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The TDLAS instrument for the detection of total inorganic chlorine in the stratosphere

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Abstract. A novel method based on tunable diode laser absorption spectroscopy is proposed for the detection of the sum of the stratospheric chlorine components HCl, $ClONO_2$, ClOOCl and ClO. All of the above species are detected as HCl following thermal decomposition ($ClONO_2$ and ClOOCl) to ClO which is converted to Cl via reaction with NO; the Cl atom is then rapidly reacted with a hydrocarbon to form HCl. The method has been investigated in the laboratory for detection of $ClONO_2$, for which the conversion efficiency was found to be 100% under suitable conditions.

1. Introduction

The emission of anthropogenic chlorofluorocarbons has resulted in a present-day stratospheric chlorine burden of nearly 4 ppbv (parts per billion volume mixing ratio) [World Meteorological Organization, 1992]. The observation of a significant negative trend in ozone concentrations at mid-latitude [Herman et al., 1994] and, more spectacularly, in the Antarctic [Farman et al., 1985] are closely linked to chemical reactions involving chlorinated radical species. This chemistry is initiated by the photolysis of the otherwise chemically inert chlorofluorocarbons (CFCs) to yield a chlorine atom; the Cl atom can react with O_3 to generate ClO (chlorine monoxide) which is the major component of the stratospheric reactive chlorine species Cl_x (= Cl + Cl_2 + ClO + ClOOCl + OClO + HOCl). In the normal stratosphere, most of the chlorine is found as the less reactive "reservoir species" HCl and $ClONO_2$ ($Cl_y = Cl_x + HCl + ClONO_2$), which are mainly formed from Cl and ClO via the following reactions:

$$Cl + CH_4 + O_2 \rightarrow HCl + CH_3O_2 \quad (1)$$

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \quad (2)$$

The stratospheric partitioning between the reactive chlorine species Cl_x and the reservoir species $ClONO_2$ and HCl to a large extent determines the rate of the halogen-initiated ozone depletion. Under "normal" conditions, inorganic chlorine is to a first approximation partitioned between the two reservoir species HCl and $ClONO_2$ in the mid-latitude stratosphere. Under "ozone hole" conditions this situation is changed and extensive activation of these chlorine reservoirs into active forms takes place. Up to 1.2 ppbv of ClO have been measured [Anderson et al., 1991], but direct *in situ* measurements of the Cl reservoir species are few. A clear requirement to better our understanding of the chemical composition of the stratosphere (and thus the ability to predict the rates of halogen-catalyzed O_3 depletion) is needed in the form of *in situ* measurements of total inorganic chlorine. Only very recently have direct measurements of stratospheric HCl been reported by Webster et al. [1993a, 1993b]; *in situ* concentrations of $ClONO_2$ have thus far been obtained only indirectly by a modeling study based on NO, ClO, and O_3 measurements [Kawa *et al.*, 1992]. Estimates of $ClONO_2$ have also been made by comparing calculated HCl to Cl_y burdens derived from measurements of speciated organic chlorine and the tracers N_2O and CO_2 [Kawa *et al.*, 1992, Woodbridge *et al.*, 1995]. Specific $ClONO_2$ measurement schemes have been proposed and demonstrated as laboratory prototype experiments [Viggiano *et al.*, 1994, Bonne *et al.*, 1995, Perkins *et al.*, 1995]. Other than these measurements, stratospheric $ClONO_2$ concentrations have thus far only been obtained by remote sensing experiments from either satellites [e.g. Dessler et al., 1995], the space shuttle [e.g. Zander *et al.*, 1990], or balloon soundings [e.g. Oelhaf *et al.*, 1994], as well as ground- and aircraft-based FTIR absorption spectroscopy [e.g. Reisinger *et al.*, 1995, Toon *et al.*, 1992].

The focus of the present work, therefore, is on developing a new measurement technique for stratospheric Cl_y both in the form of HCl and $ClONO_2$, as well as other Cl_y components including ClO and ClOOCl. We have investigated a scheme whereby the $ClONO_2$ is thermally decomposed into ClO and NO_2; the liberated ClO reacts with added NO to give Cl and NO_2. Finally, the Cl radical reacts with a proton donor such as H_2 or an alkane to yield HCl:

$$ClONO_2 \rightarrow ClO + NO_2 \ (>570\text{ K}) \quad (3)$$

$$ClO + NO \rightarrow Cl + NO_2 \quad (4)$$

$$Cl + H_2 \rightarrow HCl + H \quad (5)$$

The HCl produced in the final step, as well as that originally present in the air sample, is detected directly and specifically using tunable diode laser absorption spectroscopy (TDLAS),

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as demonstrated by Harris et al. [1992] and Webster et al. [1993b, 1994].

2. Experimental Methods

A $ClONO_2$ calibration source was constructed by first synthesizing a pure sample of $ClONO_2$ and using this in a dynamic dilution system. The $ClONO_2$ was synthesized by mixing Cl_2O with an excess of N_2O_5 as described previously [Davidson et al., 1987]. Substantial efforts were made to ensure purity of the final product. Broadband infrared spectra (600 - 4000 cm^{-1}) of the vapor in a 10 cm cell were recorded with a Bomem DA8.02 spectrometer both at 0.5 and 0.02 cm^{-1} resolution. Infrared spectra were monitored specifically for $ClNO_2$, Cl_2O, ClO, NO_2, NO, HNO_3 and other impurities, until the product showed only the spectrum of pure $ClONO_2$ [Davidson et al., 1987]. To check against possible Cl_2 and OClO impurities, long path (9.75 m) UV absorption measurements were undertaken; the impurity levels were found to be OClO ~0.01% and $Cl_2 < 1\%$. After all spectroscopic checks the vapor pressure of the pure compound at -78 C was measured using a 10-Torr Baratron gauge to be 1.23 Torr (1.64 mBar); we estimate the absolute purity to be ≥ 99%.

A flow of He at 1000 mBar was bubbled through the purified $ClONO_2$ held at -78 C to generate a saturated He/$ClONO_2$ flow of between 0 and 5 cm^3 STP min^{-1} (sccm) (Fig. 1). In order to avoid potential decomposition of the $ClONO_2$ in a mass flow controller (MFC), the system was constructed to dilute the $ClONO_2$ flow by adding N_2 gas through MFC#2, most of which was then pumped off through MFC#3. Typically, the ~1 sccm flow from the source was diluted by 420 sccm N_2, and of this only ~35 sccm was fed to the converter tube inlet, where it was further diluted in a flow of 7.5 L STP min^{-1} (slm) zero air to yield a final mixing ratio in the approximate range 8 to 100 ppbv. All tubing prior to the converter was made of Teflon; all contact materials after the converter were of either glass or stainless steel. All mass flow controllers were multiply calibrated over the range in which they were used.

The thermal converter was a 70 cm long, 5 mm ID solid Au tube heated to 570 K over a 20 cm length near the tube center, and was originally constructed for use as a "master blaster" NO_y converter. Several such NO_y catalysis instruments have been described [e.g. Fahey et al., 1985]; details of the present system are described elsewhere [Zenker et al., manuscript submitted, 1996]. The converter output was coupled to the TDL White cell inlet. The TDL spectrometer used a Pb-salt laser tuned to scan the P(5) HCl line at 2775.76 cm^{-1} and operated with 7.5 kHz modulation and standard 2f lock-in detection [Roths et al., 1996]. The White cell (Fig. 1) had a base length of 45 cm and a total optical path of 45.9 m [Wienhold et al., 1994]. The beam exiting the White cell was collected and focused by a 190 mm focal length off-axis parabolic mirror onto an HgCdTe detector. The cell was maintained at 40.6 mBar pressure with the pressure drop occurring at a calibrated glass capillary at the White cell inlet which limited the total flow to ~7.5 slm. Because of the relatively short optical path and lack of high frequency modulation techniques, the absolute detection limits for HCl were moderate in this experiment (~300 pptv); HCl detection limits an order of magnitude better can be obtained using TDLAS [Harris et al., 1992, Webster et al., 1994]. However, the present system has sufficient sensitivity to test the proposed detection method at realistic Cl_y levels (approximately 5 ppbv Cl).

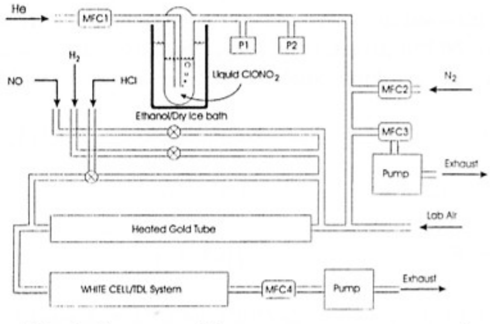

Figure 1. Block diagram of the converter system. See text for details. MFC = Mass Flow Controller.

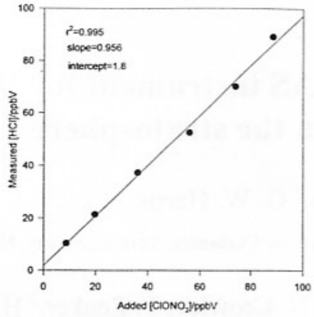

Figure 2. Plot of TDLAS measured HCl mixing ratio versus the $ClONO_2$ mixng ratio introduced into the converter.

In order to calibrate HCl mixing ratios, either of two permeation sources were used. These operated by flowing N_2 gas through a Teflon tube immersed in one of two thermostatted concentrated HCl solutions. The HCl flow rates were confirmed both by optical density measurement (high concentration permeation source only) and collection of aqueous HCl samples followed by ion chromatographic (IC) analysis. A third HCl calibration source (a certified standard mixture of 500 ppbv HCl in N_2 - Messer Griesheim) was used to cross-calibrate the permeation sources. We performed multipoint calibrations using the high concentration permeation source (~75 ppbv HCl), the low concentration source (~8 ppbv), as well as the tank mixture in the range 2 to 15 ppbv. $ClONO_2$ flow rates were calculated using the 1.64 mBar vapor pressure of $ClONO_2$ in He along with the flow rates of the various controllers F1 - F4: reliable mixing ratios in the 10 to 120 ppbv range were obtained. The $ClONO_2$ flow rates were verified for several samples by IC analysis for nitrate ion after a timed collection of the $ClONO_2$ flow into an aqueous bubbler. For the IC measurements, several samples were collected in a 2-flask cascade fashion in order to establish collection efficiency at various flows; all IC samples had blanks subtracted. In most cases synthetic air (Messer Griesheim, alkane free, Product 0131) was used as the carrier gas entering the converter to which were added flows of NO (1.6 ppm) and H_2 (~1%) to obtain conversion of $ClONO_2$ to HCl. Measured HCl values were derived from least-squares fits of the TDL 2f signal to the calibration signal; reported values were corrected for drift in detector response and line centering.

3. Results

The most important result is displayed in Figure 2's plot of measured HCl mixing ratio versus the $ClONO_2$ mixing ratio introduced into the converter. The linear and stoichiometric response of measured HCl versus input $ClONO_2$ clearly establishes the possibility of using such a system for determination of stratospheric Cl_y. For each injected $ClONO_2$ flow the HCl signal was allowed to equilibrate to a reasonably stable value, approximately 10 readings (30 s averages) were recorded, and the $ClONO_2$ input withdrawn from the converter in order to collect an IC sample (requiring from 3 to 60 min), and finally the $ClONO_2$ was re-introduced to the converter. After re-equilibrating, ~10 additional values were recorded. Each point in Figure 2 thus represents the mean of the ~20 values from before and after the IC collection. The plot in Figure 2 yields a slope of 0.956 (± 0.034) with an intercept of 1.8 (±1.9) and a correlation coefficient of $r^2 = 0.995$. If one follows the Cl atom through reactions (3) - (5), then, provided the chemistry is complete, the stoichiometry for $ClONO_2$ conversion to HCl is 1:1; hence the slope in Figure 2 is predicted to be unity. The slight positive intercept results from a memory effect which we observed whenever the inlet system and White cell had been exposed to high levels (≥ 50 ppbv) of HCl. Even after ~1 hour, a residual outgassing signal equivalent to ~1.5 ppbv HCl persisted. This residual signal was not observed if only moderate levels of HCl or $ClONO_2$ (in the range 5 - 10 ppbv) were introduced into the system. In these cases the signal disappeared below the detection limit in less than 5 minutes after the calibration gas was removed.

The chemistry delineated in reactions (3) - (5) is relatively straightforward. However, for stratospheric measurements the questions of either spectroscopic interferences or unknown side reactions naturally present themselves. Brassington [1989] has shown that the HCl line we used is free of spectroscopic interference to at least the 10s of ppt level. Possible further spectroscopic interferences were investigated by replacing the bulk gas carrier flow of synthetic air (~7.5 slm) by laboratory air which is relatively rich in hydrocarbons, NO_x, as well as water: No spectroscopic interferences were observed. The momentary pressure change often led to a spike in the HCl signal, but after several minutes equilibration the detected HCl returned to the same value, minus but a small fraction, typically 3%. The deviation was well within the accuracy of the HCl measurement (± 10%), and we attribute the small deviations to either slight variations in pressure and flow rates, or possibly different pressure broadening coefficients in laboratory air as compared to synthetic air. A heterogeneous reaction between $ClONO_2$ and water may also have an effect, but the measured HCl signal versus input $ClONO_2$ again showed the same linearity over the full domain of the measurement. We also note that when using either laboratory or synthetic air, the proton donor (here H_2) is almost superfluous since any proton donor at the ppm level (e.g. CH_4 zero-air impurity) is sufficient for reaction (5) to proceed quickly. Only by using long purges with very alkane free air could we limit the final conversion step to HCl.

The converter temperature is a very important parameter, since the initial dissociation process is known to have a strong thermal dependence [Knauth, 1978]. Anderson and Fahey [1990] have investigated the rate constant for dissociation of $ClONO_2$ in such a gold converter and obtained the value $10^{-6.16}$ exp(-90.7 kJ mol^{-1}/RT) cm^3 s^{-1} $molecule^{-1}$ as measured at lower pressures (60-160 Torr). This temperature dependence is of concern in the present instance because the converter has a 20 cm copper sleeve heating element in the center with a significant temperature gradient toward either end. To investigate the temperature dependence of the conversion efficiency, a constant flow of 70.3 ppbv $ClONO_2$ was maintained with large excesses of NO and H_2 while monitoring the HCl signal as a function of nominal converter temperature. The experiment showed that temperatures ≥ 550 K are needed to ensure ≥ 95% dissociation and conversion to HCl.

4. Discussion

The present experiments validate the approach of using the reaction scheme (3) - (5) for detection of stratospheric Cl_y (at least the $ClONO_2$/HCl components) as HCl at (sub-)ppbv levels using TDL spectroscopy. The error associated with Figure 2 must incorporate uncertainties in both the x- and y-values. We estimate the total error on the $ClONO_2$ concentration in the White cell to be approximately 15%. A major source of this is the $ClONO_2$ flow dilution system, in particular the differential addition/removal scheme using MFC #2 and MFC #3, since each of these flows are only accurate to 0.25% of the full scale reading (1000 and 500 sccm, respectively), along with the smaller but non-negligible uncertainty in the $ClONO_2$ vapor pressure measurement. The total error for the HCl concentration in the White cell is estimated to be ~10%, including the error of the HCl permeation sources, the fit error, and the HCl "sticking" phenomenon during and after calibration, as discussed above. This gives a total error on the entire measurement scheme estimated at ~25%, although the regression values indicate that this estimate may be somewhat liberal. Glass and heated metals have proven to have the least memory effect for HCl. Future designs will incorporate these materials, as well as heated inlets to further reduce response times. Further known technological improvements should also help realize better detection limits. Use of an InSb detector, high frequency modulation techniques [Johnson *et al.*, 1991], and longer pathlengths will all help bring about higher sensitivity.

The present study has focused on the detection of $ClONO_2$ (and, of course, HCl) for which the method has been tested. We now discuss the detection of the other major Cl-containing stratospheric compounds ClO and ClOOCl, and the experimental modifications that would enable separation of the HCl, $ClONO_2$, ClOOCl and ClO signals. One such variation might be the use of isotopically labeled species that could be used to differentiate the Cl_y components. For example, the reaction

$$Cl + D_2 \rightarrow DCl + D \qquad (5a)$$

could be used to differentiate between HCl and $[Cl_y]$ - [HCl]. One can also envision a system with a dual inlet to distinguish between the HCl and $ClONO_2$ by using different temperatures in the inlet/converter. The thermal dissociation of ClOOCl (to 2 ClO) has recently been reinvestigated by Nickolaisen et al. [1994]. As the thermal decomposition rate of ClOOCl is a factor of 100 faster than for $ClONO_2$ at 600

K, we expect that ClOOCl will also be stoichiometrically converted to HCl in our reactor. Additionally, the thermal decomposition rate constants of $ClONO_2$ and ClOOCl have different temperature dependencies and variations of temperature may provide a means to differentiate between the two. The detection of ambient ClO is ensured with this method (we have shown that ClO is 100% converted to HCl) and, in theory, it can be selectively detected in the presence of HCl, $ClONO_2$, and ClOOCl by simply switching the NO in and out of a cool reactor (where there is no thermal decomposition of $ClONO_2$ or ClOOCl) and measuring the signal modulation due to HCl (NO off) and HCl + ClO (NO on). Such experiments are still speculative, though, as our system has only been tested for linearity in HCl and $ClONO_2$ inputs.

The conversion of ClO to Cl under the present conditions takes place in only 12 ms ($\tau_{1/2} = 1/(k_{ClO+NO})[NO] = 4$ ms), while the conversion of Cl To HCl requires only 30 μs ($\tau_{1/2} = (1/k_{Cl+H2})\ [H_2] = 10\mu s$). Clearly, diffusion to walls cannot compete on such short time scales, and the 100% conversion efficiency of $ClONO_2$ to HCl is ensured. This is an advantage of the present method over those in which the ClO or Cl radials are detected following thermal decomposition of the $ClONO_2$ since our method avoids uncertainties as to the rate of loss of the Cl or ClO radical (via e.g. diffusion from the viewing zone or to the reactor wall).

5. Summary

We have demonstrated that the thermal fragmentation of $ClONO_2$ to ClO and NO_2 followed by reactions with NO and H_2 quantitatively converts $ClONO_2$ to HCl. The reaction sequence (3) - (5) has been shown to be linear and stoichiometric in $ClONO_2$ input in the range 5 - 120 ppbv. More sensitive detection promises a system that can measure Cl_y with sufficient sensitivity and accuracy for stratospheric measurements. We are currently constructing such a system.

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