In situ HNO₃ to NOy instrument comparison during SOLVE

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Received 25 January 2002; revised 9 August 2002; accepted 9 August 2002; published 27 March 2003.

[1] Measurements of HNO₃ mixing ratios from the chemical ionization mass spectrometer have been critically compared with simultaneous measurements of total gas phase NOy from the NO chemiluminescence detector aboard the NASA DC-8 aircraft during the SAGE 3 Ozone Loss and Validation Experiment (SOLVE). The data were obtained in the arctic upper troposphere and lower stratosphere in the winter of 1999–2000. A brief comparison to the NOy instrument aboard the NASA ER-2 is also presented. The time responses, detection limits, relative precision, and stability of relative calibrations for the instruments were in excellent agreement throughout the mission. However, the average slope of the HNO₃ to NOy correlation was 1.13 ± 0.03 overall and 1.06 ± 0.03 in stratospheric air, indicating that the two measurements had a systematic calibration offset. Possible sources for the offset error are presented, and methods to reduce the calibration error in future flights are suggested. INDEX TERMS: 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; KEYWORDS: nitric acid, reactive nitrogen, chemical ionization mass spectrometry, HNO₃, NOy, instrumentation


1. Introduction

[2] Reactive nitrogen in the atmosphere, collectively called NOy, comprises a variety of molecules including NO, NO₂, N₂O₅, nitric acid (HNO₃), HNO₄, ClONO₂, and PAN (peroxyacetyl nitrate). Reactive nitrogen plays a central role in the aeronomy of the atmosphere, in tropospheric pollution, and in stratospheric ozone loss. Significant effort has been devoted to accurate and comprehensive measurements of total NOy and its component species.

[3] A well-established method for measuring total NOy involves catalytically converting all the reactive nitrogen species to NO on a gold catalyst [Bollinger et al., 1983; Fahey et al., 1985; Kliner et al., 1997] and then measuring the total NO concentration with a chemiluminescence detector [Ridley and Grabek, 1990]. This technique has been applied to aircraft measurements both in the stratosphere [Fahey et al., 1989a] and troposphere [Kondo et al., 1997b; Ridley et al., 1994; Sandholm et al., 1992] as well as ground-based [Parrish et al., 1993] and balloon [Kondo et al., 1992] measurements.

[4] More recently, a number of research groups have developed the chemical ionization mass spectrometry (CIMS) method for detecting a variety of trace gases in the atmosphere [Arnold et al., 1997; Eisele and Berresheim, 1992; Hunton et al., 2000; Möhler et al., 1993; Spreng and Arnold, 1994; Viggiano, 1993; Viggiano and Hunton, 1999]. In this technique, the trace gas of interest reacts with ions injected into the flow of ambient gas to produce product ions that are a unique tracer for the presence of the neutral. The reactant and product ions are detected with a quadrupole mass spectrometer. CIMS has proven to be a valuable technique for detecting HNO₃ in the atmosphere [Arnold et al., 1992; Ballenthin et al., 1998; Huey et al., 1998; Miller et al., 2000; Schneider et al., 1998] and has also been used to detect a variety of other species including SO₂, HNO₂, CH₃COCH₃, HCN, HCl, and HF.

[5] In the 1999–2000 winter/spring season, the National Aeronautics and Space Administration (NASA) sponsored the SAGE 3 Ozone Loss and Validation Experiment (SOLVE). A heavily instrumented DC-8 aircraft was stationed in Kiruna, Sweden, for three measurement campaigns in December 1999 and January and March 2000. It made a total of 17 science flights into the lowest levels of the stratosphere and the upper troposphere in the arctic. The in situ chemistry suite of instruments included a chemiluminescence instrument from the University of Tokyo for measuring NO, NO₂, NOy, and particulate NOy, and a CIMS instrument from the Air Force Research Laboratory/Space Vehicles Directorate, Hanscom Air Force Base, Massachusetts, USA.

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0148-0227/03/2002JD002136S09.00
Air Force Research Laboratory for detecting HNO$_3$ as well as other trace gases. Both instruments collected extensive data sets throughout the three campaigns.

While the distribution of individual species within the total NO$_x$ is variable in the troposphere, the single species HNO$_3$ often makes up 75% or more of total NO$_x$ for improving accuracy for future campaigns. In future work and we conclude the paper with suggestions ever, systematic differences in calibration could be reduced the measurements agree to within their error limits. However, systematic differences in calibration could be reduced in future work and we conclude the paper with suggestions for improving accuracy for future campaigns.

2. Chemiluminescence NO$_y$ Detector

2.1. Instrument Description

The University of Tokyo NO$_y$ instrument has been described in detail in other publications [Koike et al., 2002; Koike et al., 2000; Kondo et al., 1997a]. Therefore we provide only a short overview here. The instrument consisted of the inlet system in a pod outside the aircraft boundary layer, the catalytic converter, a gas handling system, the chemiluminescence detector, and an in-flight calibration system. For SOLVE, the NO$_y$ instrument was mounted on the starboard side of the DC-8 aircraft above the wing.

NO was measured directly using a chemiluminescence detector. NO$_x$ was measured simultaneously by catalytically converting all of the component NO$_y$ species to NO on the surface of heated gold tubes with carbon monoxide (CO) acting as a reducing agent. The converter system was contained in a pod mounted outside the cabin to minimize the length of the inlet tubes. The inside diameter of the inlet tubes was 0.7 cm. Gas phase NO$_y$ measurements were made by sampling air through the rearward facing inlet, which discriminated against particles of diameter larger than 1 µm. The mixing ratios of total NO$_x$ (gas phase-NO$_3$ + amplified particulate NO$_y$) were measured by sampling air through the forward facing inlet, which was heated to 100°C. The mixing ratios of gas phase and total NO$_y$ were measured independently. A humidifier maintained the H$_2$O mixing ratio in the sample flows at a few percent in order to stabilize the instrument background against humidity variations in the ambient air.

The pressure in the gold catalytic converter for gas phase NO$_y$ was maintained at a constant value of about 50 hPa, independent of the ambient pressure. The pressure was held constant by controlling the sample flow using a servo-controlled Teflon valve mounted upstream of the converter tube. The sample flow rate for the NO$_y$ measurement was 1 standard liter per minute (sLpm). All parts of the inlet system upstream of the gold catalyst were made of Perfluoralkoxy (PFA) Teflon and were temperature controlled at 40°C.

2.2. Laboratory Calibrations

The conversion efficiencies of the various NO$_y$ species on the gold catalyst were measured prior to and after the SOLVE deployments. The efficiency was greater than 98% for NO$_2$ and greater than 95% for HNO$_3$. The conversion efficiencies of other species, such as HCN, that might cause interferences or backgrounds in the NO signal were found to be negligibly low.

In laboratory tests, the time response of the instrument to HNO$_3$ test gases through a 1 m Teflon sampling line was measured by adding about 10 ppbv of HNO$_3$ to a dry, synthetic airflow at a pressure of 1000 hPa. After terminating the HNO$_3$ flow, the initial e-folding time of the NO$_y$ signal was found to be 20 s. [Kondo et al., 1997a] Because the total length of the inlet line upstream of the gold catalyst was reduced to 27 cm in the flight instrument, the time response in flight was expected to be on the order of 5 s. This expectation was borne out by analysis of the flight data presented below.

2.3. In-Flight Calibrations

The absolute sensitivities of the NO and NO$_2$ channels were measured every 70 min by adding known flows of NO and NO$_2$ standard gases into the ambient gas stream. The NO$_2$ conversion efficiency in the ambient air was also checked at the same time and was found to be greater than 98% throughout the whole mission. These methods of calibration are described in detail in other publications [Koike et al., 2000; Kondo et al., 1997a].

2.4. Error Assessment

The precision and detection limit for NO$_y$ were estimated under the assumption that the count rate followed a Poisson distribution. Typical count rates in the upper troposphere (8 – 12 km) were 900 s$^{-1}$ background and 8700 s$^{-1}$ for 1000 pptv at a sensitivity of 7.8 counts s$^{-1}$ pptv$^{-1}$. For 10-s averages at 1000 pptv, the error due counting statistics was approximately 0.4% or 4 pptv. The actual fluctuations in the observed NO$_y$ mixing ratio were about 1.2 times larger than the precision estimated from counting statistics. The detection limit (S/N = 2) was estimated to be 4 pptv for a 10-s integration time. The absolute accuracy of NO$_y$ measurements estimated from uncertainties in calibration gas NO concentration (2%), sample gas flow rate (2%), calibration gas flow rate (2%), conversion efficiency (2%) and other factors was 10% for an NO$_y$ value of 1000 pptv.

3. Chemical Ionization Mass Spectrometer

3.1. Instrument Description

A schematic diagram of the AFRL CIMS instrument as it flew in the SOLVE mission is shown in Figure 1. Ambient air passed through a flow tube from an inlet outside the aircraft’s boundary layer. CO$_3$ ions generated in a corona discharge ion source reacted with the air sample to give unique product ions that were detected by the mass spectrometer. In the case of HNO$_3$, the product ion was CO$_3$(HNO$_3$) at 123 u. Because no other species with appreciable concentrations react with CO$_3$ to produce a product ion at the same mass, the detection of HNO$_3$ was
essentially free of interference from other neutral species. The largest source of background signal was due to adsorption and desorption of HNO₃ itself within the flow system, as discussed below. CO₃/HNO₃ and product ions from other neutrals were orders of magnitude less intense than CO₃, indicating that the instrument was far from saturation. For HNO₃ during SOLVE, detection sensitivities in the range of 4000–8000 counts s⁻¹ ppbv⁻¹ were obtained.

The instrument has been described in detail in previous publications [Ballenthin et al., 1998; Hunton et al., 2000; Miake-Lye et al., 1998; Miller et al., 2000; Talbot et al., 1999; Viggiano and Hunton, 1999; Viggiano et al., 2003].

For the SOLVE campaign we made several important improvements to the CIMS instrument, most notably in the inlet design, ion source, mass spectrometer, and calibration system. In earlier missions, we used a curved, forward facing inlet that relied on the ram pressure of the atmosphere to force gas through the flow tube. For SOLVE, a straight, 3.5 cm ID, Teflon-coated, stainless steel tube was mounted perpendicular to the aircraft fuselage inside an aerodynamic fairing, beyond the boundary layer of the aircraft skin. The inlet end of the tube protruded 3 cm beyond the fairing and was cut at a 30° angle to the horizontal so that the opening in the tube faced away from the direction of flight. The length of the inlet tube outside the aircraft was 43 cm, and the total length of the inlet tube from the inlet aperture to the corona ion source was 104 cm. This inlet design was intended to prevent larger aerosol particles from entering the instrument. By comparison with other inlets of similar design, we estimate that the aerosol cutoff size was on the order of 0.5–1 μm.

During the first two SOLVE deployments an exhaust pipe perpendicular to the aircraft and cut off at 45° with the opening facing rearward was used. For the March deployment, the exhaust end of the sampling tube was terminated with a rear facing venturi, as shown in Figure 1, to increase aspiration and to stabilize the flow through the sampling tube. Throughout the mission, a high-speed fan was installed in the exhaust line to keep the flow velocity relatively constant (at about 8 m s⁻¹) at different altitudes. The gas flow through the instrument varied as a function of altitude from approximately 45 sLpm at 10.5 km to 35 sLpm at 12.5 km.

The entire inlet tube, except for the outermost 5 cm at the end of the fairing, was wrapped with heating tapes and heated to 80°C to inhibit adsorption of water vapor or HNO₃ on the walls of the tube. Measurements at various points along the sampling tube showed that the air sample was near cabin temperature as it entered the cabin, rose to about 35°C by the time it passed through the ionization region, and was at 55°C following the fan in the exhaust line.

A straight section of the exhaust line contained a corona needle followed by two electrodes 20 and 40 cm downstream of the needle. The velocity of the air flow in the sampling tube was obtained by pulsing a high voltage on the corona needle to produce ions in the flow tube and using an oscilloscope and high-gain amplifier to measure the time of flight of the ions at the downstream electrodes. This measurement was made during calibration events in flight. The ion flight time was corrected to give average, bulk neutral flow velocity using data from postflight laboratory
experiments in which the time of flight was directly calibrated to a bulk neutral flow of nitrogen gas introduced into the CIMS flow tube through a gas flow controller. Measurements of gas flow velocity with a Pitot tube were unsuccessful because turbulence in the flow tube caused large fluctuations in the Pitot tube differential pressure.

[19] The ion source used during SOLVE differed in an important respect from that used in previous missions. Because CO$_3^-$ ions are required for the chemical ionization process, a dilute mixture of CO$_2$ in O$_2$ was used in the ion source for earlier missions. However, subsequent laboratory work showed that the corona discharge with this gas mixture generated radical species that gave interfering ion signals at important masses. Notably, production of CO$_4^-$ led to HCO$_4^-$. These ions clustered weakly with N$_2$ and H$_2$O to give a small interference signal at the same mass that was monitored for HNO$_3$ (123 u). This interference accounted for some of the 50 pptv detection limit that was reported for data obtained during the SONEX mission [Miller et al., 2000]. The subsequent laboratory work showed that it was not necessary to mix CO$_2$ into the oxygen source gas, and that HCO$_4^-$ could be virtually eliminated by so doing. Therefore, for SOLVE, O$_3$ ions were created in the corona from pure O$_2$ and were injected into the flow tube instead of CO$_2$. Injection of O$_3$ ions into the air sample led to CO$_3^-$ within microseconds as a result of reactions with CO$_2$ in the air. The CO$_3^-$ ions then reacted with the trace gases. Furthermore, we found that running the corona discharge in the ion source at very low current (8 nA) minimized production of radicals, though slightly lowering total ion yield. Thus we sacrificed about a factor of two in detection efficiency in order to virtually eliminate interfering signals. Even so, the CO$_3^-$ ion intensity at the detector was typically 5 × 10$^6$ s$^{-1}$ for the low pressure, dry air of the SOLVE mission. A typical CO$_3^-$(HNO$_3$) ion intensity in the stratosphere was 10$^6$ s$^{-1}$. A typical mass spectrum obtained with the CIMS instrument is shown by Viggiano et al. [2003].

[20] The rf quadrupole mass filter used in the CIMS was greatly improved prior to the SOLVE mission by the addition of rf-only focusing rods to the entrance and exit of the mass filter. The main function of the focusing rods was to force ions to enter the mass filter near to its axis with little transverse velocity. This focusing maximized the abundance sensitivity. The ratio of ion intensity to the intensity 1 u lower due to wings on the side of the mass peak), increased transmission and minimized mass discrimination. The intensity of isolated mass peaks was independent of mass resolution for peak widths ≥1 u, implying that all ions of the selected mass were being passed by the spectrometer. This improvement is not simply aesthetic. The detection efficiency of the CIMS depends on the transmission efficiency of the mass filter, while the dynamic range (about 5 orders of magnitude for 1-s integration) and detection limit of the CIMS instrument depends on the abundance sensitivity. The detector was a discrete dynode electron multiplier used in the pulse counting mode.

3.2. In-Flight Calibrations

[21] The calibration system for the SOLVE mission was based on permeation tubes (Kim-tek Laboratories, Inc., LaMarque, Texas) kept in a Teflon-coated, copper reservoir. HNO$_3$ and sulfur dioxide permeation tubes were used throughout the SOLVE campaigns and hydrogen cyanide was added for the March deployment. Beginning a month prior to the mission, the permeation tubes were kept in the reservoir at all times under conditions of constant temperature (35°C), constant gas flow (0.4 sLpm) and constant pressure (930 hPa). A battery pack kept the system powered whenever aircraft or laboratory power was not available. Flow through the permeation tube reservoir was normally pumped into the exhaust line of the sampling tube except during a calibration event, when closure of a Teflon solenoid valve on the pump forced the flow through ~45 cm of 0.4 cm ID Teflon tubing to a point 5 cm inboard from the end of the inlet tube.

[22] Ion signals from a typical calibration event are shown in Figure 2. The SO$_5^-$ signal at mass 112 u comes from the addition of the SO$_2$ calibration gas and the CO$_3^-$(HNO$_3$) at mass 123 u is produced from HNO$_3$. The instrument was programmed to measure the mass 123 signal much more frequently than 112, which is why the 1-s CO$_3^-$(HNO$_3$) data are smoother than the 5-s averages plotted for SO$_5^-$. SO$_2$ and HCN gases and permeation tubes proved to be trouble-free. These two gases did not adhere to the walls of the reservoir or to transfer lines. Mass spectrometer signal levels rose and fell with time constants less than 0.5 s as the calibration flow was switched on and off. HNO$_3$ was a different matter because of its low vapor pressure and tendency to adhere to surfaces. All surfaces in contact with the HNO$_3$ vapor had to be Teflon-coated or manufactured from solid Teflon to minimize adsorption and desorption of the vapor. The HNO$_3$ permeation tubes took many days to come to equilibrium once under constant temperature and carrier gas flow conditions. In the flow tube, the time response to the HNO$_3$ calibrant was slower than for SO$_2$. [23]
Figure 2 shows that the calibration signal did not stabilize until around 50 s after the flow of calibrant started. Approximately the same time was required for the signals to return to ambient levels after the calibration. When the ambient HNO₃ concentration was very low, as in tropospheric air, the effects of calibrations lingered for longer periods. An example of a calibration under such conditions, where the ambient HNO₃ signal was approximately \(400 \text{s} / C_0\) rather than \(10,000 \text{s} / C_0\), is shown in Figure 3. The \(CO_3 / C_0\) (HNO₃) signal was dominated by the calibration event for approximately 1000 s after the calibration gas was shut off, but began to respond to changes in ambient HNO₃ after a universal time of 42250 s.

The data in Figure 3 can be modeled accurately by the product of three exponential decays. Sixty-nine percent of the total signal is accounted for by an exponential with a time constant of 1.7 s, 22% has a time constant of 22 s, and the remaining 9% of the signal has a long time constant of 420 s. In each case the time constant refers to a single e-folding time. Because the SO₂ calibration signal shows that the time constant of the calibration gas handling system and the CIMS flow tube is significantly faster than 1 s, all three of the HNO₃ time constants must represent equilibration of various walls and surfaces in the flow system. The effects of these time constants on the measurements of ambient HNO₃ are discussed in section 4.

Figure 3. HNO₃ and SO₂ calibration responses for low ambient HNO₃ concentrations. The logarithm of the calibration signal is plotted against time to emphasize the time response of the system at lower signal levels. The 1-s averages for \(CO_3\) (HNO₃) and 5-s averages for SO₅ are plotted.

3.3. Error Assessment

Calibration data were used to calculate a calibration factor by which the \(CO_3\) (HNO₃) count rate was multiplied to give HNO₃ volume mixing ratios. The calibration factor was obtained from the measured change in ion count rate during calibrations and from the ratio of the emission rate of HNO₃ from the permeation tubes to the total gas flow in the flow tube. This ratio is equal to the volume mixing ratio of calibrant HNO₃ in the flow tube. The total flow was calculated from the measured temperature, pressure, and flow velocity. The effects of errors in each of these individual measurements are considered below.

Count rates for \(CO_3\) (HNO₃) were typically on the order of 5000 counts s⁻¹ ppbv⁻¹ and the instrument typically devoted at least 50% of its measurement time to this ion. With this sensitivity and an integration time of 1 s (actual measurement time of 0.5 s), 10% precision in the Poisson statistics is obtained at a detection limit of 40 pptv. For the stratospheric data presented here, where the concentrations are at least 500 pptv and the averaging times are 1 s or longer, counting statistics account for a 4% error or less.

A balance with 0.1-mg resolution was used to measure the mass loss from each permeation tube (HNO₃, SO₂, and HCN) periodically throughout the mission. The mass loss rate over time was used to calculate the instantaneous emission rate. We note that in at least one other group, this method has given emission rates that agree to

Figure 4. Average values of the HNO₃ calibration factor as a function of altitude for the March 2000 SOLVE deployment. The error bars represent 1-σ uncertainties.
within a few percent with ion chromatography calibrations of emission rates (P. Wennberg, private communication, 2000). The permeation tubes were kept under constant pressure, temperature, and flow conditions for the entire 4-month SOLVE mission. They were removed from the reservoir only for minutes at a time for weighing. The scale used could reproducibly produce weights with a precision of <0.5 mg. The total mass loss over the course of a 1-month deployment was approximately 0.02 g. However, the rate of weight loss over the course of the entire mission was not linear with time for the HNO₃ tubes but rather decreased by a factor of nearly 40% by the end of the 4 months. Over the course of a single, 1-month deployment, the variation was no more than 10%, but a linear approximation for any one deployment introduced some error. The humidity of the environment where the weighing was done was not controlled and variable adsorption of water onto the outside of the permeation tube could have affected the accuracy of the weights. However, the weights showed essentially no scatter about the trend, suggesting that water adsorption on the tubes was a minimal problem.

[29] A mass loss calibration will suffer from a systematic error if other species besides the species of interest are emitted. The HNO₃ tubes were stabilized with sulfuric acid to reduce the amount of water emission. However, the water emission rate was not measured. Emission of NOₓ from HNO₃ tubes has also been reported [Ryerson et al., 1999]. During in-flight calibrations, large emissions of NO or NO₂ from the permeation tubes would have been detected as NO₂-H₂O at mass 64 or as NO₃ at mass 62, respectively. No change in either signal level was detected, but because the sensitivity to these gases was lower than for HNO₃ [Arnold et al., 1995], upper limits on their concentrations were not useful. Because the weight fraction of NOₓ emissions from the tubes was previously reported to be 8% [Ryerson et al., 1999] and because the tubes were stabilized with sulfuric acid, we feel a reasonable estimate of the accuracy of the permeation tube emission rates is ±20%.

[30] Total gas flow in the flow tube was calculated from the measured temperature, pressure, and flow velocity of the gas. The emission rate of the permeation tube divided by the total gas flow in the flow tube yields the mixing ratio of calibrant HNO₃ in the flow tube. Because the calibrant gas was injected as far upstream in the flow tube as possible into a turbulent flow, we assume perfect mixing. Measurements of the temperature and pressure are straightforward. However, because both parameters change somewhat with position in the flow tube, we assign a ±5% error to each to account for the variability. As described above, the gas flow velocity was measured using ion time of flight. We estimate that the total flight time of ~25 ms was measured to an accuracy of 3 ms, giving an error of ±12%.

[31] In previous experiments, we estimated that the instrumental background of HNO₃ in the CIMS was approximately 50–100 pptv. As mentioned above, this background has been reduced by changes in the ion source chemistry and by care in Teflon coating and heating of the flow tube. For the SOLVE campaign we attempted to measure the HNO₃ background in the CIMS directly by injecting zero air into the flow tube and excluding ambient air. However, it proved to be impossible to match the flow and ion chemistry conditions to the actual measurement conditions accurately enough, and the results were not useful. Throughout the SOLVE deployments there were several occasions when the DC-8 flew through tropospheric air at cruise altitudes. The HNO₃ concentration measured in these air masses dropped to as low as 40 pptv. An example of such data is shown here in Figure 11. From this observation we conclude that the instrumental background under these measurement conditions must have been lower than 40 pptv. For stratospheric air, we estimated the instrumental background from the data in Figure 5. The intercept of the least squares fit of the stratospheric points (selected by restricting ozone concentrations to greater than 250 ppbv) was 57 pptv. The background compared to the tropospheric measurements may have increased slightly with higher ambient levels of HNO₃ because of increased adsorption onto the flow tube walls. However, the background is largely independent of ambient concentration because adsorption and desorption reach equilibrium within several time constants. Wall interactions affect the time constant of the instrument more than the background. The background levels were higher immediately after calibrations, as shown in Figures 2 and 3, but these data were removed from the final data sets. While this level of background is important for tropospheric measurements where ambient concentrations are very low, it is a relatively small effect for the SOLVE data, 2–5%, where the ambient concentrations are much higher. No background subtraction was done for the CIMS data in the SOLVE data archive or for the data presented here.
In summary, propagation of errors gives the accuracy of the HNO₃ mixing ratios presented here for the stratosphere as ±30%. We estimate that the precision is ±10–15%. The bulk of this uncertainty in accuracy (±20%) is due to determining the emission rate of the HNO₃ permeation tube used as the calibration standard. Of the remainder, most is due to uncertainty in the measurement of the mass flow in the sample tube, needed to express HNO₃ concentrations as mixing ratios. The uncertainty in precision is due to changes in the flow properties between calibration events and to turbulence effects on the ion signals.

4. Results

A scatterplot of CIMS HNO₃ concentrations against simultaneous total, gas phase NOₓ measurements is shown in Figure 5. The data points represent 60-s averages from all flights in the March 2000 deployment. When the data are limited to stratospheric air masses with ozone concentrations greater than 250 ppbv, the NOₓ and HNO₃ measurements are highly correlated ($r^2 = 0.83$) as they should be because HNO₃ is the primary constituent of total reactive nitrogen under these conditions. However, the slope of the correlation is 1.06, indicating that the CIMS multiplicative calibration factors are systematically too high or that the CIMS measurements were affected by an interfering species. Below 1000 ppbv, the HNO₃ concentration falls off faster than at higher altitudes, as shown by the shoulder in the scatterplot.

Previous measurements of the HNO₃/NOₓ ratio in the high latitude stratosphere show some variability. Examples of these include ER-2 aircraft measurements from the 1987 AAOE campaign where the ratio was 0.9 [Fahey et al., 1989b], balloon measurements from Esrange in Sweden in 1990 where the ratio was 0.75 [Kondo et al., 1992], and lower altitude aircraft measurements in 1997 where the ratio ranged from 0.96 in January to 0.59 in March [Schneider et al., 1999]. A ratio of 0.8 was also obtained in midlatitudes during the SONEX campaign [Talbot et al., 1999]. The experimental uncertainty in the CIMS and NOₓ measurements presented here, combined with the systematic error in calibration, prevent an accurate assessment of the NOₓ budget. However, if we assume that HNO₃ should account for 80% of NOₓ, then the two measurements disagree by a factor of approximately 25%, an error that is encompassed by the error estimates for the CIMS measurements. The SOLVE measurements are more consistent with an HNO₃/NOₓ ratio near or above 0.80 than with lower values. We also note that the offset between HNO₃ and NOₓ was consistent throughout the SOLVE missions and there is no indication of a seasonal variation of the HNO₃/NOₓ ratio as reported by Schneider et al. [1999].

A different view of the same data is shown in Figure 6 where the ratio of the HNO₃ to NOₓ concentration is plotted against the simultaneously measured ozone concentration. Above an ozone mixing ratio of 250 ppbv, the ratio of HNO₃ to gas phase NOₓ is essentially constant but slightly above one. The least squares best fit to the data above 300 ppbv of ozone has a value of 1.10 at 300 ppbv of ozone and decreases slightly to 1.05 at 800 ppbv. Below 250 ppbv of ozone, the ratio decreases steadily.

If the assumption that the HNO₃/NOₓ ratio is 0.80 is correct, then the systematic offset between the two instruments is within the accuracy limits specified for the HNO₃ measurements and is nearly encompassed by the error limits for the NOₓ measurement. The possible sources for systematic errors are the same as for random errors outlined in the instrumental sections above. If the actual HNO₃ emission...
rate from the permeation tube were lower than the mass loss measurements indicated or some HNO₃ calibration gas were lost in the transfer to the flow tube, then the actual HNO₃ mixing ratio during calibrations would be lower than our calculations indicate. The final values of the ambient concentrations would be lowered proportionately. HNO₃ loss in Teflon tubing was measured by Neuman et al. [1999] and was negligible at the elevated temperature of the line from the Teflon valve to the flow tube inlet. Equilibration of this length of tubing probably contributes to the slow rise and fall time of the calibration signals, but is not a likely net sink for the HNO₃. The other Teflon tubing in the calibration system was exposed to a constant HNO₃ flow at all times so that wall interactions there should have been in equilibrium. The possibility of a systematic error in the weight loss calibrations is discussed above, and this remains the most likely source of the systematic calibration error. If the flow velocity of the gas in the flow tube were systematically higher than the time of flight measurements indicated, then the actual HNO₃ mixing ratios during calibrations would be lower than calculated and again would reduce the final ambient HNO₃ mixing ratios. However, the postflight calibration of the time of flight system with the flow controller was designed to eliminate this source of systematic error. The NO₃ measurement could, in principal, also be affected by a systematic calibration error. For example, if the conversion efficiency of HNO₃ in the NO₃ instrument was less than measured or if losses of HNO₃ are larger, then the actual NO₃ mixing ratios would be higher than reported. However, the agreement of the two NO₃ instruments outlined in Figure 7 argues against a systematic error. Changes in HNO₃ or NO₃ concentrations were subject only to relative precision limitations and were measured with smaller error than the absolute concentrations.

On 23 January 2000, the NASA ER-2 aircraft that was also deployed to Kiruna as part of SOLVE flew along the same flight track as the DC-8 for a period of around 25 min. This flight leg was at an altitude of 11.3 km (37,000 feet) in the upper troposphere. The ER-2 carried an NO₃ chemiluminescence detector of similar design to that on the DC-8 [Fahey et al., 2001; Popp et al., 2001]. The data from both aircraft offer an additional opportunity for NO₃ comparisons and are shown in Figure 7. Figure 7 is similar to that presented by Koike et al. [2002], with the addition of the simultaneously observed HNO₃ values. The times of the common flight segment are shown on the graph. Note that because the ER-2 flew more slowly than the DC-8, the time axis for the ER-2 is compressed compared to that for the DC-8. In this way, data obtained by both aircraft at the same position in space, rather than at the same time, are plotted together. Slight differences between the two NO₃ data sets are probably due to the fact that the ER-2 flew a few kilometers northwest of the DC-8 and sampled the same air masses as much as 500 s after the other aircraft. These differences prevent a perfect cross calibration. Nevertheless, the agreement between the two instruments is remarkably good and suggests that the relative error between them was no more than 10–15%. The CIMS HNO₃ data obtained at the same time are also plotted in Figure 7 and are lower than NO₃ because the flight was in the troposphere.

The time responses of the two DC-8 instruments can be assessed by examining data from two periods when the concentrations of HNO₃ and NO₃ were both changing rapidly. In the first instance, data from early in the 16 January 2000 flight are plotted in Figure 8. The overall concentrations of NO₃ were low and the scatterplot between HNO₃ and NO₃ has the higher slope corresponding to mixing between tropospheric and stratospheric air. As a result, the amplitudes of the structures are greater in the HNO₃ data but the time development of the structures is nearly identical to that detected in NO₃. The smallest structures are on the order of a few seconds across and are well resolved by both instruments.
At the other extreme of concentration, a similar plot of HNO₃ and NOₓ when the concentrations were large is shown in Figure 9. These data are from the end of the 9 March 2000 flight. To estimate the time responses of both instruments more quantitatively, we have followed the Fourier analysis techniques presented by Murphy [1989] and Ryerson et al. [1999]. The Fourier transforms of the 1-s HNO₃ and NOₓ time series in Figure 9 are plotted in Figure 10. From DC to approximately 0.1 Hz, the Fourier amplitudes show a power law decrease that is characteristic of actual atmospheric structure. At faster frequencies, the Fourier amplitudes are independent of frequency, which is characteristic of white or instrumental noise. The transition frequency between these two regimes is an estimate of the instrumental time response [Murphy, 1989]. As shown by the least squares fits to the data in Figure 10, the transition frequency for the NOₓ instrument is approximately 0.19 Hz. This frequency corresponds to a time constant of about 5 s, which is in excellent agreement with the estimate derived by scaling the laboratory results by the length of the inlet tube. The transition frequency for the CIMS HNO₃ measurements is 0.13 Hz. This frequency corresponds to a time constant of 8 s, which probably represents a convolution of the two faster time constants derived from the calibration data presented in Figure 3. For comparison, the frequency response of the ozone measurements from the same time period is also shown in Figure 10. The ozone instrument has a faster time response than either of the other two and the Fourier transform of the ozone concentrations does not show the transition to white noise at higher frequencies.

A final example of data from the SOLVE campaign in shown in Figure 11. The volume mixing ratio of particulate NOₓ is plotted in the top graph for a portion of the 23 January 2000 flight. The forward facing inlet in the NOₓ instrument measured gas phase plus amplified particulate NOₓ. The particulate NOₓ concentration is calculated by subtracting the NOₓ signal at the rearward facing inlet from the signal obtained at the forward facing inlet and dividing by an enhancement factor that depended on the size distributions of the particles. Large structures in particulate NOₓ such as these were detected only in the upper troposphere. Note that at the end of the time period plotted in Figure 11, the gas phase NOₓ concentration begins to rise to lower stratospheric levels while the particulate signal drops to essentially zero. In the bottom graph, the NOₓ concentration from the rear facing inlet and the HNO₃ concentration from the CIMS instrument are plotted for the same time period. There is no visible correlation between the particulate NOₓ and either of the gas phase concentrations observed. A scatterplot of particulate NOₓ against gas phase NOₓ in this region has negative slope and a correlation coefficient, r², of 0.12. Between 52860 and 52940 s UT, the particulate NOₓ signal decreased by 70 pptv. The CIMS HNO₃ signal decreased by 7 pptv in the same time period, a change that was smaller than the statistical scatter in the data of approximately 10 pptv. Thus
Figure 11. A comparison of particulate NO\textsubscript{y} (top) forward facing inlet minus rearward facing inlet divided by an enhancement factor to gas phase NO\textsubscript{y} and HNO\textsubscript{3} (bottom) rearward facing inlets for a portion of the 23 January 2000 flight. The absence of strong correlation suggests that the gas phase measurements were not contaminated by evaporation of entrained aerosols.

the contribution of any particulate NO\textsubscript{y} to the CIMS HNO\textsubscript{3} signal cannot be larger than 10–15% of the total particulate NO\textsubscript{y} concentration. We conclude that neither the CIMS inlet nor the rear facing NO\textsubscript{y} inlet admitted large quantities of particles that could evaporate in the flow tube systems of either instrument and thereby affect the observed gas phase concentrations.

5. Conclusions

[41] Gas phase volume mixing ratios of HNO\textsubscript{3} and total NO\textsubscript{y} were measured simultaneously aboard the NASA DC-8 aircraft during the SOLVE campaign conducted from Kiruna, Sweden. The measurements were made during the winter and spring of 1999–2000 in the arctic upper troposphere and lower stratosphere. A detailed comparison has shown that the data sets from both instruments were very tightly correlated in the lower stratosphere where HNO\textsubscript{3} shown that the data sets from both instruments were very tight. A detailed comparison has shown that the data sets from both instruments were very tightly correlated in the lower stratosphere where HNO\textsubscript{3} comprises most of NO\textsubscript{y} and the concentrations of both species ranged between 1000 and 5000 pptv. Below 1000 pptv, the correlation between HNO\textsubscript{3} and NO\textsubscript{y} follows a steeper slope due to the mixing of upper tropospheric air with a lower fraction of HNO\textsubscript{3} in NO\textsubscript{y}. The time responses of both instruments were on the order of 5–8 s and appeared to be sufficiently fast to resolve all atmospheric structures encountered. Neither instrument was affected by ingestion of NO\textsubscript{y}-containing aerosol particles that might have boosted measured gas phase concentrations above the correct ambient levels.

[42] On one occasion during the 3-month campaign, the NASA ER-2 aircraft flew along the same flight path as the DC-8 in order to permit direct comparisons of the measurements on both aircraft. The ER-2 carried a total NO\textsubscript{y} instrument of similar design to the DC-8 experiment. Although the conditions for the comparison were not controlled tightly enough to permit an accurate cross calibration, the agreement of the two measurements was excellent. The relative calibration differences are not likely to be larger than 10–15%.

[43] The CIMS measurements of HNO\textsubscript{3} and the DC-8 measurements of NO\textsubscript{y}, however, were affected by a systematic, multiplicative, calibration offset of approximately 25% based on the assumption that HNO\textsubscript{3} should be 80% of NO\textsubscript{y} in the regions of the stratosphere that were sampled. This calibration offset was very consistent throughout the SOLVE mission. The calibration differences are within the error limits estimated for the CIMS instrument. Possible sources of the error include measurements of the HNO\textsubscript{3} emission rates from the permeation tubes used as calibration sources for the CIMS measurements; measurements of the total gas flow within the CIMS flow tube; loss of HNO\textsubscript{3} calibrant gas in the CIMS calibration system before it enters the flow tube; errors in measurement of the HNO\textsubscript{3} conversion efficiency in the NO\textsubscript{y} apparatus; or loss of ambient HNO\textsubscript{3} within the chemiluminescence instrument flow apparatus or conversion catalyst.

[44] In future flights, calibration offsets such as these can be reduced by cross calibration between the CIMS and NO\textsubscript{y} instruments. One approach is to calibrate the CIMS HNO\textsubscript{3} source by measuring the HNO\textsubscript{3} flow from the permeation tube oven directly with the NO\textsubscript{y} instrument. The disadvantage of this method is that the cross calibration does not occur under actual flight conditions. A better approach, and the one we recommend, is to install a joint calibration system that could be used alternately or simultaneously for both instruments. Such a joint calibration system would not substitute for the independent calibrations of the two instruments that would still be the basis for the absolute measurement levels. Rather, it would be used in addition to them to assess systematic differences in calibration such as those outlined in this paper. Joint calibration would be used to address specifically the fraction of NO\textsubscript{y} that is composed of HNO\textsubscript{3}.

[45] Acknowledgments. The authors are pleased to thank David Fahey and Rushan Gao of the NOAA Aeronomy Laboratory, Boulder, Colorado, for permission to include their NO\textsubscript{y} data from the NASA ER-2 mission plotted in Figure 7. We also thank Melody Avery and Bruce Anderson of NASA Langley Research Center for permission to use their ozone concentration data obtained on the DC-8 in Figure 5 and in the analysis of the instrument time constants. The funding support of the NASA Upper Atmosphere Research Program, the NASA Atmospheric Effects of Aviation Program, and the Air Force Office of Scientific Research is gratefully acknowledged.

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