Stratospheric correlation between nitric acid and ozone

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[1] An extensive data set of nitric acid (HNO3) and ozone (O3) measurements has been collected in the lower and middle stratosphere with in situ instruments onboard the NASA WB-57F aircraft and remote sounding instruments that include the JPL MkIV Interferometer, the Aura Microwave Limb Sounder, and the Atmospheric Chemistry Experiment Fourier Transform Spectrometer. The measurements utilized in this study span a broad latitudinal range between the deep tropics and northern high latitudes. The data are used to establish the robustness of the HNO3-O3 correlation in the stratosphere and the latitudinal dependence in the correlation. Good agreement is found among the HNO3-O3 correlations observed with the various instruments. Comparing HNO3-O3 correlations relaxes the coincidence criteria necessary when making direct comparisons of HNO3 measurements and allows meaningful comparisons between data sets that are not closely matched in time or space. The utility of this correlation is further demonstrated by establishing vertical profiles of proxy HNO3 mixing ratios using the observed correlation and widely available ozonesonde data. These profiles expand the range of data available for validating remote measurements of HNO3. The HNO3-O3 correlation is also demonstrated as a diagnostic for identifying locally enhanced HNO3 in the upper troposphere. In situ measurements of HNO3 near the tropical tropopause during the Aura validation campaigns are consistent with ACE-FTS observations, with both revealing extremely low mixing ratios (<125 ppt) and a HNO3 minimum in this region.

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1. Introduction

[2] Nitric acid (HNO3) is a principal component of total reactive nitrogen (NOx) in the stratosphere. NOy also includes the other oxides of nitrogen, such as NO2 (the sum of NO and NO2). Since the catalytic destruction of ozone (O3) by NOy is one of the dominant O3 loss mechanisms in the stratosphere, HNO3 is indirectly involved in controlling stratospheric ozone concentrations [Farman et al., 1985; Brasseur and Solomon, 2005]. HNO3 also plays a key role in the formation of polar stratospheric clouds (PSCs) in polar winters. Surface reactions on PSCs cause the formation of reactive chlorine species in the wintertime polar stratospheres, and thus facilitate ozone loss processes in these regions [Solomon, 1999; Gao et al., 2001]. Outside of the polar regions, O3 can generally be considered a long-lived tracer in the lower stratosphere and has been used as a diagnostic for transport and dynamic processes [Bregman et al., 2000; Heggin and Shepherd, 2007; Marcy et al., 2007]. HNO3 and O3 exhibit a strong positive correlation in the lower stratosphere [Neuman et al., 2001]. Correlations between HNO3 and O3 have previously been used to characterize air masses in the Arctic and midlatitude lower stratospheres [Bregman et al., 1995; Schneider et al., 1999; Neuman et al., 2001], validate HNO3 profiles [Irie et al., 2006] and describe tracer relationships in the tropical tropopause layer (TTL) [Marcy et al., 2007].

[3] We report here an extensive data set of HNO3 and O3 measurements collected in the lower and middle stratosphere. The data were collected using both in situ instruments onboard the NASA WB-57F aircraft and a suite of balloon- and satellite-borne remote sounding instruments. The measurements are used here to establish the robustness of the HNO3-O3 correlation in the stratosphere, characterize the
latitudinal variability in the correlation, and illustrate the utility of the correlation for validating remote sounding instrumentation.

2. Observations

Measurements of HNO$_3$ and O$_3$ mixing ratios were made in situ with instruments onboard the NASA WB-57F high-altitude research aircraft. HNO$_3$ was measured using the NOAA Chemical Ionization Mass Spectrometer (CIMS) [Neuman et al., 2000; Marcy et al., 2005], with a reported accuracy of $\pm$25% and a 1-$\sigma$ precision of 40 ppt or better. O$_3$ was measured with an overall uncertainty of $\pm$5% by the NOAA Ozone Photometer [Proffitt et al., 1983]. Measurements were made in the tropical lower stratosphere during four flights conducted as part of the NASA Pre-Aura Validation Experiment (Pre-AVE) in January and February 2004 and Costa Rica Aura Validation Experiment (CR-AVE) in February 2006 (Figure 1). We believe these data represent the first in situ measurements of HNO$_3$ in the tropical lower stratosphere. The flights originated and terminated at Juan Santamaria International Airport near San Jose, Costa Rica (10°N, 84°W). In situ measurements were also made in the midlatitude lower stratosphere over the continental United States during six flights as part of the Aura Validation Experiment-Houston (AVE-Houston) campaign in June 2005 (Figure 1). These flights originated and terminated at Ellington Field in Houston, Texas (30°N, 95°W).

This study also utilizes HNO$_3$ and O$_3$ measurements from three different remote sounding instruments; the Aura Microwave Limb Sounder (MLS), the JPL MkIV Interferometer (MkIV), and the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS). Of the data available from each of these instruments, we have chosen to utilize limited subsets that are coordinated temporally and/or geographically with the in situ measurements and each other as much as possible. The MLS instrument, onboard the Earth Observing System Aura satellite, quantifies HNO$_3$ and O$_3$ by measuring thermal emission from the limb of Earth’s atmosphere [Waters et al., 2006]. The MLS version 2.2 data has an overall uncertainty of $\pm$2 ppb or better in the HNO$_3$ retrievals and $\pm$10% in the O$_3$ retrievals throughout the vertical range of the data described here (147–22 hPa) [Santee et al., 2007; Froidevaux et al., 2008]. Vertical and horizontal resolutions of the MLS measurements are 3–4 km and $\sim$400 km, respectively. We utilize MLS data from four Aura overpasses in each of 3 distinct latitudinal regions; 0°–10°N over the tropical eastern Pacific Ocean, 31°N–41°N over the continental United States, and 68°N–74°N over the Canadian Arctic (Figure 1). The tropical MLS data were chosen to match the location and season of the WB-57F Costa Rica flights and ACE-FTS occultations, but were collected between 29 January and 4 February 2005 because MLS data are not available during this time period in 2004. The midlatitude MLS data were collected during the WB-57F AVE-Houston campaign, on 13, 15, 17 and 22 June 2005. Two of the WB-57F flights (on 13 and 22 June) were coordinated to align with the Aura ground tracks near the time of the satellite overpass for validation purposes [Santee et al., 2007]. The Arctic MLS data were collected on the same days as ACE-FTS occultations in this region (15 September and 29 October 2005, and 30 October and 20 November 2006).

The MkIV Interferometer is a balloon-borne solar-occultation Fourier transform spectrometer that measures infrared spectra at sunrise or sunset with a spectral resolution of 0.01 cm$^{-1}$ [Toon, 1991]. Systematic uncertainties for MkIV retrievals of HNO$_3$ and O$_3$ in the stratosphere are 12% and 6%, respectively. The vertical resolution of the MkIV measurements is 2–3 km. We utilize MkIV profiles of HNO$_3$ and O$_3$ observed during three balloon flights from Fort Sumner, New Mexico (34°N, 104°W), on 19 September 2003, 23 September 2004, and 20 September 2005 (Figure 1).

The ACE-FTS instrument, also a solar-occultation Fourier transform spectrometer, is onboard the Canadian Space Agency’s SCISAT-1 satellite [Bernath et al., 2005; Boone et al., 2005]. ACE-FTS measures high-resolution (0.02 cm$^{-1}$) infrared spectra with global coverage from 85°S to 85°N. The ACE-FTS statistical fitting errors are $\sim$5% or better for stratospheric mixing ratios of HNO$_3$ and O$_3$ in the version 2.2 (and version 2.2 “O$_3$ update”) data.
Vertical and horizontal resolutions of the ACE-FTS measurements are 3–4 km and ~500 km, respectively. We utilize 4 ACE-FTS profiles from three latitudinal regions similar to those chosen for the MLS data; 3°N–8°N over the tropical eastern Pacific Ocean (7 February and 6 April 2004, 25 April 2006, and 22 February 2007), 35°N–40°N over the continental United States (29 and 30 July 2004, and 5 June and 31 July 2005), and 70°N–73°N over the Canadian Arctic (15 September and 29 October 2005, and 30 October and 20 November 2006) (Figure 1). The tropical profiles were chosen to match as closely as possible the location and season of the WB-57F Costa Rica flights and MLS overpasses, and the midlatitude profiles were chosen to match the location and season of the WB-57F AVE-Houston flights and MLS overpasses. Some of these profiles were not sampled in the same year as the WB-57F or MLS data owing to the relatively sparse sampling of the ACE-FTS occultations in the tropics and midlatitudes.

Vertical profiles of \( O_3 \) mixing ratio were measured at the NOAA Earth Systems Research Laboratory (NOAA/ESRL) ozonesonde station in Boulder, CO (40°N, 105°W) (Figure 1). The NOAA/ESRL network uses electrochemical-concentration-cell ozonesondes with an accuracy of ±10% [Newchurch et al., 2003]. We utilize the \( O_3 \) profiles from sounding flights on June 20 and 24 of 2005 during the WB-57F AVE-Houston campaign.

### 3. Results and Discussion

In situ measurements onboard the NASA WB-57F during the AVE-Houston campaign reveal a robust and compact correlation between \( \text{HNO}_3 \) and \( O_3 \) in the midlatitude lower stratosphere (Figure 2a). A least squares regression analysis of the decile averages (unfilled black symbols) in Figure 2a indicates a linear relationship between \( \text{HNO}_3 \) and \( O_3 \) over the range of the data shown. Deciles, defined as representing an equal number of data points, have the advantage over binned averages in that they reveal the density of points in Figure 2a. The regression algorithm is only applied to data with \( O_3 \) greater than 150 ppb to prevent enhanced values of \( \text{HNO}_3 \) in the troposphere from compromising the fit (see large values of \( \text{HNO}_3 \) at ~100 ppb \( O_3 \) in Figure 2a). These enhanced values of \( \text{HNO}_3 \) in the troposphere will be discussed later. There is no observable latitudinal dependence in the \( \text{HNO}_3-O_3 \) correlation greater than the natural variability over the limited latitudinal range of the data shown (24°N–43°N). The observed dependence over a larger latitude range is discussed in section 3.2. The precisions of the in situ measurements near 2 ppb \( \text{HNO}_3 \) and 750 ppb \( O_3 \) are displayed with the error bar symbol in the bottom right corner of Figure 2a. The precision of each tracer measurement is derived as the standard deviation of the 10-s averages during flight segments with near-constant average values. These values are substantially less than the observed scatter in the 10-s data (Figure 2a), indicating that the latter results primarily from the small-scale geophysical variability of \( \text{HNO}_3 \) and \( O_3 \) in the stratosphere.

A comparison of in situ measurements onboard the WB-57F and remote measurements from the MkIV, ACE-FTS and MLS instruments in the midlatitude lower stratosphere is shown in Figure 2b. The remote sounding data do...
not represent decile averages, but rather averages of data as reported at their respective retrieval levels (see Figure 2 caption). All of these data were collected at latitudes between 24°N and 43°N (Figure 1), and during the months of June, July or September to coincide temporally and geographically with the WB-57F data set. Thus, seasonal effects are not expected to contribute significantly to the differences in the HNO<sub>3</sub>-O<sub>3</sub> correlations shown here. All of the data averages above 150 ppb O<sub>3</sub> in Figure 2b, with the exception of the MLS values at 265 ppb and 315 ppb O<sub>3</sub>, lie within ±15% of a linear fit calculated using all 4 data sets combined with equal weighting. The low values of HNO<sub>3</sub> observed in the MLS correlation (at O<sub>3</sub> mixing ratios less than 400 ppb) result from the known low bias in the MLS HNO<sub>3</sub> data in the upper troposphere and lowermost stratosphere [Santee et al., 2007]. The equation for the least squares linear regression is given by

\[
\text{HNO}_3 = (0.00256 \pm 0.000154) \cdot (O_3) - (0.0922 \pm 0.0886)
\]

with HNO<sub>3</sub> and O<sub>3</sub> expressed in ppb for the range 150 ppb < O<sub>3</sub> < 1100 ppb. The coefficient of determination (R<sup>2</sup>) for the linear fit to the combined data set is 0.93, indicating that the HNO<sub>3</sub>-O<sub>3</sub> correlation is robust in the midlatitude lower stratosphere and comparable between data sets that are measured with a variety of in situ and remote techniques.

[1] The use of in situ data for the validation of remote sounding instruments can be influenced by two issues that make meaningful comparisons between the data sets challenging. First, in situ measurements from aircraft platforms typically have horizontal resolutions of a few kilometers (~1.8 km for the 10-s data in Figure 2a) and are reported at a specific altitude, whereas the remote measurements considered here have horizontal resolutions of hundreds of kilometers and vertical resolutions up to several kilometers. Thus, the small-scale geophysical variability of HNO<sub>3</sub> observed in in situ measurements (as seen in Figure 2a) cannot be detected by remote sounding instruments that report average conditions over considerably larger sampling volumes. Second, most remote measurements are ideally validated using data sets that are approximately coincident in time and space. Coincidence criteria vary depending on the measurements being compared [e.g., Walker et al., 2005; Santee et al., 2007; Considine et al., 2008] but most comparisons involve data obtained within a few hours and 500 km of each other [Hegglin et al., 2008]. Given these requirements, sufficient data are not always available to provide statistically significant comparisons. Both of these issues can largely be overcome, however, if a robust relationship exists between the species A of interest and another species B, like that shown in Figure 2, and if measurements of both species are simultaneously available from the same platform. The best cases occur when species A and B are long-lived tracers. Tracer correlations provide a so-called “instantaneous climatology” that reduces the influence of small-scale geophysical variability observed in in situ data sets and has allowed a meaningful comparison between data sets with measurements having vastly different sampling volumes [e.g., Hegglin et al., 2008; Nightingale et al., 1996; Khosrawi et al., 2004]. For example, Murphy et al. [1993] have demonstrated that the variability of the NO<sub>Y</sub> to O<sub>3</sub> ratio (HNO<sub>3</sub> is a primary component of NO<sub>Y</sub>) is significantly lower than the variability of either species observed individually in the lower stratosphere. Furthermore, the instantaneous climatology provided by robust tracer correlations relaxes the coincidence criteria necessary when making direct comparisons of HNO<sub>3</sub> measurements and allows statistically meaningful comparisons between a variety of data sets that are not closely matched in time or space (Figure 2b).

[12] When using HNO<sub>3</sub>-O<sub>3</sub> correlations as a tool for validating HNO<sub>3</sub> measurements, there is an implicit assumption that the uncertainty in the O<sub>3</sub> measurement is less than the uncertainty in the HNO<sub>3</sub> measurement from the same platform. This assumption is valid in many cases because O<sub>3</sub> is usually given a higher measurement priority than HNO<sub>3</sub>, and there are usually more options available for validating O<sub>3</sub> measurements. The relative uncertainty for O<sub>3</sub> is less than the relative uncertainty for HNO<sub>3</sub> in all of the data sets utilized here with the exception of the ACE-FTS measurements. (The ACE-FTS data set has a reported error of ~5% in both the HNO<sub>3</sub> and O<sub>3</sub> measurements.) Nonetheless, when a comparison between data sets using HNO<sub>3</sub>-O<sub>3</sub> correlations reveals systematic differences, the possibility that the differences result from the O<sub>3</sub> measurements rather than the HNO<sub>3</sub> measurements must also be considered. Identifying the origin(s) of differences then requires more than one diagnostic. Ideally, the HNO<sub>3</sub>-O<sub>3</sub> correlations are but one diagnostic in a comprehensive validation of remote HNO<sub>3</sub> and O<sub>3</sub> measurements.
Profiles are correlated (Figure 3 and Table 1) to the average of the two ozonesonde profiles (Figure 4). The $\text{HNO}_3^*$ profile agrees within expected uncertainties with the WB-57F and MLS data throughout most of the vertical range shown in Figure 4. The average MLS value at 22 hPa is approximately 1 ppb lower than $\text{HNO}_3^*$, consistent with known biases in the MLS data set in this region [Santee et al., 2007]. The variability in $\text{HNO}_3^*$ results from the uncertainties associated with the specific $\text{HNO}_3$-$\text{O}_3$ correlation relation and $\text{O}_3$ measurements being used. If an averaged and smoothed $\text{O}_3$ profile is used to estimate $\text{HNO}_3^*$, then the variability in the real atmospheric $\text{HNO}_3$ abundances will be underrepresented by $\text{HNO}_3^*$.

The use of $\text{HNO}_3$-$\text{O}_3$ correlations to calculate $\text{HNO}_3^*$ from in situ ozonesonde profiles expands the range of data available for validating remote measurements of $\text{HNO}_3$. Unlike a direct comparison of $\text{HNO}_3$-$\text{O}_3$ correlations for the purpose of validation, as described above, this method does not require a simultaneous $\text{O}_3$ measurement from the platform being validated. We also note that the utility of $\text{HNO}_3^*$ profiles is not limited to the validation of remote sounding instrumentation, since they can be used whenever high-resolution vertical profiles of $\text{HNO}_3$ are required. This method offers the advantage that daily variations in the vertical structure of the stratosphere, particularly near the tropopause, will be evident in the ozonesonde data and thus accounted for in the calculation of $\text{HNO}_3^*$.

### 3.2. Latitudinal Dependence in the $\text{HNO}_3$-$\text{O}_3$ Correlation

The near-global coverage of satellite-borne remote sounding instruments makes them ideally suited to studying latitudinal variations in the $\text{HNO}_3$-$\text{O}_3$ correlation. Measurements in the Northern Hemisphere tropical, midlatitude and polar stratosphere by the ACE-FTS and MLS instruments reveal a strong latitudinal dependence in the correlation and good agreement between the two instruments (Figure 5). The coefficients for the second-order polynomial fits to the correlations are given in Table 1. The latitudinal dependence illustrated in Figure 5 is best explained as an evolution from initial conditions represented by the tropical correlation. When air moves poleward and ages, $\text{HNO}_3$ results from in situ ozonesonde data and thus accounted for in the calculation of $\text{HNO}_3^*$.

![Figure 3](image-url)  
**Figure 3.** $\text{HNO}_3$-$\text{O}_3$ correlations observed by the MkIV, ACE-FTS and MLS instruments in the midlatitude stratosphere (see Figure 1). Different symbols shapes represent individual occultations (three for MkIV, four for ACE-FTS) or different satellite overpasses (MLS, with eight profiles averaged during each of four overpasses). Lines represent second-order polynomial fits to the combined data set of each instrument. The coefficients for the polynomial fits are shown in Table 1.

### 3.1. Calculating Proxy $\text{HNO}_3$ Profiles

In situ measurements of $\text{HNO}_3$ onboard the NASA WB-57F have proven to be useful for the validation of MLS $\text{HNO}_3$ retrievals in the lower stratosphere [Santee et al., 2007]. Despite the higher natural variability displayed in the in situ measurements, coincident $\text{HNO}_3$ measurements from the WB-57F and MLS on 22 June 2005 generally show fair-to-good agreement when the two data sets are compared without smoothing for a single day as shown in Figure 4. A limitation of such comparisons is that the maximum flight altitude of the WB-57F allows comparison only as high as the 68 hPa MLS retrieval level (Figure 4). Using the well-characterized stratospheric correlation between $\text{HNO}_3$ and $\text{O}_3$, however, we can calculate a proxy profile of $\text{HNO}_3$, designated $\text{HNO}_3^*$, from in situ ozonesonde data. Vertical profiles of $\text{O}_3$ mixing ratio from ozonesondes are more widely available and typically extend to higher altitudes than aircraft data sets. $\text{O}_3$ profiles were available from the NOAA/ESRL Boulder ozonesonde station on 20 and 24 June 2005, 2 days before and after the WB-57F and MLS measurements shown in Figure 4. A $\text{HNO}_3^*$ profile was calculated by applying the polynomial equation for the midlatitude ACE-FTS $\text{HNO}_3$-$\text{O}_3$ correlation (Figure 3 and Table 1) to the average of the two ozonesonde profiles (Figure 4). The $\text{HNO}_3^*$ profile agrees within expected uncertainties with the WB-57F and MLS data throughout most of the vertical range shown in Figure 4. The average MLS value at 22 hPa is approximately 1 ppb lower than $\text{HNO}_3^*$, consistent with known biases in the MLS data set in this region [Santee et al., 2007]. The variability in $\text{HNO}_3^*$ results from the uncertainties associated with the specific $\text{HNO}_3$-$\text{O}_3$ correlation relation and $\text{O}_3$ measurements being used. If an averaged and smoothed $\text{O}_3$ profile is used to estimate $\text{HNO}_3^*$, then the variability in the real atmospheric $\text{HNO}_3$ abundances will be underrepresented by $\text{HNO}_3^*$.

The use of $\text{HNO}_3$-$\text{O}_3$ correlations to calculate $\text{HNO}_3^*$ from in situ ozonesonde profiles expands the range of data available for validating remote measurements of $\text{HNO}_3$. Unlike a direct comparison of $\text{HNO}_3$-$\text{O}_3$ correlations for the purpose of validation, as described above, this method does not require a simultaneous $\text{O}_3$ measurement from the platform being validated. We also note that the utility of $\text{HNO}_3^*$ profiles is not limited to the validation of remote sounding instrumentation, since they can be used whenever high-resolution vertical profiles of $\text{HNO}_3$ are required. This method offers the advantage that daily variations in the vertical structure of the stratosphere, particularly near the tropopause, will be evident in the ozonesonde data and thus accounted for in the calculation of $\text{HNO}_3^*$.

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<table>
<thead>
<tr>
<th>Instrument and Location</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>Range (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACE-FTS (70°N–73°N)</td>
<td>−0.42279</td>
<td>0.0048101</td>
<td>−5.7629 × 10⁻⁷</td>
<td>150 &lt; $\text{O}_3$ &lt; 6600</td>
</tr>
<tr>
<td>ACE-FTS (35°N–40°N)</td>
<td>0.17878</td>
<td>0.0022653</td>
<td>−2.1521 × 10⁻⁸</td>
<td>150 &lt; $\text{O}_3$ &lt; 8800</td>
</tr>
<tr>
<td>ACE-FTS (3°N–8°N)</td>
<td>0.11311</td>
<td>0.00074318</td>
<td>−4.4215 × 10⁻⁸</td>
<td>150 &lt; $\text{O}_3$ &lt; 8800</td>
</tr>
<tr>
<td>MkIV (34°N)</td>
<td>0.15818</td>
<td>0.0022216</td>
<td>−2.0400 × 10⁻⁷</td>
<td>150 &lt; $\text{O}_3$ &lt; 8800</td>
</tr>
<tr>
<td>MLS (68°N–74°N)</td>
<td>−1.1311</td>
<td>0.0045093</td>
<td>−5.2908 × 10⁻⁷</td>
<td>150 &lt; $\text{O}_3$ &lt; 6600</td>
</tr>
<tr>
<td>MLS (31°N–41°N)</td>
<td>−0.27047</td>
<td>0.0025794</td>
<td>−2.6100 × 10⁻⁷</td>
<td>150 &lt; $\text{O}_3$ &lt; 8800</td>
</tr>
<tr>
<td>MLS (0°–10°N)</td>
<td>1.1949</td>
<td>9.9836 × 10⁻⁵</td>
<td>−1.1119 × 10⁻⁹</td>
<td>150 &lt; $\text{O}_3$ &lt; 1 × 10⁵</td>
</tr>
</tbody>
</table>

*The polynomial equation takes the form $\text{HNO}_3 = a + b(\text{O}_3) + c(\text{O}_3)^2$, with $\text{HNO}_3$ and $\text{O}_3$ both in units of parts per billion.*

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owing to the greater net production of HNO$_3$. The only significant loss of HNO$_3$ (or, more generally, loss of NO$_y$) meanwhile, occurs at altitudes greater than 40 km owing to the photolytic destruction of NO and the subsequent repartitioning of the NO$_y$ reservoir [Fahey et al., 1990].

[17] Murphy et al. [1993] have described a similar latitudinal dependence on linear NO$_y$-O$_3$ correlations observed at altitudes up to 21 km in the lower stratosphere. NO$_y$/O$_3$ ratios do not increase smoothly between the tropics and high latitudes, but are instead separated by two regions with very strong gradients in the ratio; in the subtropics between $12^\circ/$C176$^\circ$ and $22^\circ/$C176$^\circ$ latitude, and at the edge of the polar regions at $\sim$65$^\circ$. The strong gradients are due to weak horizontal mixing in these regions [Murphy et al., 1993; Fahey et al., 1996]. In regions between these two sharp gradients, namely in the tropics, midlatitudes and polar regions (as depicted in Figure 5), the NO$_y$/O$_3$ correlation is much less variable. We expect the HNO$_3$/O$_3$ ratio to exhibit a similar behavior in the lower stratosphere with only minor variability in the tropics, midlatitudes and polar regions, and sharp gradients in the transition regions because HNO$_3$ is generally a large fraction of NO$_y$ in the lower stratosphere [Neuman et al., 2001]. Hegglin and Shepherd [2007] have observed that the correlation between O$_3$ and nitrous oxide (N$_2$O) is compact in the lower stratosphere but relatively less compact in the middle stratosphere, revealing a fan-like structure in the correlation when data over a broad and continuous latitudinal range are included. We note that the HNO$_3$-O$_3$ correlations in Figure 5 are expected to display a similar change in compactness if data from a broad and continuous latitudinal range were to be included.

[18] Murphy et al. [1993] reported little seasonal variation in the NO$_y$-O$_3$ correlation in the tropics and midlatitudes, and a more significant seasonal variation displayed in the correlation measured at high latitudes primarily associated with processes in the wintertime polar vortex. For this

Figure 4. Vertical profiles of HNO$_3$ mixing ratio from the WB-57F and MLS on 22 June 2005 during the AVE-Houston validation campaign. WB-57F data are colored as a function of latitude. MLS data represents eight vertical profiles at latitudes of 31$^\circ$N–41$^\circ$N as reported at standard MLS retrieval levels. HNO$_3^*$ was calculated using the average of two ozonesonde profiles at 40$^\circ$N on 20 and 24 June 2005 and the polynomial fit for the midlatitude ACE-FTS HNO$_3$-O$_3$ correlation shown in Table 1. The HNO$_3^*$ error bars represent the combined uncertainties of the ozonesonde profiles and polynomial fit to the midlatitude HNO$_3$-O$_3$ correlation.

Figure 5. (a) HNO$_3$-O$_3$ correlations observed by the ACE-FTS instrument in the Northern Hemisphere tropics (3$^\circ$N–8$^\circ$N), midlatitudes (35$^\circ$N–40$^\circ$N), and polar regions (70$^\circ$N–73$^\circ$N). The correlations were established using data from four occultations in each region, represented by the different symbol shapes. The coefficients for the second-order polynomial fits to each correlation are shown in Table 1. Approximate measurement altitudes are represented by black circles, squares, and triangles at 20, 25, and 30 km, respectively. (b) HNO$_3$-O$_3$ correlations observed by the MLS instrument in the Northern Hemisphere tropics (0$^\circ$–10$^\circ$N), midlatitudes (31$^\circ$N–41$^\circ$N), and polar regions (68$^\circ$N–74$^\circ$N). The correlations were established using data from four overpasses in each region, represented by the different symbol shapes. The coefficients for the second-order polynomial fits to each correlation are shown in Table 1.
reason, the polar correlations shown in Figure 5 were chosen from data collected in the late summer or early fall in order to minimize any potential effects from denitrification [Santee et al., 2000; Fahey et al., 1990] and chemical ozone loss [Solomon, 1999] that might perturb the HNO$_3$-O$_3$ correlation.

### 3.3. HNO$_3$-O$_3$ Correlations in the Midlatitude Upper Troposphere

[10] The HNO$_3$-O$_3$ correlation in the upper troposphere can be linear and compact owing to the mixing of air masses between the stratosphere and troposphere. Similar linear and compact HCl-O$_3$ correlations in the upper troposphere were used previously to derive the fraction of stratospheric air in the midlatitude upper troposphere [Murcy et al., 2004]. The HNO$_3$-O$_3$ correlation in the upper troposphere, however, is typically less compact than the stratospheric correlation [Murphy et al., 1993; Neuman et al., 2001]. The source of this variability lies in the fact that O$_3$ is long-lived and generally well mixed throughout the upper troposphere while HNO$_3$ is subject to local production and removal. For example, redistribution through uptake and sedimentation by cirrus cloud particles is considered an important term in the upper tropospheric budget of HNO$_3$ [Lawrence and Crutzen, 1998; Popp et al., 2004, 2007; Krämer et al., 2008]. Nonetheless, the correlation between HNO$_3$ and O$_3$ can serve as a useful diagnostic for locally enhanced values of HNO$_3$ in the upper troposphere. Enhanced HNO$_3$ mixing ratios as large as 1.5 ppb were observed over the midlatitude upper troposphere during four of six AVE-Houston WB-57F flights (Figure 6, at 50–125 ppb O$_3$). We argue that this enhanced HNO$_3$ is produced locally in the upper troposphere by the oxidation of lightning-produced NO$_x$ [Murphy et al., 1993; Martin et al., 2007, and references therein]. The upper tropospheric lifetime of NO$_x$ against conversion to HNO$_3$ is $\sim$5 days [Jaeglé et al., 1998]. These enhancements cannot be stratospheric in origin because the stratospheric HNO$_3$-O$_3$ correlation (at O$_3 >$ 150 ppb in Figure 6) would be preserved upon transport and dilution in the upper troposphere. It is also unlikely that the enhanced HNO$_3$ mixing ratios are due to anthropogenic or natural emissions at Earth’s surface, since most NO$_x$ is converted to HNO$_3$ in the boundary layer. This HNO$_3$ is unlikely to reach the upper troposphere in convection since the rainout lifetime of a highly soluble species like HNO$_3$ near the surface is typically less than 3 days [Giorgi and Chameides, 1986] and HNO$_3$ is efficiently removed during upward transport. Previous NO$_x$ measurements in the outflow of summertime thunderstorms over the continental United States revealed lightning-produced NO$_x$ mixing ratios as large as 4 ppb at 9–12 km altitude, consistent with the altitudes of enhanced HNO$_3$ shown in Figure 6 [Ridley et al., 1996, Martin et al., 2007].

### 3.4. HNO$_3$ and O$_3$ in the Tropical Upper Troposphere and Lower Stratosphere

[20] HNO$_3$ and O$_3$ measurements have unique features in the tropical upper troposphere and lower stratosphere. In situ measurements of HNO$_3$ in the deep tropics (3°S–10°N) onboard the WB-57F indicate a minimum in HNO$_3$ at altitudes of 14–17 km in the TTL (Figure 7). Observed HNO$_3$ mixing ratios were typically 125 ppt or less throughout this region. Remote measurements by the ACE-FTS instrument show slightly larger HNO$_3$ mixing ratios that are nonetheless consistent with the upper range of the in situ measurements (Figure 7). While the HNO$_3$ minimum is not apparent in the ACE-FTS measurements reported here because the minimum measurement altitude is 15.5 km, a previous study utilizing a larger subset of the ACE-FTS measurements does indicate a similar HNO$_3$ minimum in the tropical upper troposphere [Folkins et al., 2006]. Convective transport models have been used to simulate the HNO$_3$ minimum observed in the tropics [Folkins et al., 2006], although the minimum predicted by the models occurs at 13–14 km altitude, which is 3–4 km lower than found in the in situ data set presented here. The models attribute the HNO$_3$ minimum to the convective outflow of air that is depleted in HNO$_3$ [Folkins et al., 2006]. Simulations with a wet-convection plume model indicate that HNO$_3$ scavenging is highly efficient in deep convective updrafts, and that as little as 3% of HNO$_3$ entrained in the cloud column will be detrained at anvil height [Mari et al., 2000]. We note that condensed-phase HNO$_3$ has been observed in subvisible cirrus clouds at altitudes of 16–18 km in the tropics [Popp et al., 2007]. Under appropriate conditions, the vertical redistribution of HNO$_3$ by uptake and sedimentation in cirrus ice particles could provide an additional sink of HNO$_3$ in the TTL. The convective plume model described by Folkins et al. [2006] does not account for the redistribution of HNO$_3$ in ice particles, and would tend to underpredict the height of the HNO$_3$ minimum if this process is a significant factor in the HNO$_3$ budget in the TTL. Finally, although the increase in HNO$_3$ above 18 km (Figure 7a) is due to photochemical production and transport from the middle stratosphere, HNO$_3$ mixing ratios are lower in the tropics than at higher latitudes (at similar altitudes) in part because air entering the tropical lower stratosphere through the TTL is depleted in HNO$_3$.

[21] The elevated HNO$_3$ mixing ratios at altitudes less than 14 km in Figure 7 suggest a source of HNO$_3$ in the tropical troposphere, which is most likely the oxidation of
lightning-produced NO$_x$. Martin et al. [2007] have reported that nearly 80% of the HNO$_3$ between 8.5 km and 12.5 km altitude in the tropics can be explained by lightning production. Since the data shown in Figure 7 represent maritime measurements, and lightning occurs more frequently over the continents, we caution that the tropospheric HNO$_3$ data in Figure 7 might be biased low compared to continental data and thus should not be interpreted as a tropical climatology.

In situ measurements of O$_3$ in the tropics show a largely monotonic increase in O$_3$ between the upper troposphere and lower stratosphere, with no evidence of an O$_3$ minimum in the TTL (Figure 7b) since O$_3$ is not efficiently scavenged in convective updrafts. Remote measurements by the ACE-FTS instrument indicate O$_3$ mixing ratios that are largely consistent with the in situ measurements but show a slight high bias with respect to the in situ observations. A high bias of ACE-FTS O$_3$ in the extratropical upper troposphere was noted by Heglin et al. [2008]. Like HNO$_3$, the increase in O$_3$ above 18 km altitude is due to photochemical production and transport from the middle stratosphere. Unlike HNO$_3$, O$_3$ is not produced in significant amounts by lightning in the upper troposphere and O$_3$ is not removed in convective updrafts. Approximately half of the O$_3$ in the TTL is photochemically produced in situ, with the remainder contributed either by the tropospheric background or mixing from the stratosphere [Marcy et al., 2007].

[23] The HNO$_3$-O$_3$ correlation for the in situ data in the tropics is shown in Figure 8. The data are separated into three groups representing air in the lower stratosphere, TTL, and troposphere. The upper and lower boundaries of the TTL, defined using criteria by Marcy et al. [2007], are approximately 17.5 km and 14.5 km, respectively. The data in the tropical lower stratosphere (red symbols in Figure 8) reveal a compact linear correlation between HNO$_3$ and O$_3$, as described above. The TTL data (blue symbols), which contain the minimum HNO$_3$ values illustrated in Figure 7, are clustered at the lower end of the stratospheric correlation. The remaining data in the troposphere (green symbols), at altitudes less than 14.5 km, are more variable than the data in the TTL and show no apparent correlation between HNO$_3$ and O$_3$. A pronounced feature is the high HNO$_3$ mixing ratios (>0.05 ppb) at low values of O$_3$ (<100 ppb). These data are most likely influenced by HNO$_3$ produced by lightning.

4. Summary

[24] An extensive data set of HNO$_3$ and O$_3$ measurements has been collected in the lower and middle stratosphere with in situ instruments onboard the NASA WB-57F and a suite of remote sounding instruments that includes the MkIV, MLS and ACE-FTS. The measurements reveal a compact linear correlation between HNO$_3$ and O$_3$ in the midlatitude lower stratosphere. This correlation is robust and comparable between data sets measured using a variety of in situ and remote techniques. Validating remote measurements of HNO$_3$ by comparing HNO$_3$-O$_3$ correlations allows a meaningful comparison between data sets with greatly different sampling volumes. In addition, the use of tracer correlations for validation relaxes the coincidence criteria necessary
correlation between HNO$_3$ and O$_3$ can also serve as a useful diagnostic for enhanced values of HNO$_3$ in the upper troposphere. Enhanced HNO$_3$ mixing ratios as large as 1.5 ppb were observed in the midlatitude upper troposphere that likely result from the oxidation of lightning-produced NO$_x$. Finally, in situ measurements of HNO$_3$ in the TTL revealed low mixing ratios (<125 ppt) and a minimum in HNO$_3$ at altitudes of 14–17 km. This minimum in HNO$_3$, which has also been observed in remote measurements by the ACE-FTS instrument, has previously been attributed to the convective outflow of air that has been depleted of HNO$_3$ in the updraft column.

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