general agreement with each other [*Rinsland et al.*, 1994; *Clarmann et al.*, 1993; *Roche et al.*, 1993; *Toon et al.*, 1992]. However, all these measurements are based on observations of the same spectroscopic feature, the ν_4 Q branch at 780.2 cm^{-1}, which leaves open the possibility that the difference between theory and measurement may be due to a systematic error in the spectroscopic parameters for either chlorine nitrate or another species having spectral features in this region.

In this work we present new laboratory measurements of the ν_5 band of $ClONO_2$ centered at 563 cm^{-1}. We then use stratospheric observations of the ν_5 band to retrieve the daytime and nighttime vertical mixing ratio profiles of $ClONO_2$, and compare the results with a profile obtained simultaneously using the ν_4 Q branch and with the results of a 1-D photochemical model.

Laboratory Measurements of the ν_5 Band

Absorption cross sections of $ClONO_2$ were first measured in Orsay in 1992 as part of the Infrared Spectroscopy of Ozone and Related Atmospheric Constituents program [*Diallo et al.*, 1994]. The measurements were made using a stepping-mode Fourier-transform spectrometer with a KCl beamsplitter at a maximum unapodized resolution of 0.0027 cm^{-1}. The early measurements were made using a 4.85 cm stainless steel absorption cell, cooled by liquid nitrogen and equipped with AgCl windows [*Orphal et al.*, 1994]. The measurements were repeated in 1994 using a 15 cm Pyrex absorption cell cooled by an ethanol flow [*Orphal, 1995*]. The cross sections presented here are derived from the latter measurements.

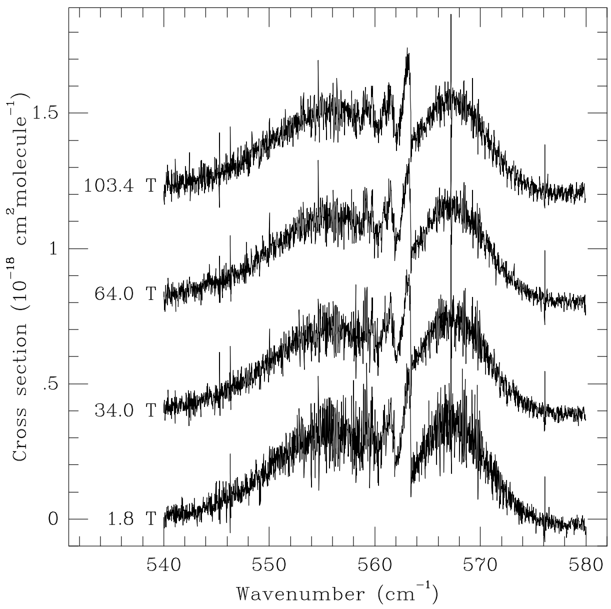

Figure 1. Absorption cross sections at 223 K in the vicinity of the ν_5 band of $ClONO_2$. The partial pressure of $ClONO_2$ was 1.8 torr; the total pressure was increased by adding N_2. The measurements at 34.0, 64.0, and 103.4 torr have been offset by 0.4, 0.8, and 1.2×10^{-18}, respectively.

The $ClONO_2$ sample was synthesized by reacting Cl_2O and N_2O_5, and purified by repeated low-temperature distillation. The sample purity was checked after each distillation by recording low-resolution infrared spectra. No absorption due to HNO_3, NO_2, or N_2O_5 was observed in the final sample used for cross section measurements. Another likely impurity, Cl_2, has no spectral features in the infrared, and so as a final check we compared the pressure above the condensed sample with the vapor pressure of $ClONO_2$ [*Orphal, 1995*]. The uncertainty in the vapor pressure curve leads to an upper limit of 5% for Cl_2 in the sample.

We added 1.8 torr of $ClONO_2$ to the cell through a Pyrex vacuum system equipped with greaseless fittings and Teflon taps, and increased the total pressure by adding N_2. The cell was cooled to 223 K and spectra were recorded at an unapodized resolution of 0.02 cm^{-1}. The absorption cross sections near the ν_5 band are shown in Figure 1 for total pressures of 1.8, 34.0, 64.0, and 103.4 torr. While the fine structure visible at 1.8 torr disappears at higher pressures, the overall band shape is quite similar at all observed pressures. The estimated uncertainty in the cross section is $-5, +11\%$, which includes the 5% upper limit for Cl_2.

The 1992 spectra have poor sensitivity in the vicinity of the ν_5 band and do not provide a direct confirmation of the present measurements. However, measurements of the ν_2 (1293 cm^{-1}) and ν_3/ν_4 (780 and 809 cm^{-1}) bands were made in both years and the results are internally consistent. For example, at 212 K the peak cross sections observed at 1292.69 cm^{-1} were 3.50 ± 0.15 and $3.53 \pm 0.15 \times 10^{-18} cm^2\,molecule^{-1}$ in 1992 and 1994, respectively. For comparison, *Ballard et al.* [1988] obtained $3.70 \pm 0.15 \times 10^{-18} cm^2\,molecule^{-1}$ at 213 K.

The temperature dependence of the band strength was derived from measurements made by *Davidson et al.* [1987], who reported the integrated cross sections (535–580 cm^{-1}) to be 6.2 and $11.6 \times 10^{-18}\,cm\,molecule^{-1}$ at 223 and 296 K, respectively. Our measurements are in good agreement at 223 K, having an integrated cross section of $6.3 \times 10^{-18}\,cm\,molecule^{-1}$. We assume that the overall band shape for typical stratospheric temperatures (207–253 K for May 1994) can be approximated by the 223 K measurements.

For convenience in fitting stratospheric spectra, we approximate the absorption cross section by creating a set of equispaced spectral lines. The ground state energies of the individual lines are adjusted to reproduce the observed temperature dependence of the integrated cross section, using a procedure similar to that described by *Ballard et al.* [1988].

Stratospheric Measurements

The mixing ratio profiles presented here were obtained during a balloon flight on May 22-23, 1994. The balloon was launched from Ft. Sumner, New Mexico (34.5°N, 104.2°W) at 0830 Mountain Daylight Time on May 22, reached the float altitude of 37 km at 1045, and was terminated near the New Mexico-Arizona border at 0845 the following morning.

The gondola for this flight carried two infrared spectrometers, the Smithsonian Astrophysical Observatory (SAO) far-infrared spectrometer (FIRS-2) and the Jet Propulsion Laboratory (JPL) MkIV interferometer. The FIRS-2 is a Fourier-transform spectrometer (FTS) which is used to measure stratospheric emission spectra in the far (80–210 cm^{-1}) and mid (350–700 cm^{-1}) infrared at a maximum (unapodized) resolution of 0.004 cm^{-1}. The MkIV, also a FTS, measures solar absorption spectra in the mid to near infrared (650–5650 cm^{-1}) at a maximum resolution of 0.0075 cm^{-1}. Both instruments have been described previously [*Johnson et al.*, 1995; *Toon*, 1991] and have been providing remote-sensing measurements of stratospheric composition from both aircraft and balloon platforms for many years, although this is the first time they have flown together on the same gondola.

The JPL observations of $ClONO_2$ were made during sunset on May 22. The analysis of the ν_4 band has already been described [*Toon et al.*, 1992; *Toon et al.*, manuscript in preparation, 1996], and so the discussion here will be brief. First, we estimate the slant column N_{ij} for each target gas i in each spectrum j, using a nonlinear least squares (NLLS) fitting routine to adjust an initial mixing ratio profile until the calculated spectrum best matches the observed spectrum in a small spectral window. Next, we construct a model atmosphere with 1 km layers and calculate the slant path n_{jk} in each layer k for each spectrum j. We then use a linear equation solver to find the mixing ratio profile m_{ik} which solves the equation $N_{ij} = \sum m_{ik} n_{jk}$, subject to a second-derivative constraint [e.g., *Sen et al.*, 1995]. The one notable change in the JPL analysis since 1992 has been the use of the spectroscopic parameters determined by *Bell et al.* [1992] in place of the absorption cross sections measured by *Ballard et al.* [1988], which reduces previously-retrieved $ClONO_2$ mixing ratios by roughly 10%. The uncertainty in the spectroscopic parameters for the ν_4 band is 12%.

As mentioned above, the SAO observations were made over a 22-hour period beginning on the morning of May 22. The spectra were binned by elevation angle and summed to form daytime and nighttime averages. The SAO analysis procedure is described in detail by *Johnson et al.* [1995], and will be summarized here. We fit spectra in onion-peeling fashion using a NLLS routine and spectroscopic data from the SAO92 database [*Chance et al.*, 1994]. The temperature profile and pointing-angle corrections are derived from measurements of different sets of lines of CO_2. We take the preliminary profile resulting from the onion peeling, calculate the slant columns N_{ij}, and retrieve m_{ik} on a 2 km grid with a procedure similar to that used by JPL. Our error estimate includes fitting residuals (which dominate), the effects of interfering species, and errors in intensity calibration and pointing.

A portion of an averaged spectrum corresponding to a tangent height of 21 km is shown in Figure 2. The spectral region shown, which is used for $ClONO_2$ retrievals, is dominated by strong lines of CO_2 and N_2O but also contains a few strong lines of H_2O and weaker lines of HNO_3, as well as a wing of the N_2O_5 band at 580 cm^{-1}. We simultaneously fit $ClONO_2$, H_2O, CO_2, and N_2O. The abundance of N_2O_5, which contributes a gradual slope from 545 to 575 cm^{-1}, is kept fixed. The es-

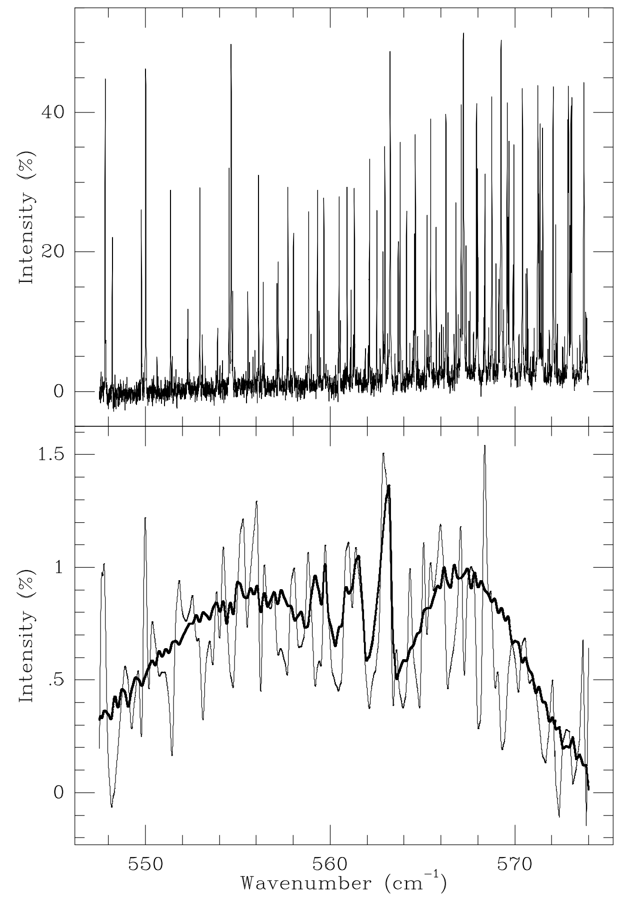

Figure 2. Top panel: Flight spectrum at a tangent height of 21 km showing the spectral region containing the ν_5 band of $ClONO_2$. Bottom panel: The heavy curve shows a calculated $ClONO_2$ reference spectrum, and the light curve shows the residuals after fitting a calculated spectrum containing no $ClONO_2$ to the spectrum shown in the top panel. Both the calculated spectrum and residuals have been smoothed to a resolution of 0.18 cm^{-1}. Intensity in both panels is normalized to the intensity of a 277 K blackbody source.

timated $ClONO_2$ is only weakly correlated with the abundance assumed for interfering species; the largest correlation coefficient (with H_2O) is -0.09.

The bottom panel of Figure 2 compares a calculated $ClONO_2$ spectrum with the residuals after fitting a calculated spectrum containing no $ClONO_2$ to the spectrum shown in the top panel. Both the calculated spectrum and residuals have been smoothed to a resolution of 0.18 cm^{-1} for ease in comparing broadband features. There is an excellent correspondence between the residuals and the calculated $ClONO_2$ reference spectrum.

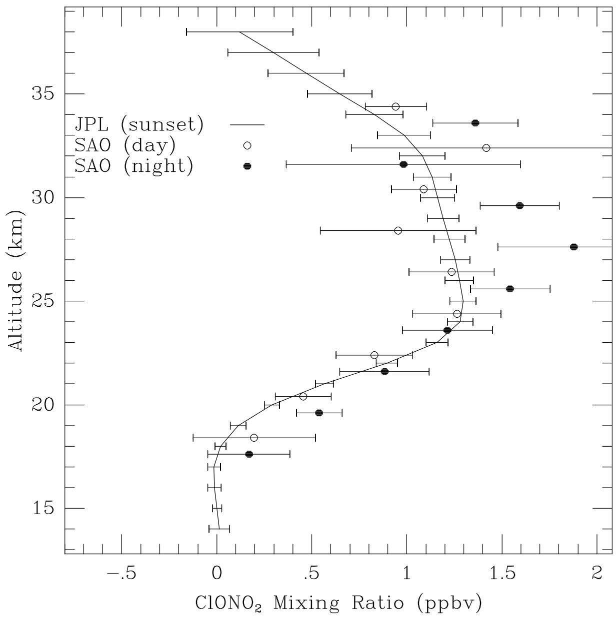

Figure 3. Comparison of $ClONO_2$ mixing ratio profiles retrieved by JPL (using the ν_4 band) and SAO (using the ν_5 band). The JPL measurements (curve) were made at sunset. The SAO measurements were made during both day and night (open and closed symbols, respectively). One-sigma (68%) confidence limits are indicated, including both random and systematic errors (but not spectroscopic errors). The SAO day and night measurements have been offset by ± 0.4 km.

Results and Discussion

In Figure 3 we compare the daytime and nighttime $ClONO_2$ mixing ratio profiles retrieved by SAO with the sunset profile retrieved by JPL. The SAO and JPL profiles are in good qualitative agreement, with the JPL sunset profile tending to fall between the SAO daytime and nighttime profiles. The nighttime increase in $ClONO_2$ is readily apparent.

The ratio SAO/JPL provides an estimate of the relative systematic error in the SAO and JPL measurements. Specifically, $\mathrm{SAO/JPL} = \varepsilon_S/\varepsilon_J$, where ε_S and ε_J are the systematic errors in the SAO and JPL profiles, respectively. Assuming that ε is dominated by spectroscopic errors, we expect the ratio to fall in the range 0.83–1.23. The average ratio in the altitude range 20–34 km (where the amount of $ClONO_2$ measured by both groups is statistically significant), calculated using the daytime SAO profile, is 0.98 ± 0.11, where the 1-σ error in the mean includes both random and known systematic errors (excluding spectroscopic errors). After using the Caltech/JPL 1-D photochemical model [*Froidevaux et al.*, 1985], (Mark Allen, personal communication, 1989) to correct for the diurnal variation we find the ratio to be 1.10 ± 0.12, which is within the expected range. This indicates that the systematic difference between the JPL and SAO profiles is consistent with known spectroscopic errors.

We noted in the Introduction that previous measurements of $ClONO_2$ have not agreed well with model calculations, calling into question the use of a model to correct for the time difference between the JPL and SAO profiles. We test the model by comparing the observed and calculated diurnal variation as follows. We first average the model calculations over the same period as the observations to produce daytime and nighttime profiles which correspond to the measured profiles. At each altitude we calculate R_o, the ratio of measured daytime to nighttime $ClONO_2$, and R_m, the ratio of modelled daytime to nighttime $ClONO_2$. We then calculate the ratio $R = R_o/R_m$ at each altitude in the range 20–34 km. The weighted average of all 8 determinations of R is 0.98 ± 0.14, where the 1-σ error in the mean includes only the random error in the stratospheric measurements of $ClONO_2$. The fact that R is consistent with 1 shows that the modelled diurnal variation is in agreement with the observations.

Conclusion

We find that measurements of $ClONO_2$ made from observations of the ν_4 band at 780 cm^{-1} in solar occultation spectra are in excellent agreement with measurements made from observations of the ν_5 band at 563 cm^{-1} in thermal emission spectra, once we have corrected for the observed diurnal variation. We also find that the observed relative diurnal variation is in good agreement with the results of a 1-D model.

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