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Using chemical ionization mass spectrometry for detection of HNO_3, HCl, and $ClONO_2$ in the atmosphere

T.P. Marcy[a,b,*], R.S. Gao[a], M.J. Northway[a,b], P.J. Popp[a,b], H. Stark[a,b], D.W. Fahey[a,b]

[a] *Aeronomy Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway R/AL6, Boulder, CO 80305, USA*
[b] *Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80305, USA*

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Abstract

Ion chemistry schemes involving three different reagent ions are described for measuring nitric acid (HNO_3), hydrochloric acid (HCl), and chlorine nitrate ($ClONO_2$) in the upper troposphere and lower stratosphere using chemical ionization mass spectrometry (CIMS). These schemes were evaluated in the laboratory for sensitivity and selectivity of the neutral species. The use of one scheme, based on the SF_5^- reagent ion, is described for airborne measurements. Initial atmospheric measurements show that HNO_3, HCl, and $ClONO_2$ can be measured using SF_5^- with high precision and accuracy.

Keywords: Chemical ionisation; Atmospheric; HCl; Nitric acid

1. Introduction

Chemical ionization mass spectrometry (CIMS) has been used as a sensitive measure of nitric acid (HNO_3) and a number of other trace species in the atmosphere [1–16]. Quantification of many of these species in the atmosphere is of interest for our understanding of homogeneous and heterogeneous chemical and physical processes. Measurement of some trace species such as hydrochloric acid (HCl) and chlorine nitrate ($ClONO_2$) are also of interest because these molecules can be useful as tracers of stratospheric air masses and stratospheric ozone that have penetrated into the upper troposphere [1]. More detailed knowledge of HCl and $ClONO_2$ concentrations in the lower stratosphere will also lead to a better understanding of the stratospheric chlorine budget because both are principal reservoirs of inorganic chlorine [17,18].

The CIMS technique ideally employs reagent ions that react selectively with the trace species of interest to produce a unique product ion, with minimal interference from other reactions. Measurement of the product ion is then used to quantify the abundance of the trace gas in the atmosphere. Reactions of many reagent ions with HNO_3, HCl, and $ClONO_2$, as well as other atmospheric trace gases, have been studied in the laboratory for the expressed purpose of using the reactions for atmospheric CIMS measurements [2–4,19–23]. In addition, several of these reactions have been used to make measurements of these three species in the atmosphere. For example, CIMS instruments have been used to measure atmospheric HNO_3 using SiF_5^- as the reagent ion and $HNO_3{\cdot}SiF_5^-$ as the product ion [2,5–9]. The yield of $HNO_3{\cdot}SiF_5^-$ is proportional to the amount of HNO_3 in the sample and is calibrated by adding a known amount of HNO_3 to the instrument from a permeation tube source [5]. HNO_3 has also been measured in the atmosphere using Cl_n^- or CO_3^- reagent ions [10–13]. HCl can be detected by CIMS using the reagent ions $NO_3^-{\cdot}H_2O$, CF_3O^-, and SF_5^- [1,3,14,24]. A fluoride transfer from CF_3O^- or SF_5^- to HCl produces the product ion $HFCl^-$. CF_3O^- has also been shown to react with $ClONO_2$ by fluoride transfer [21]. In the present study, we have investigated three reagent ions (SF_5^-, CF_3O^-, and $CH_3SiF_4^-$) in the laboratory and evaluated their suitability for use in the

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[*] Corresponding author. Tel.: +1 303 497 7873; fax: +1 303 497 5373.
E-mail address: Timothy.P.Marcy@noaa.gov (T.P. Marcy).

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measurement of HNO_3, HCl, and $ClONO_2$ in the atmosphere. We show that, in addition to previously demonstrated reactions, the reagent ion $CH_3SiF_4^-$ reacts via fluoride transfer to HCl and that SF_5^- transfers fluoride to $ClONO_2$. On the basis of the laboratory work, the SF_5^- reagent ion was determined to be the best candidate for use in atmospheric measurements of HCl and HNO_3, and is suitable for measurement of $ClONO_2$, which is a secondary objective of the airborne studies. The SF_5^- ion was used in flight in the NOAA airborne CIMS instrument during the NASA Cirrus Regional Study of Tropical Anvils and Cirrus Layers–Florida Area Cirrus Experiment (CRYSTAL–FACE) mission in July 2002. During this mission, HNO_3, HCl, and $ClONO_2$ were measured in the upper troposphere and lower stratosphere (UT/LS).

2. Laboratory studies

The primary objective of the laboratory tests was to establish whether any of the reagent ions was suitable for use in airborne CIMS measurements of HCl or HNO_3 in the UT/LS. The criteria for suitability includes (i) no significant detection interference for the product ion from contaminant ions of the same, or nearly the same mass, (ii) a well defined relationship between the measured product ion count rates and the concentrations of the species measured, and (iii) no significant reactive interference from the presence of other atmospheric species, such as ozone or water.

The laboratory studies were conducted with a CIMS instrument that is functionally equivalent to the flight instrument, which has been described in detail elsewhere [5]. The laboratory instrument is arranged in a configuration that allows relative ease of operation and modification. As diagrammed in Fig. 1, the instrument has a 35 cm long and 5 cm diameter flow tube. A 2 standard liter per minute (slm) flow of N_2 carries the reagent ion precursor gas through a commercial ^{210}Po radioactive source (NRD Incorporated, Grand Island, NY) [5,6] where the reagent ions are produced. This source is a 20 mCi alpha emitter that produces secondary electrons in the primarily nitrogen flow, which then attaches to the reagent ion precursor molecules to give the reagent ions. The reagent ion flow enters on the opposite side of the flow tube entrance from the “sample” flow. In the laboratory, the sample is a flow of 2 slm dry N_2 rather than an inlet flow from the atmosphere as used in the flight instrument. Known amounts of HCl from a standard bottle or HNO_3 from a permeation tube can be added to the laboratory sample line to determine sensitivities and detection limits for each of the reagent ions. The laboratory flow tube is operated at room temperature and maintained at a pressure of 22 hPa by a scroll pump when the total flow is 4 slm. The size of the flow tube and the pressure, temperature, and rate of gas flow result in a residence or reaction time in the flow tube of 0.18 s. At the downstream end of the flow tube, ions pass into a quadrupole mass spectrometer through a 0.5 mm diameter aperture. The quadrupole chamber is pumped to 0.01 Pa by two turbo-molecular pumps. The spectrometer can either be scanned through a range of masses, or set to monitor a single mass for a given period of time. The ions that are transmitted through the quadrupole are detected by a Channeltron-type electron multiplier (Detector Technology, Palmer, MA) in a chamber pumped to 10^{-3} Pa by a third turbo-molecular pump.

2.1. Reagent ion options

The reagent ion SF_5^- is produced from trifluoromethyl sulfur pentafluoride (SCF_8, Apollo Scientific, UK). Electron attachment to SCF_8 in the ^{210}Po source in the CIMS instrument primarily produces SF_5^- [25,26]. (SCF_8 has been detected in the atmosphere at concentrations of 0.12 parts per trillion by volume (pptv) [27]. It is thought to be produced in SF_6-gas-insulated high voltage equipment that contains flu-

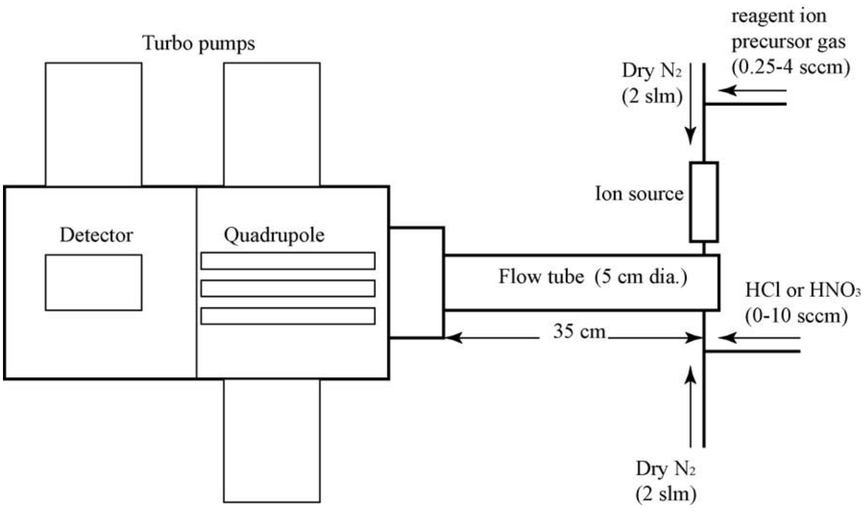

Fig. 1. Schematic of the laboratory CIMS instrument. Flow tube pressure = 22 hPa and residence time = 0.18 s. Reagent precursor gas flow ranges from 0.25 to 4.0 sccm depending on the gas being used.

orinated polymers. It is chemically inert, and is only broken down in the atmosphere by electron attachment reactions, giving it an atmospheric lifetime of about 1000 years [25–28].) Flow through the ion source is a mixture of 600 parts per million by volume (ppmv) SCF_8 in N_2 added to a 2 slm N_2 flow. A flow of 4 standard cubic centimeter per minute (sccm) of the 600 ppmv SCF_8 in N_2 mixture produces the maximum quantity of SF_5^- ions.

Known reactions of SF_5^- with HNO_3, HCl, and $ClONO_2$ include:

$$SF_5^- + HNO_3 \rightarrow SF_4 + HFNO_3^- \quad (1)$$

$$SF_5^- + HCl \rightarrow SF_4 + HFCl^- \quad (2)$$

$$SF_5^- + HCl \rightarrow HF + SF_4Cl^- \quad (3)$$

$$SF_5^- + ClONO_2 \rightarrow SF_4 + ClONO_2F^- \quad (4)$$

Reactions (1), (2), and (4) are all fluoride transfers, and reaction (3) is a fluoride–chloride exchange. Reactions (1)–(3) have been observed in quadrupole ion trap experiments [24] and all four product ions are observed with the CIMS instrument. The relative yields of reactions (2) and (3) have been determined to be 25 and 75%, respectively [24]. These yields cannot be directly determined with the present CIMS instrument due to an unknown degree of mass discrimination in the quadrupole mass spectrometer.

The reagent ion CF_3O^- is produced by adding a 3 sccm flow of 1200 ppmv CF_3OOCF_3 (Prof. Darryl DesMarteau, Clemson University, Clemson, SC) in N_2 to the 2 slm flow passing through the ^{210}Po source. CF_3O^- reacts as follows:

$$CF_3O^- + HNO_3 \rightarrow CF_2O + HFNO_3^- \quad (5)$$

$$CF_3O^- + HCl \rightarrow CF_2O + HFCl^- \quad (6)$$

$$CF_3O^- + ClONO_2 \rightarrow CF_2O + ClONO_2F^- \quad (7)$$

where the products of reactions (5) and (6) have been observed in the CIMS instrument. The reaction of $ClONO_2$ with CF_3O^- was not evaluated in our tests, but reaction (7) has been observed previously [21]. All of these reactions are fluoride transfers analogous to reactions (1), (2), and (4).

The reagent ion $CH_3SiF_4^-$ is produced from a flow of 0.25 sccm of a mixture of 1200 ppmv methyl trifluorosilane (CH_3SiF_3, Apollo Scientific, UK) and 370 ppmv SF_6 (Scott Specialty Gases, Plumsteadville, PA) added to the 2 slm flow through the ^{210}Po source. Reactions with the trace gases analogous to reactions (1)–(4) are:

$$CH_3SiF_4^- + HNO_3 \rightarrow CH_3SiF_3 + HFNO_3^- \quad (8)$$

$$CH_3SiF_4^- + HCl \rightarrow CH_3SiF_3 + HFCl^- \quad (9)$$

$$CH_3SiF_4^- + HCl \rightarrow HF + CH_3SiF_3Cl^- \quad (10)$$

$$CH_3SiF_4^- + ClONO_2 \rightarrow CH_3SiF_3 + ClONO_2F^- \text{(proposed)} \quad (11)$$

Reaction (11) may occur, but has not been confirmed.

During the laboratory studies, HCl and HNO_3 were added to the sample gas to verify the products of reactions (1)–(3), (5), (6), and (8)–(10). At a later date, $ClONO_2$ was added to the sample inlet of the flight instrument to confirm reaction (4).

2.2. Sensitivities and detection limits

Known quantities of HCl, HNO_3, and $ClONO_2$ were added to determine the sensitivity (ion counts per second (cps) per pptv of analyte entering the sample inlet) and detection limit (sample inlet pptv, 1σ, 1s) for each of the trace species with each proposed reagent ion. A comparison of these numbers, presented in Table 1, was used as a first step in determining which reagent ion is most suitable for airborne studies. HNO_3 results are listed both with and without 4 sccm ammonia (NH_3) added to the reagent flow. When HNO_3 is measured in the atmosphere, NH_3 is added to the reagent flow to reduce the background signal by preventing HNO_3 that absorbs on the walls of the system from later desorbing [5,6]. Some HNO_3 may also be produced in the ion source. The results show that sensitivity to HNO_3 with SF_5^- is 2.6 cps/pptv, which is greater than what has been achieved with SiF_5^- in the past [5,8,29]. The sensitivities using the other two reagent ions are also lower than with SF_5^-. The HNO_3 detection limits using SF_5^-, CF_3O^-, and $CH_3SiF_4^-$ all represent improvements over those previously found using the SiF_5^- reagent ion.

The SF_5^- chemistry has the highest sensitivity to HCl, an order of magnitude better than with CF_3O^-. The detection limit for HCl using SF_5^- is about 5 pptv (1s, 1σ), which is also much better than that found using $CH_3SiF_4^-$. Preliminary laboratory tests of $ClONO_2$ detection using SF_5^- show an approximate sensitivity of 2 cps/pptv. The background for the $ClONO_2F^-$ product ion is nearly zero, so the detection limit for $ClONO_2$ is less than 3 pptv (1s, 1σ). The range of HCl abundance in the region of the atmosphere, in which the airborne instrument is operated, is from nominally zero to about 3500 pptv, so the ideal detection method for HCl should give good coverage within this range. The above detection limit and sensitivity with SF_5^- indicate that we will be able to measure HCl values from 0.2% of the maximum expected to well above the 3500 pptv maximum.

Based on the results presented in Table 1, SF_5^- appears to be the best choice for airborne HCl and HNO_3 measurements, and will be suitable for our secondary objective of measuring $ClONO_2$. It is, therefore, the focus of the following more detailed studies.

2.3. SF_5^- product ions

The first criterion for an ion chemistry scheme to be suitable for airborne measurements is that it produces a sufficiently clean mass spectrum without interference of contaminant ions with the desired product ions. All three reagent ions considered here are satisfactory in this respect. Representa-

Table 1
Sensitivities and detection limits of reagent ions tested

Reagent ion	Molecule	Product ion	Background (cps)	Sensitivity (cps/pptv)	Detection limit 1σ, 1s (pptv)
SF_5^- (laboratory)	HNO_3	$HFNO_3^-$	3400	5.4	11
			200 w/NH_3	2.6	8
	HCl	$HFCl^-$	400	3.7	5
		SF_4Cl^-	40	0.4	15
	$ClONO_2$	$ClONO_2F^-$	30	2	3
CF_3O^- (laboratory)	HNO_3	$HFNO_3^-$	3300	3.8	15
			500 w/NH_3	1.8	10
	HCl	$HFCl^-$	1000	0.23	140
	$ClONO_2$	$ClONO_2F^-$	<10		
$CH_3SiF_4^-$ (laboratory)	HNO_3	$HFNO_3^-$	1400	3	13
			150 w/NH_3		
	HCl	$HFCl^-$	400	1.2	13
		$CH_3SiF_3Cl^-$	30	0.06	90
	$ClONO_2$	$ClONO_2F^-$	<10		
SiF_5^- (flight)	HNO_3	$HNO_3{\cdot}SiF_5^-$	300 w/NH_3	0.73	24[a]
			500	1.1	24[b]
			1100	1.1	30[c]

[a] Reference [5].
[b] Reference [8].
[c] Reference [29].

tive mass spectra using SF_5^- ions with and without HCl and HNO_3 added are shown in Fig. 2. The $HFCl^-$ and $HFNO_3^-$ product ions clearly dominate the spectrum, apart from SF_5^-, when the calibration gases are added.

The second criterion is that there is a well-defined, monotonic relationship between the measured product ion count rates and the concentrations of the species measured. To investigate this, different known amounts of HCl or HNO_3 were added to the flow in the laboratory instrument and the reagent ion loss and product ion yields were observed. The relationships between the amount of trace gas added and both the depletion of the reagent ion and production of the product ion are expected to follow the rate law for a simple, direct reaction of the trace gas with the reagent ion. The trace gas is in excess over the reagent ion, so the reaction is pseudo-first-order. The results of these studies are shown in Figs. 3 and 4 for the SF_5^- reaction with HNO_3 and HCl, respectively. The

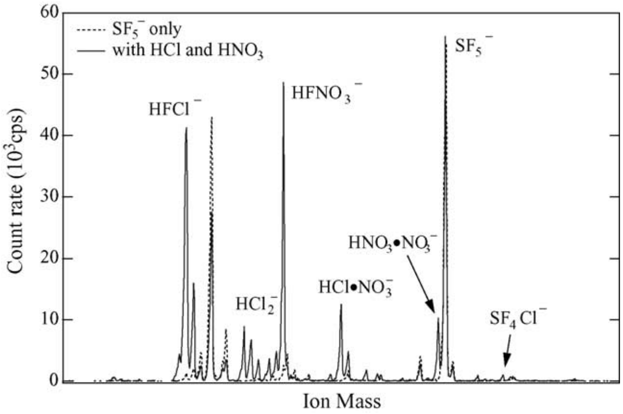

Fig. 2. Typical mass spectra produced from the SF_5^- chemistry scheme with (solid line) and without (dotted line) 10,000 pptv of HCl and 7200 pptv HNO_3 added to the sample flow. The $HFCl^-$ and $HFNO_3^-$ product ion peaks dominate the spectrum when HCl and HNO_3 are added. Several minor products also appear.

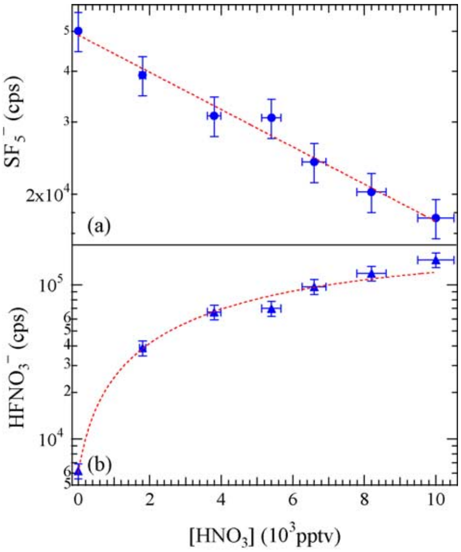

Fig. 3. $SF_5^- + HNO_3$ kinetics. (a) Reagent ion as a function of HNO_3 added to the sample flow. The fit is consistent with pseudo-first-order kinetics with $k_{HNO_3} = 2.1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. (b) $HFNO_3^-$ product ion as a function of HNO_3 can be fit by an equation of the form: $HFNO_3^- = C(1 - [SF_5^-])$, suggesting that it is a primary product of the $SF_5^- + HNO_3$ reaction.

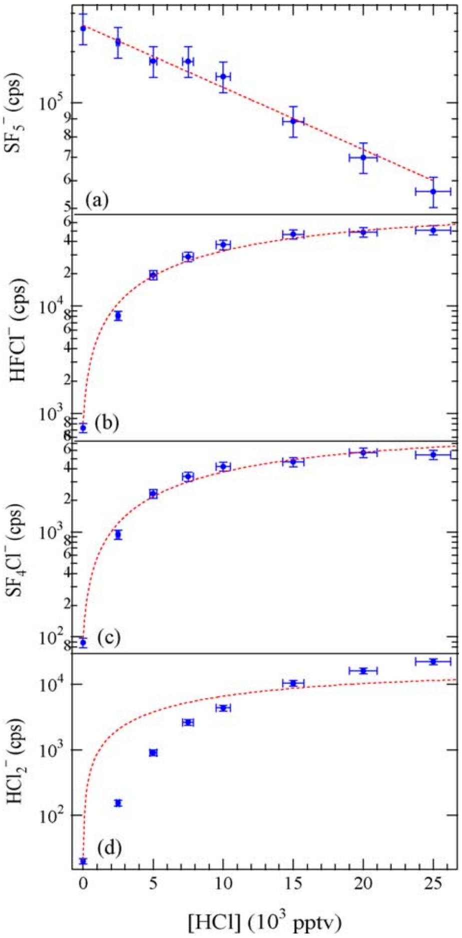

Fig. 4. SF_5^- + HCl kinetics. (a) The exponential fit of SF_5^- vs. [HCl] is consistent with pseudo-first-order kinetics with $k_{HCl} = 1.0 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}; (b) $HFCl^-$ and (c) SF_4Cl^- can be fit by equations of the form: product ion = $C(1 - [SF_5^-])$, suggesting that these are primary products of the SF_5^- + HCl reaction; (d) HCl_2^-, cannot be a primary product of SF_5^- + HCl and cannot be fit to $C(1 - [SF_5^-])$.

exponential loss of SF_5^- with increasing HNO_3 or HCl concentration confirms the expected pseudo-first-order kinetics for both reactions.

The loss of the SF_5^- reagent ion with addition of HNO_3 (Fig. 3a) can be fit to the equation: $[SF_5^-]$ (cps) = 49,000 exp($-105[HNO_3]$ (ppmv)). The pre-exponential factor is the reagent ion count rate produced in the absence of HNO_3. This results in an overall rate constant, k_{HNO_3}, of $(2.1 \pm 0.3) \times 10^{-9}$ cm^{-3} $molecule^{-1}$ s^{-1} in good agreement with the value of $(2.1 \pm 0.4) \times 10^{-9}$ cm^{-3} $molecule^{-1}$ s^{-1} from Lovejoy and Wilson [24]. The fit to the reagent ion depletion in Fig. 4a yields a rate constant of $(1.0 \pm 0.2) \times 10^{-9}$ cm^{-3} $molecule^{-1}$ s^{-1} for the reaction with HCl, which agrees within the uncertainties with the previously reported value of $(1.2 \pm 0.2) \times 10^{-9}$ cm^{-3} $molecule^{-1}$ s^{-1} [24].

The plots of product ions with addition of HCl or HNO_3 are fit with equations of the form: product ion = $C(1 - [SF_5^-])$, where C is a factor that depends on the mass discrimination of the quadrupole for each product ion in addition to the rate constant for the reaction. The good fits of the product ions $HFNO_3^-$ (Fig. 3b), $HFCl^-$ (Fig. 4b), and SF_4Cl^- (Fig. 4c) demonstrate that the product ions that will be used to measure HCl and HNO_3 are primary products that are not created or depleted by other reactions to any significant degree. These products are, therefore, suitable for measuring HCl and HNO_3. The plot of HCl_2^- (Fig. 4d) is provided for comparison to show a product ion that cannot be produced directly from the HCl + SF_5^- reaction and accordingly shows an HCl dependence that cannot be fit by the above equation.

2.4. Atmospheric interferences

The third criterion is that species present in the atmosphere, but not in the initial lab tests, do not interfere with the proposed measurements using the SF_5^- reagent ion. An interference would occur if another neutral species in the atmosphere were to significantly deplete the reagent ion, or produce or react with one of the product ions of interest. Two of the most abundant and reactive (with negative ions) atmospheric species are ozone and water. To ensure that the SF_5^- chemistry would not be compromised in the real atmosphere, ozone and water were added to the sample flow in amounts of 4 and 100 ppmv, respectively, comparable to expected maximum values in the UT/LS, and the effects on the sensitivities and detection limits were observed. Table 2 summarizes the results of these tests. The SF_5^- reagent ion count rate does not change significantly with the addition of either water or ozone. Within the uncertainty of the measurements, up to 4 ppmv of ozone does not affect either $HFNO_3^-$ or $HFCl^-$ product ion count rates and 100 ppmv of H_2O does not affect the HNO_3 measurement. Adding 100 ppmv of water does cause the $HFCl^-$ product ion to decrease by a small but significant amount. This effect results in a 12 ± 5% decrease in HCl sensitivity under 100 ppmv H_2O conditions. It is most

Table 2
SF_5^- atmospheric interference tests

	7200 pptv HNO_3 added	10,000 pptv HCl added	
	$HFNO_3^-$ [a]	$HFCl^-$ [a]	SF_4Cl^- [a]
Zero N_2 + HCl or HNO_3	0.509 ± 0.018	0.362 ± 0.015	0.034 ± 0.002
100 ppm H_2O added	0.485 ± 0.015	0.317 ± 0.010	0.026 ± 0.001
4 ppm O_3 added	0.48 ± 0.08	0.32 ± 0.04	0.033 ± 0.005

[a] Normalized to SF_5^-, which remains constant within the uncertainties.

likely due to the anion clustering with H_2O. With 100 ppmv water addition, there is a small increase in the signal from $H_2O{\cdot}HFCl^-$.

2.5. Laboratory conclusions

Overall, SF_5^- provides the best sensitivity and detection limit for both HCl and HNO_3, has a mass spectrum that is reasonably free of interferences, and results in product ions that have well defined relationships with the analytes. The potential of atmospheric interferences from O_3 and H_2O are small in the cloud-free UT/LS. However, the HCl measurements may be compromised if sufficiently humid ambient conditions are encountered, such as in clouds and in the lower troposphere. Taken together, these results suggest that the SF_5^- chemistry will be the best of the three reagent ions for measurement and detection of HNO_3, HCl, and $ClONO_2$ in the UT/LS.

3. Airborne studies

The SF_5^- reagent ion was chosen for measurements with the flight CIMS instrument based on the detection limit and interference tests. The CIMS instrument was flown during the NASA CRYSTAL–FACE mission in July 2002, from Key West, FL to measure HCl, HNO_3, and $ClONO_2$. Most of the flights during the mission used the SiF_5^- chemistry to measure only HNO_3 [29]. SF_5^- was used as the reagent ion on the last three flights of the mission (July 28, 29, and 31) [1]. Changing reagent ions required changing the source gases passing through the ^{210}Po source from the SiF_4/SF_6 mixture to SCF_8 and retuning the quadrupole mass spectrometer to detect the product ions from reactions (1)–(4).

3.1. Calibration

Throughout the mission, the HNO_3 measurement was calibrated in flight by addition to the flow of a known amount of HNO_3 from a permeation tube (Kintek Inc., Galveston, TX) to account for any drift in sensitivity through the flight. The ratio of the sensitivities to HCl and HNO_3 is assumed to be constant throughout a flight. The measurements are zeroed during flight by periodically adding dry nitrogen in place of ambient air to the sample line. HCl and $ClONO_2$ were not calibrated in flight. After the mission HCl was cross-calibrated with HNO_3 in order to establish a relationship between the production of $HFNO_3^-$ and $HFCl^-$ from HNO_3 and HCl, respectively, in the flight CIMS instrument. This allowed the HCl mixing ratio to be calculated using the in-flight HNO_3 calibrations.

The flight CIMS instrument was operated in the laboratory after the mission, under conditions as close to those encountered in flight as possible. The sample inlet pressure was set to 130 hPa using an external mechanical pump and servo-controlled valve. This is the pressure at 14 km altitude. A portable refrigeration unit was used to insure uniform flow tube temperatures that matched flight conditions. HCl from a standard bottle (GASCO, Sarasota, FL) was added to the dry nitrogen flow in the sample inlet. The flow of HCl was set to 3.9 sccm to give 10,000 ± 1000 pptv of HCl in the 2.0 slm inlet flow using the 5 ± 0.5 ppmv bottle concentration certified by the manufacturer. The HNO_3 permeation tube, as calibrated in our laboratory and by the manufacturer, produced 7200 pptv of HNO_3 in the sample flow.

The instrument was operated for 1 h for the CIMS system to equilibrate before calibration measurements were made. The calibration sequence cycled through the product and reagent ions $HFCl^-$, $HFNO_3^-$, SF_4Cl^-, and SF_5^- for 1 min each to insure that the signal from each ion was stabilized. This sequence was repeated with dry N_2 only entering the inlet and with known amounts of either HNO_3 or HCl added to the flow in order to establish a relationship between the production of $HFCl^-$ and $HFNO_3^-$. The average ratio of $HFNO_3^-$ to $HFCl^-$ from a series of calibration runs was 1.38 ± 0.14.

A similar calibration of $ClONO_2$ was also performed in the laboratory. $ClONO_2$ was added to the sample flow by passing 5 sccm of N_2 over a sample of liquid $ClONO_2$ in a glass trap in a dry ice/ethanol bath (193 K) with a trap pressure of 920 hPa. The vapor pressure of $ClONO_2$ at this temperature is approximately 1.3 hPa [30]. The $ClONO_2/N_2$ mixture is diluted to a mixing ratio of about 0.02 ppmv in the CIMS sample flow by addition of N_2 in a manner similar to that used for previous studies [31]. The resulting $ClONO_2F^-$ signal gave a sensitivity of 2 pptv/cps (Table 1), which was used in conjunction with the in-flight HNO_3 calibration to produce ambient $ClONO_2$ mixing ratios, as with the HCl measurements.

3.2. Data reduction method

Sufficiently high concentrations of HNO_3 or HCl can significantly deplete the concentration of the SF_5^- reagent ion, which affects the sensitivity to both species. Fig. 3a and Fig. 4a show the depletion of SF_5^- with increasing HNO_3 and HCl, respectively. Based on Fig. 3a, 2000 pptv of HNO_3, a value commonly encountered by the flight instrument, causes a 20% drop in SF_5^-. In the data reduction process, we must account for this change in sensitivity. The production of $HFCl^-$ and $HFNO_3^-$ (the amount of SF_4Cl^- produced is small enough to neglect) are governed by the relationships for two competing pseudo-first-order reactions of the form: A + B → C + D, and A + E → F + G. When B and E are in sufficient excess over A, then

$$\frac{d[C]}{dt} = k_1[A]_t[B]_0,$$

$$\frac{d[F]}{dt} = k_2[A]_t[E]_0$$

and

$$[A]_t = [A]_0\{1 - \exp(-k_1 t[B]0 - k_2 t[E]_0)\},$$

where k_1 and k_2 are the rate constants for the two reactions above, respectively, and $[X]_0$ and $[X]_t$ are the concentrations of species X initially and at time t, respectively. In the present case, it follows that each of the product ions is related to ambient values of each of the trace gases, HNO_3 and HCl, by the following equations:

$$\mathrm{HFCl}^- = \frac{ak_1[\mathrm{HCl}]_0[\mathrm{SF_5}^-]_0 \times \{1 - \exp(-k_1 t[\mathrm{HCl}]_0 - k_2 t[\mathrm{HNO_3}]_0)\}}{k_1[\mathrm{HCl}]_0 + k_2[\mathrm{HNO_3}]_0} \tag{12}$$

$$\mathrm{HFNO_3}^- = \frac{bk_2[\mathrm{HNO_3}]_0[\mathrm{SF_5}^-]_0 \times \{1 - \exp(-k_1 t[\mathrm{HCl}]_0 - k_2 t[\mathrm{HNO_3}]_0)\}}{k_1[\mathrm{HCl}]_0 + k_2[\mathrm{HNO_3}]_0} \tag{13}$$

where the constants a and b account for the combination of the mass discrimination of the quadrupole and the conversion from concentration units in the flow tube to measured counts per second for the product ions. $[HCl]_0$ and $[HNO_3]_0$ are the ambient concentrations of HCl and HNO_3, respectively. $[SF_5^-]_0$ is the concentration of the reagent ion in the absence of HCl or HNO_3, and the reaction time, t, is the residence time in the flow tube, which is 0.18 s. From the laboratory results above, $k_1 = 1.0 \times 10^{-9}\ \mathrm{cm^{-3}\ molecule^{-1}\ s^{-1}}$ and $k_2 = 2.1 \times 10^{-9}\ \mathrm{cm^{-3}\ molecule^{-1}\ s^{-1}}$. The values of a and b are derived from the observed $HFCl^-$ and $HFNO_3^-$ ion signals that arise when a known amount of HCl or HNO_3 is added during calibration. An additional complication could occur due to the ligand switching reaction: $HFCl^- + HNO_3 \leftrightarrow HFNO_3^- + HCl$. However, this reaction is not significant in this case, because when both HCl and HNO_3 are added simultaneously, the results can still be described by Eqs. (12) and (13), within experimental uncertainty.

In order to derive values of $[HCl]_0$ from the flight data, the value of $HFCl^-$ during calibration, which was not measured in flight, must be known. The ratio of $HFCl^-$ to $HFNO_3^-$ produced during post flight calibration will be used to estimate the amount of $HFCl^-$ that would have been produced by HCl calibrations coincident with HNO_3 calibrations in flight.

The average ratio of $HFNO_3^-$ to $HFCl^-$ from the calibration runs of 1.38 ± 0.14 is used along with the in flight HNO_3 calibration to calibrate the HCl flight data. Given this ratio, Eqs. (12) and (13) can be solved numerically using the flight data to find $[HCl]_0$ and $[HNO_3]_0$. The calibrations also give a sensitivity to HCl of 10 ± 3 cps/pptv and a detection limit of 3 ± 1 pptv. These numbers are better than those from the laboratory instrument (Table 1) because the reagent ion count is higher in the flight CIMS.

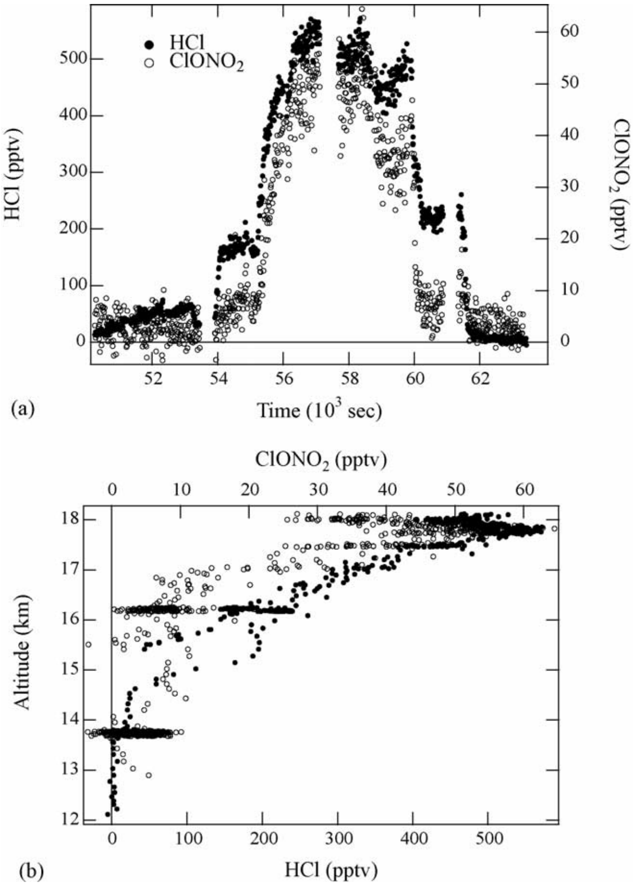

Fig. 5. (a) Mixing ratio measurements of HCl and $ClONO_2$ as a function of universal time during a flight from Key West, FL, to Houston, TX, on July 31, 2002. (b) Altitude profiles of the measurements.

3.3. Flight data

HCl and $ClONO_2$ mixing ratios from flight data obtained on July 31, 2002 [1] are shown in Fig. 5 as time series and as altitude profiles. These data provide an example of the ranges of HCl and $ClONO_2$ values encountered in a region of the atmosphere where the instrument is typically flown. The vertical gradient in both species is expected since both are produced in the stratosphere. The overall uncertainties in the measurements are ±25% for HCl and ±50% for $ClONO_2$ due primarily to uncertainties in the calibrations performed on the ground. The near zero HCl data have a standard deviation of less than 5 pptv, which is consistent with the 3 pptv detection limit derived from the calibrations. The variance of the $ClONO_2$ data when the value is near zero is less than 3 pptv. Flights at the maximum altitude for the WB-57F or higher latitudes would encounter higher values of HCl and $ClONO_2$.

4. Summary

We have evaluated the three reagent ions, SF_5^-, CF_3O^-, and $CH_3SiF_4^-$, for their potential to be used for airborne

CIMS measurements of HCl, HNO_3, and $ClONO_2$. Based on the three criteria for suitability listed above, all three could be used successfully in atmospheric measurements. However, the new SF_5^- ion chemistry has proved to be the preferred scheme for measuring HCl, HNO_3, and $ClONO_2$ with high precision and accuracy in the upper troposphere and lower stratosphere. The laboratory studies show that overall SF_5^- is superior to the other two reagent ions tested and that it is insensitive to interference from ozone and water typical in most situations that a flight instrument will encounter in the UT/LS. The product ions provide well-characterized relationships to HCl, HNO_3, and $ClONO_2$ that allow reliable measurements to be made. Successful measurements of HCl, HNO_3, and $ClONO_2$ were made in the upper troposphere and lower stratosphere during the NASA CRYSTAL–FACE mission in July 2002.

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