

General Comments:

Item 1--We agree that the source of the spectral data is important for anyone who may want to compare the LIMS V6 HNO₃ results with the profile data from satellite experiments having higher spectral resolutions. When we were preparing to update the LIMS profile retrievals to Version 6, the status of the line parameters for HNO₃ was still uncertain in the versions of HITRAN that were available during the late 1980s and 1990s. Therefore, we elected to regenerate a LIMS emissivity data table using the HNO₃ cross section parameters of Goldman et al. [Applied Optics, 1981], the same laboratory-measured, band parameters that were used to process the LIMS V5 profiles (see also Giver et al., [JOSA Part B1, 1984]). Their laboratory cross section measurements were available at 5 temperatures (from 240 K to 313 K), although they found essentially no variation of absorption cross section with temperature. It is also noted that the HNO₃ line intensities in the 11- μ m region for HITRAN 96 were normalized to the band intensity of Giver et al. [1984].

The LIMS instrument was essentially a limb-viewing radiometer. The filter for its HNO₃ channel extended from 842 to 915 cm⁻¹, its 5% transmission points [Drayson et al., JGR, 1984]. That channel measured the radiance emitted by the ν_5 and $2\nu_9$ bands (in the region of 11.3 micrometers). Therefore, the primary improvements in spectroscopy for the V6 retrieval of HNO₃ come from the CO₂ laser band centered at 10.4 micrometers for the upper stratosphere plus the underlying emissions from the CFCs and aerosols for the lower stratosphere.

The filter for the LIMS NO₂ channel has its 5% transmission points at 1561 and 1631 cm⁻¹. The effects of the spin splitting are included in the line parameters of HITRAN 92 that we used. The band intensity for the primary NO₂ ν_3 cold band on HITRAN 92 was not altered for HITRAN 96, although the strengths of its assigned lines had been altered according to the analyses of Toth [JOSA B9, 1992]. We will add all the foregoing information to the revised manuscript.

Items 2 and 3—We will add the pertinent measurement and retrieval descriptions for LIMS V6 from Remsberg et al. [JQSRT, 2004]. Single limb radiance profiles were measured about every 12 seconds along an orbital track of the LIMS tangent point locations. Radiance samples were obtained every 0.375 km in altitude for HNO₃ and 0.75 km for NO₂, but with channel IFOVs at the horizon of 1.8 km and 3.6 km, respectively. LIMS V6 retrievals used the onion-peeling approach along with the emissivity growth approximation (EGA) of Gordley and Russell [Appl.

Opt., 1981]. Emissivity tables for the forward limb-radiance algorithm were developed as a function of temperature and pressure for each of the gases that make contributions in the NO₂ and HNO₃ channels. The LIMS NO₂ radiances are interfered with substantially by H₂O in the lower stratosphere, so an additional emissivity table was developed to account for the effects of their overlapping lines [Remsberg et al., JQSRT, 2004]. Since the HNO₃ channel measurements occurred in a spectral region that is optically thin and because we used spectral cross section data for both HNO₃ and its interfering CFC species, there was no need to prepare separate emissivity tables to account for the overlapping of their lines.

There were 13 to 14 orbits of data per day from LIMS, following the Sun-synchronous geometry for the Nimbus 7 satellite. Separate, daily zonal averages of the retrieved NO₂ profiles were obtained for Figure 2 from the ascending (at bottom, from south to north and during local daytime) orbital passes and then from the descending (at top, from north to south and during local nighttime) orbital passes. Because the diurnal variations of HNO₃ are no greater than 5% or so, zonal averages were taken from the combination of its ascending and descending orbital results (as in Figure 1). Hopefully, this summary description provides much of the general information that you wish to have about the LIMS experiment. Further details are in Gille and Russell (JGR, 1984, and references therein).

Specific comments:

Abstract: p. 2770, lines 17-20: This conclusion is based on the significant changes that were found for the LIMS-retrieved V6 NO₂ of the upper stratosphere, due primarily to spin-splitting effects for the lines of this molecule and their inclusion in the line list for the first time in HITRAN 92.

Background: p. 2771, lines 7-11: Reviewer 1 wanted some examples, too. We will add Mlynchak et al. [JGR, p. 6039, 1999], Leovy et al., [JAS, p. 230, 1985], and Froidevaux et al., [JGR, p. 6389, 1989].

Section 2, General: This information was provided in our response to your overall general concerns (see above, items 1 through 3).

p. 2773, lines 20-21: We will refer to the modeled HNO₃ profiles of Jackman et al. [1985].

p. 2773, lines 22-24: We have not calculated non-LTE radiances from CO₂ and O₃ near the stratopause for this channel, relying instead on their indicated effects from the forward radiance simulations of Edwards et al. [1996]. It is also possible that we have not adequately accounted

for the effects of the temperature tides on the LIMS HNO₃ radiances of the upper stratosphere. Therefore, we will note this latter possibility in the revised manuscript and also remove the phrase “most likely due to not having accounted for ...”

p. 2774, lines 7-11: The enhancements in the NO₂ of the upper stratosphere in Figure 2b at high northern latitudes are really because the LIMS ascending profiles along the orbit crossed the terminator zone near 75N into polar nighttime for 15 November 1978. We will emphasize that point in the revised manuscript. The results shown in the references that you cite are for periods when there was significant solar storm activity, which enhances the NO_y in the upper stratosphere directly. Such solar activity was notably absent during the time frame of the LIMS experiment, so it is unlikely that one would see any significant, positive correlations between the LIMS HNO₃ and NO₂ in the upper stratosphere.

p. 2774, lines 11-14: We do not wish to generate and interpret sequences of daily maps of HNO₃ on potential vorticity surfaces, in order to quantify its changes with time within the polar vortex itself. Instead, we generated a time series plot of HNO₃ poleward of 75N in the manner of Leovy et al., [1985, their Figure 18], who estimated the effects of diabatic descent of zonal-average, polar ozone with respect to potential temperature levels of the middle stratosphere from early winter through mid March from the LIMS V5 data. However, our plots of V6 HNO₃ and ozone (not shown) indicate that both gases essentially behave as tracers in the lower stratosphere from late February through early April (mixing ratio values remain constant on a theta surface). Therefore, we will change the sentence to say “... indicates that there was also an accumulation of HNO₃ in the lower stratosphere at polar latitudes during wintertime”.

Section 3.1

General: Spectral range and resolution will be addressed according to our reply to Item 1 above.

p. 2776, lines 11 and elsewhere: We will replace “hot band” with “laser band.”

p. 2776, line 13 to p. 2777, line 6: Again see our reply in “General, Item 1” above.

p. 2777, lines 12-14: Zonal mean distributions of the background aerosol extinction were not available for the seven months of LIMS. Hitchman et al. [JGR, p. 20689, 1994] reported finding both seasonal and QBO-like variations for the aerosol extinction distributions from the SAGE II dataset.

p. 2777, lines 14-17: The revised manuscript will note the subsequent work of Funke et al.

p. 2778, line 21 and following: We will shorten the discussion, as requested.

Section 3.2

General: The entry in Table 1 will be changed to Spectral Band Model Error. Its uncertainties are according to the estimates of Goldman et al. [1981].

p. 2779, lines 19-26: The titles of Tables 1 and 2 will be changed to say “Calculations of precision and accuracy...” Estimates of the precision were also obtained from the standard deviations of sets of profiles along orbits near 30S (in the summer hemisphere where the effects of the zonal waves are small). Minimum standard deviation results from the profile sets are plotted in Figure 4, and they are comparable to the calculated precisions at most pressure levels.

Section 4

p. 2782, lines 24-25: We will add the following references:

Callis et al. (Geophys. Res. Lett., 10, 945–948, 1983); Considine et al. (Geophys. Res. Lett., 19, 397–400, 1992); Jackman et al. (JGR, 90, 7923–7930, 1985); Natarajan et al. (JGR, 91, 1153–1166, 1986); Solomon et al. (JGR, 91, 5455–5464, 1986).

Section 4.1

p. 2784, lines 18-21: We are NOT suggesting that the higher values of HNO₃ in the upper stratosphere are somehow caused by delayed photolysis. There is no such hypothesis to be confirmed or disproved. Our intention in referring to the photolysis rate was solely to point out the uncertainties that would be introduced if HNO₃ mixing ratios were estimated from other LIMS observations by making use of the instantaneous equilibrium assumption. This method was suggested in Jackman et al. [1985] as a means of deriving HNO₃ above the 5-hPa level. We cited that reference on p. 2783, lines 6 and 18. We realize that the short discussion about the photolysis and equilibrium assumption should have been inserted in p. 2783 immediately following the reference to Jackman et al., instead of on p. 2784. We plan to remove this discussion from p. 2784 and add appropriate comments on p. 2783, thereby assuring continuity in our discussion.

Section 4.2

p. 2785, line 16: We will refer to the following: Santee, M., et al. (JGR, V112, D24S40), and Gille, J., [1987, already in the original reference list].

p. 2785, lines 23-24: The following brief description of the heterogeneous chemistry formulation will be added. We believe that the use of a two-dimensional model is appropriate for comparisons of the meridional gradients of HNO₃ with the zonal average LIMS data.

To be added to p. 2785, line 22:

The solid line corresponds to the HNO₃ from the two-dimensional model simulation [Callis et al. 2001]. The model includes heterogeneous processing of N₂O₅ and ClONO₂ on stratospheric sulfate aerosol surfaces, leading to the production of HNO₃. Data on reaction probability have been adopted from the JPL evaluation [Sander et al., 2006]. The surface area density for the background aerosol distribution is taken from the climatology based on SAGE II measurements [Thomason et al., 1997]. The model does not include reactions in polar stratospheric clouds.

Section 4.3

p. 2787, line 11: The following brief description of the diurnal photochemical model will be added.

This model is an updated version of the zero-dimensional model described in Natarajan et al. [2002] and Natarajan and Callis [1991]. The numerical procedure uses a stiff equation solver to integrate the system of species continuity equations. For each latitude and altitude considered, the model is constrained by the nighttime (descending node) LIMS observations. Initialization for species that are not measured by LIMS, e.g., the chlorine species, is based on the results of the two-dimensional model. Chemical kinetics and photochemical data are adopted from Sander et al. [2006]. During initialization, the calculations are repeated for a few diurnal cycles, and in each cycle the mixing ratios of the observed species are reset to the LIMS values at the local time of the corresponding, LIMS nighttime measurements. Once the unmeasured, reactive species reach a steady diurnal variation, the time integration is continued for another diurnal cycle and then the designated parameters are evaluated (i.e., the day/night NO₂ ratios).

p. 2787, line 26: We agree with the reviewer that the findings by Funke et al. [2005] rule out non-LTE emissions from NO₂ only below 50 km. The discrepancies in the day/night NO₂ ratios between LIMS V6 and the model are seen mostly above the 1-hPa level. It is possible that non-LTE effects in NO₂ are contributing to the errors in LIMS daytime NO₂ at these levels. We cannot make any quantitative estimate about the relative importance of the H₂O and NO₂ non-LTE emissions. We will reword the text by deleting p. 2787, line 27 to p. 2788, line 3, and inserting the following:

In a recent analysis of the spectrally-resolved NO₂ measurements from the MIPAS instrument of ENVISAT, Funke et al. [2005] found no evidence for non-LTE emissions from the higher vibrational states of NO₂, at least for altitudes below 50 km. Figure 10 shows significant

differences in the day/night NO₂ ratios between the model and the LIMS V6 data, mainly above the 1-hPa level (around 50 km). Therefore, the uncertainty in the LIMS V6 daytime NO₂ above 50 km may still be caused by a combination of non-LTE emissions from H₂O and from NO₂ itself.

Section 4.4

p. 2788, line 15: Our statement refers to the absence of a high-energy, solar proton event during January 1979. Only such events can cause in-situ production of odd nitrogen in the upper stratosphere. We will refer to Jackman et al. [JGR, 1990].

Text to be added to p. 2788, line 15:

The study by Jackman et al. [1990] on the effects of solar proton events on the middle atmosphere during the period 1963-1984 does not indicate the occurrence of any large event during January 1979.

References to be added:

Callis, L. B., Russell III, J. M., Natarajan, M., and Haggard, K. V.: Examination of wintertime latitudinal gradients in stratospheric NO₂ using theory and LIMS observations, *Geophys. Res. Lett.*, 10, 945 – 948, 1983.

Santee, M. L., et al.: Validation of the Aura microwave limb sounder HNO₃ measurements, *J. Geophys. Res.*, 112, D24S40, doi:10.1029/2007JD008721, 2007.

Sander, S. P., et al. : Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation Number 15, JPL Publication 06-2, 2006.

Thomason, L. W., Poole, L. R., and Deshler, T.: A global climatology of stratospheric aerosol surface area density deduced from Stratospheric Aerosol and Gas Experiment II measurements: 1984 – 1994, *J. Geophys. Res.*, 102, 8967, 1997.

Natarajan, M., and Callis, L. B.: Stratospheric photochemical studies with Atmospheric Trace Molecule Spectroscopy (ATMOS) measurements, *J. Geophys. Res.*, 96, 9361 – 9370, 1991.

Jackman, C. H., et al.: Effect of solar proton events on the middle atmosphere during the past two solar cycles as computed using a two-dimensional model, *J. Geophys. Res.*, 95, 7417 – 7428, 1990.