LIMS HNO$_3$ Data Above 5 mbar: Corrections Based on Simultaneous Observations of Other Species

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The LIMS HNO$_3$ values are inconsistent with other LIMS measurements above about 5 mbar. During the four time periods analyzed, the LIMS HNO$_3$ concentrations were much higher than the HNO$_3$ concentrations computed using the other LIMS measurements (O$_3$, H$_2$O, NO$_2$, and temperature). Until this inconsistency in the LIMS data is resolved, we recommend an alternative evaluation of upper-stratospheric HNO$_3$, consistent with all other LIMS measurements, for pressure levels less than 5 mbar. The alternate method of evaluating HNO$_3$ makes use of a photochemical equilibrium approximation to derive OH from LIMS H$_2$O and O$_3$; this OH is used with LIMS NO$_2$ to derive HNO$_3$ above 5 mbar.

INTRODUCTION

Recently, the 7 months (October 25, 1978 to May 29, 1979) of the Limb Infrared Monitor of the Stratosphere (LIMS) data have become available for use by the scientific community. The LIMS instrument monitored four trace gases (O$_3$, H$_2$O, HNO$_3$, and NO$_2$) and the temperature in the stratosphere and mesosphere. Several papers have appeared describing the instrument and the constituents monitored [*Gille and Russell*, 1984; *Gille et al.*, 1984a, b; *Remsberg et al.*, 1984; *Russell et al.*, 1984a, b].

These measurements are of great use in studying the dynamics and chemistry of the stratosphere. They can be used to derive other minor species as well as to check two- and three-dimensional atmospheric models. It is therefore of importance that the LIMS data be internally self-consistent. While it is not possible to check the self-consistency of all species in this data set, it is possible to argue fairly convincingly that O$_3$, H$_2$O, NO$_2$, and temperature measurements are not only qualitatively but quantitatively fairly accurate.

Remsberg et al. [1984] compare LIMS O$_3$ measurements with other O$_3$ measurements, including rocket and balloon underflights, Umkehr soundings, and Dobson measurements. All appear fairly consistent with each other. The LIMS zonal mean O$_3$ profiles are, therefore, believed to be accurate to 10–15% at most altitudes and latitudes. The LIMS H$_2$O measurements were validated in 13 balloon underflights [*Russell et al.*, 1984b]. The mean difference between the two sets of measurements was about 0.6 ppmv, approximately the same order as the estimated LIMS accuracy. LIMS and balloon NO$_2$ measurements gave agreement on the order of 20% in the 30-mbar to 3-mbar pressure range for 13 different comparisons [*Russell et al.*, 1984a]. The LIMS temperature measurements are consistent with ground-based and balloon measurements taken concurrently [*Gille et al.*, 1984a].

The LIMS HNO$_3$ appears to have a realistic behavior below 5 mbar, but above 5 mbar the LIMS HNO$_3$ appears to be too high [*Gille et al.*, 1984b]. We will discuss this LIMS HNO$_3$ behavior, explain why we feel it to be unrealistic, and present what we believe to be a better HNO$_3$ two-dimensional (2-D) distribution for one time period above 5 mbar.

LIMS HNO$_3$ BEHAVIOR COMPARED WITH OTHER EXPERIMENTAL MEASUREMENTS AND MODEL CALCULATIONS

We are aware of three publications on LIMS HNO$_3$ data: namely, *Russell et al.* [1983], *Gille and Russell* [1984], and *Gille et al.* [1984b]. In the *Russell et al.* [1983] paper, one-dimensional HNO$_3$ profiles are presented for four time periods at 52° north latitude. These data were given in the range from 100 to about 0.7 mbar. Characteristic of these data is a minimum in the HNO$_3$ at about 2 mbar with a slight increase at higher altitudes.

Gille et al. [1984b] go into greater detail about the nitric acid measurements and the validity of their values. In fact, several intercomparisons are made with balloon measurements and 2-D model calculations in this paper. The results of the comparisons are that the LIMS results are higher than the correlative measurements above 10 mbar by about 1.5 ppbv. One of the conclusions of this study is that the LIMS values are high at 5 mbar and above. *Gille et al.* [1984b] indicate that the large LIMS HNO$_3$ values could be caused by an additional radiance contribution just twice the noise level. This additional radiance contribution "could easily arise from a number of sources, including out-of-spectral-band radiance, mislocation of the zero reference, or small aberrations in the field of view function" [*Gille et al.*, 1984b, p. 5187].

Since their work, two additional observational estimates of upper stratospheric HNO$_3$ have been made. These involved the use of balloon-borne mass spectrometers to measure the abundance of stratospheric ions. From these concentrations and the known and/or estimated kinetic and thermochemical data of these ions, concentrations of neutral species that are ion ligands, such as HNO$_3$ and H$_2$SO$_4$, may be inferred.

Arijs et al. [1983] obtained upper limits for HNO$_3$ mixing ratios of 0.3 ppbv at 42.3 km, which is substantially below the values reported for LIMS [*Russell et al.*, 1983; *Gille and Russell*, 1984; *Gille et al.*, 1984b], and 20 ppbv at 45.2 km, which is substantially above any estimated value for upper stratospheric HNO$_3$. Arijs et al. note that the derivations of upper limits to HNO$_3$ concentrations are very approximate. More recently, *Arnold and Qiu* [1984] inferred upper-stratospheric HNO$_3$ mixing ratios of 0.16 ppbv at 40.8 km, which is also well below the reported LIMS results.

EVIDENCE INDICATING INACCURACY OF LIMS HNO$_3$ ABOVE 5 MBAR

In this section we present photochemical evidence that LIMS HNO$_3$ data has inaccuracies above 5 mbar. We use the

TABLE 1. Reactions and Their Rates

Reaction Number	Reaction
(R1)	$O_2 + hv \rightarrow O + O$
(R2)	$O_3 + hv \rightarrow O_2 + O$
(R3)	$O_3 + hv \rightarrow O_2 + O(^1D)^*$
(R4)	$NO_2 + hv \rightarrow NO + O$
(R5)	$NO + hv \rightarrow N + O$
(R6)	$HNO_3 + hv \rightarrow OH + NO_2$
(R7)	$NO_3 + hv \rightarrow NO_2 + O$
(R8)	$NO_3 + hv \rightarrow NO + O_2$
(R9)	$N_2O_5 + hv \rightarrow NO_2 + NO_2 + O$
(R10)	$H_2O + hv \rightarrow OH + H$
(R11)	$H_2O_2 + hv \rightarrow OH + OH$
(R12)	$HO_2NO_2 + hv \rightarrow OH + NO_3$
(R13)	$HO_2NO_2 + hv \rightarrow HO_2 + NO_2$
(R14)	$O + O_3 \rightarrow O_2 + O_2$
(R15)	$O + O_2 + N_2 \rightarrow O_3 + N_2$
(R16)	$O + O_2 + O_2 \rightarrow O_3 + O_2$
(R17)	$O(^1D) + N_2 \rightarrow O + N_2$
(R18)	$O(^1D) + O_2 \rightarrow O + O_2$
(R19)	$NO + O + M \rightarrow NO_2 + M$
(R20)	$NO_2 + O \rightarrow NO + O_2$
(R21)	$NO + O_3 \rightarrow NO_2 + O_2$
(R22)	$N + O_2 \rightarrow NO + O$
(R23)	$NO_2 + O_3 \rightarrow NO_3 + O_2$
(R24)	$NO_3 + O \rightarrow NO_2 + O_2$
(R25)	$NO_2 + O + M \rightarrow NO_3 + M$
(R26)	$NO_3 + NO \rightarrow NO_2 + NO_2$
(R27)	$N + NO \rightarrow N_2 + O$
(R28)	$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$
(R29)	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$
(R30)	$O(^1D) + H_2O \rightarrow OH + OH$
(R31)	$OH + O_3 \rightarrow HO_2 + O_2$
(R32)	$OH + O \rightarrow O_2 + H$
(R33)	$HO_2 + O_3 \rightarrow OH + O_2 + O_2$
(R34)	$HO_2 + O \rightarrow OH + O_2$
(R35)	$H + O_2 + M \rightarrow HO_2 + M$
(R36)	$H + O_3 \rightarrow OH + O_2$
(R37)	$H_2O_2 + O \rightarrow HO_2 + OH$
(R38)	$OH + HO_2 \rightarrow H_2O + O_2$
(R39)	$OH + OH \rightarrow H_2O + O$
(R40)	$H + HO_2 \rightarrow H_2O + O$
(R41)	$H + HO_2 \rightarrow OH + OH$
(R42)	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
(R43)	$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$
(R44)	$OH + OH + M \rightarrow H_2O_2 + M$
(R45)	$OH + H_2O_2 \rightarrow H_2O + HO_2$
(R46)	$NO + HO_2 \rightarrow NO_2 + OH$
(R47)	$OH + NO_2 + M \rightarrow HNO_3 + M$
(R48)	$OH + HNO_3 \rightarrow H_2O + NO_3$
(R49)	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$
(R50)	$HO_2NO_2 + O \rightarrow OH + O_2 + NO_2$
(R51)	$HO_2NO_2 + OH \rightarrow H_2O + O_2 + NO_2$
(R52)	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$

Values in this table are taken from DeMore et al. [1983].

*Spin conservation is not violated. $O_2(^1\Delta)$ is assumed to quench to O_2 rapidly.

behavior of the hydroxyl radical (OH), derived from LIMS data, to demonstrate that LIMS HNO₃ data is high above 5 mbar. One scheme to derive OH that involves HNO₃ and NO₂ was pioneered by Pyle et al. [1983]. We call this approach scheme 1. This method should work in the regions where HNO₃ is in photochemical equilibrium or close to it (above about 10 mbar for mid-latitudes). In photochemical equilibrium the production of HNO₃—P(HNO₃)—is equal to the loss of HNO₃—L(HNO₃). We use reactions given in Table 1, thus

$$P(\text{HNO}_3) = k_{47}[\text{OH}][\text{NO}_2][M] \quad (1)$$

and

$$L(\text{HNO}_3) = k_{48}[\text{OH}][\text{HNO}_3] + J_6[\text{HNO}_3] \quad (2)$$

Setting (1) equal to (2) and solving for [OH] gives

$$[\text{OH}] = \frac{J_6}{k_{47}[M](1/R) - k_{48}} \quad (3)$$

where

$$R = [\text{HNO}_3]/[\text{NO}_2] \quad (4)$$

We obtained the LIMS data tapes from the National Space Sciences Data Center (NSSDC) at the Goddard Space Flight Center. We used daytime zonally averaged HNO₃, NO₂, and temperature data from LIMS during the period of time from March 26 to April 1, 1979, in (3) to derive the OH given in Figure 1. These data were binned according to the 2-D grid given in Guthrie et al. [1984].

Since we used pressure and Pyle et al. [1983] used altitude as the ordinate axis, it was unclear if our results were similar. Discussion with Pyle (private communication, 1984) has revealed that both calculations are in agreement when plotted on a pressure-latitude coordinate system. The only difference in methods appears to be the fact that Pyle et al. compute the OH from each observed HNO₃ and NO₂ and then average the OH values, whereas we zonally average HNO₃ and NO₂ first and then compute OH.

Our OH values become quite high above 3 mbar, reaching values in excess of $1 \times 10^{+8}$ cm⁻³. These high numbers are not compatible with the measurements that exist [Anderson, 1976; Heaps et al., 1982]. In fact, by 2 mbar the numbers even become negative when the first term in the denominator of (3) becomes smaller than the second term, k_{48}. The ratio R is quite significant in this first term, and R, after falling in value between 40 mbar and 5 mbar, suddenly starts to increase again. This behavior is seen in Figure 2. This is contrary to model calculations and, also, other measurements [Harries, 1978]. It is unlikely that uncertainties in k_{47} and k_{48} would eliminate the problem of extremely large and/or negative values of OH determined from (3). See the first section in the appendix for more discussion concerning these uncertainties.

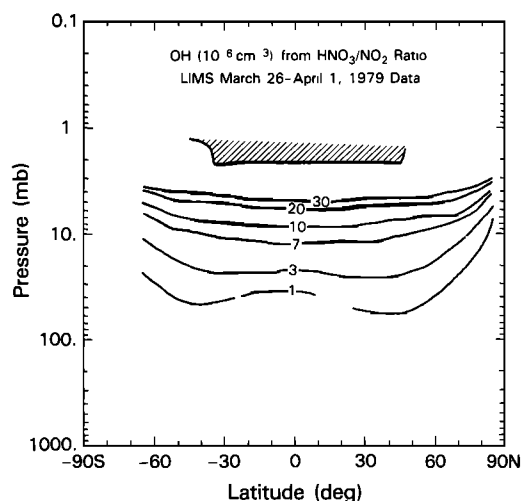We have also calculated OH during three other time

Fig. 1. OH 2-D cross section derived from LIMS daytime HNO₃, NO₂, and temperature data during the March 26 to April 1, 1979, time period, using scheme 1. Hatched area denotes negative values. Breaks in contour lines indicate lack of data.

periods, using the same method with similar findings. These other time periods are October 25 to November 1, 1978; January 19–24, 1979; and February 13, 1979. *Gille et al.* [1984*b*] use LIMS data from the time period January 15–26, 1979, in order to derive OH at 32° north by using the *Pyle et al.* [1983] approach. We plot the OH values from Figure 15 of their paper along with our OH values for the January 19–24, 1979, time period in Figure 3. Note the divergence between the *Gille et al.* [1984*b*] values and the OH values derived with the use of scheme 1. We do not know how to explain this discrepancy.

It is possible that we are neglecting some additional HNO₃ sources when setting up (1) and subsequently deriving (3) in order to calculate OH. We have carried out an extensive search in section 2 of the appendix of known reactions that lead to HNO₃ formation. We find that none of these HNO₃ production mechanisms provide the source necessary to sustain the large LIMS HNO₃ measurements above 5 mbar.

DERIVING HNO₃ ABOVE 5 MBAR FROM OTHER LIMS DATA

In the previous section we presented photochemical evidence, based on OH behavior, that LIMS HNO₃ data are too high above 5 mbar. Here we use the behavior of OH, calculated from LIMS data in another way, to correct the LIMS HNO₃ data above 5 mbar. This scheme to derive OH uses the sources and sinks of HO_x and mainly involves LIMS H_2O and O_3, as shown in (9) below. We label this approach scheme 2. Since scheme 1 mainly involves HNO₃ and NO₂ and scheme 2 mainly involves H_2O and O_3, the two schemes are fairly independent of one another. Because of this independence, the two schemes complement each other and provide a method for calculating better HNO₃ values above 5 mbar.

Scheme 2 is based on the following reasoning. The major source of $O(^1D)$ is

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \tag{R3}$$
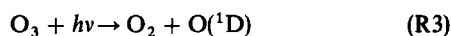
and the major sink of $O(^1D)$ is

$$O(^1D) + N_2 \rightarrow O + N_2 \tag{R17}$$
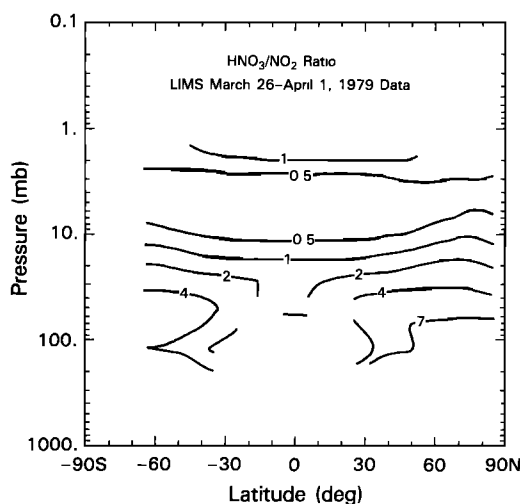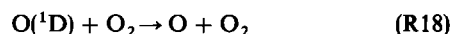
or

$$O(^1D) + O_2 \rightarrow O + O_2 \tag{R18}$$
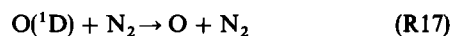
Fig. 2. The HNO_3/NO_2 ratio in a 2-D grid derived from LIMS daytime HNO₃ and NO₂ data during the March 26 to April 1, 1979, time period. Breaks in contour lines indicate lack of data.
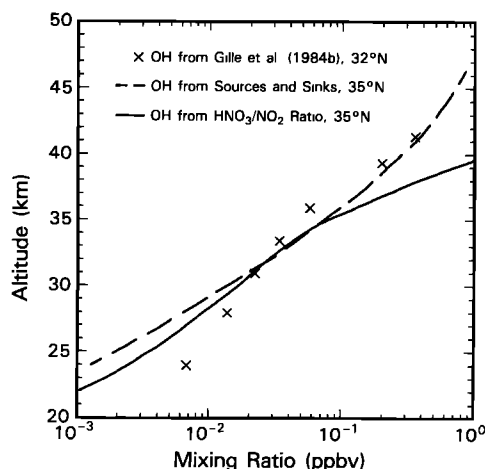
Fig. 3. OH 1-D profile at 32° north. The solid line was derived by using scheme 1 for time period January 19–24, 1979; the dashed line was derived by using scheme 2 for the same time period; the crosses were taken from the diamonds in Figure 15 of *Gille et al.* [1984*b*] for time period January 15–26, 1979.

Thus in photochemical equilibrium,

$$O(^1D) = \frac{J_3 O_3}{k_{17}[N_2] + k_{18}[O_2]} \tag{5}$$

or

$$O(^1D) = A[O_3] \tag{6}$$

where

$$A = \frac{J_3}{k_{17}[N_2] + k_{18}[O_2]} \tag{7}$$

The major source of HO_x is

$$O(^1D) + H_2O \rightarrow OH + OH \tag{R30}$$
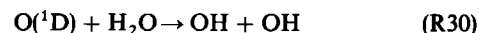
and the major sink of HO_x is

$$OH + HO_2 \rightarrow H_2O + O_2 \tag{R38}$$
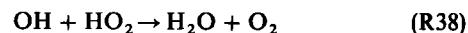
Since

$$HO_2 = B[OH] \tag{8}$$

where B is primarily a function of (R31)–(R36), O_3, O (which is dependent on O_3), and O_2 in the upper stratosphere [*Nicolet*, 1975]; we can write

$$[OH] = (k_{30}A[O_3][H_2O]/Bk_{38})^{1/2} \tag{9}$$

Relationship (9) is a reasonably accurate way to calculate OH, however, we want to calculate OH as accurately as possible. Therefore we use the 2-D model described in *Guthrie et al.* [1984] to solve for 11 minor species (O, $O(^1D)$, N, NO, NO₃, N₂O₅, H, OH, HO₂, HO₂NO₂, and H₂O₂), holding O₃, H₂O, HNO₃, and NO₂ fixed to LIMS data. The transport was set to zero, and the temperature field described in Guthrie et al. was used to derive the background N_2 and O_2; however, the temperature field used in computing reaction rates was that given by LIMS data.

All these LIMS data were binned in a daytime zonally averaged sense according to the 2-D grid given in *Guthrie et al.* [1984]. The 11 variable minor species were calculated from photochemical equilibrium considerations. Since meridional winds can move constituents, at most, a degree of latitude a
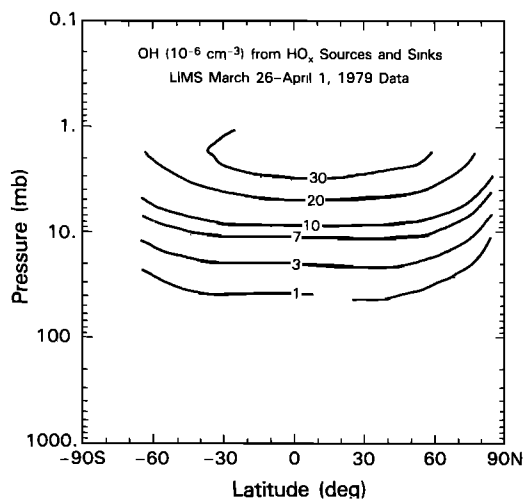
Fig. 4. OH 2-D cross section derived from LIMS daytime H_2O, O_3, HNO_3, NO_2, and temperature data during the March 26 to April 1, 1979, time period, using scheme 2. Break in contour line indicates lack of data.

day in the stratosphere (assuming, at most, a meridional wind speed of 1.3 m/s, [see, for example, *Geller*, 1983]), the zonal average calculation of the 11 species, assuming photochemical equilibrium, is good above 10 mbar and at latitudes less than 60°. The list of reactions included in these calculations is given in Table 1.

Not all of these species can be calculated correctly by assuming that they are in photochemical equilibrium. The species O, $O(^1D)$, N, NO, H, OH, HO_2, and NO_3 have short equilibrium times, and photochemical equilibrium is a good assumption. Lifetimes of N_2O_5, HO_2NO_2, and H_2O_2 with respect to photochemical loss are, at most, several days in the stratosphere at latitudes less than 60°. The lifetime of the HO_x (H, OH, HO_2) family with respect to photochemical loss is less than a day in the stratosphere only above 10 mbar and at latitudes less than 60°.

The OH derived by scheme 2 is also presented in Figure 3 for the January 19–24, 1979, time period. The OH from schemes 1 and 2 are reasonably close to each other from

about 22 to 35 km and only start diverging substantially above 35 km. Similar work by *Pyle and Zavody* [1985], using a different 2-D model, shows essentially identical results.

The OH 2-D cross section derived by scheme 2 during the time period March 26, 1979, to April 1, 1979, is given in Figure 4. Between 20 mbar and 5 mbar the OH cross sections from Figures 1 and 4 are very similar. However, above 5 mbar and below 20 mbar there are striking differences between the two. As was discussed earlier, photochemical equilibrium becomes an increasingly poor assumption at pressures greater than 10 mbar for both schemes 1 and 2. The OH-HO_2 balance in the middle and lower stratosphere is strongly dependent on the NO_x (NO and NO_2) abundance through the reaction

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (R46)$$
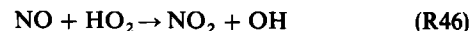
Since the estimated error given in *Russell et al.* [1984a] for the LIMS NO_2 (which is the primary influence of the NO concentration) is largest at pressures greater than 10 mbar, the OH-HO_2 balance will be most uncertain in this regime. Also, below 10 mbar, CH_4 oxidation can lead to increased HO_x production, primarily via the reactions

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \qquad (R53)$$

and

$$CH_2O + h\nu \rightarrow CHO + H \qquad (R54)$$
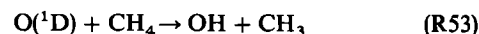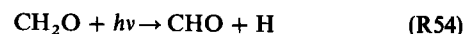
as well as shift the OH-HO_2 balance via the sequence of reactions

$$OH + CH_4 \rightarrow H_2O + CH_3 \qquad (R55)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (R56)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (R57)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (R58)$$

Since we do not include CH_4 and its oxidation in this version of scheme 2, we probably underestimate OH below 10 mbar. These reactions are numbered (R53) through (R58), following sequentially from the numbering scheme used for the chemical reactions given in Table 1.

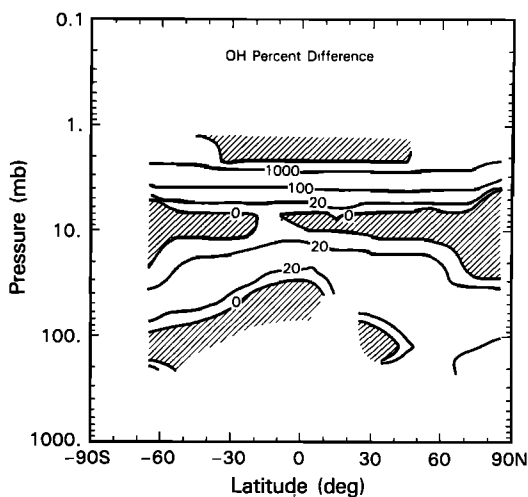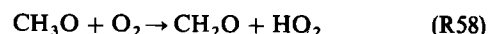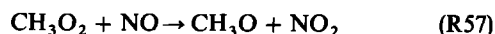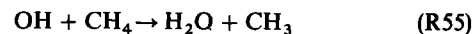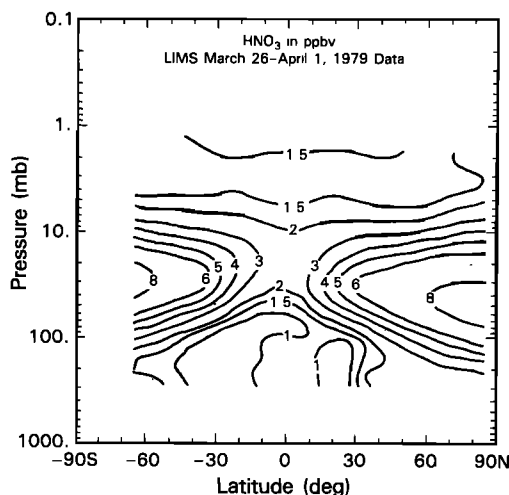We next calculate the percent difference between the OH

Fig. 5. Percentage difference between OH cross sections given in Figures 1 and 4. Use (10) for these values. The hatched areas indicate regions of negative values. Breaks in contour lines indicate lack of data.

Fig. 6. LIMS daytime HNO_3 measurements during the March 26 to April 1, 1979, time period.

presented in Figure 1 and that in Figure 4. This is given by

$$P = \frac{[OH]_{\text{scheme 1}} - [OH]_{\text{scheme 2}}}{[OH]_{\text{scheme 2}}} \qquad (10)$$

The value P is calculated at each point in the 2-D grid and presented in 2-D form in Figure 5. Above 5 mbar the OH from scheme 1 is much larger than the OH from scheme 2. By about 2.5 mbar the OH is up to 1000% larger from scheme 1. In fact, above about 2 mbar the values of P are negative because of the negative OH values resulting from scheme 1.

We next calculate the HNO₃ that would be predicted by assuming the OH from scheme 2 and the NO₂ from LIMS data. This process simply involves inverting (3) to solve for HNO₃. Thus

$$[HNO_3] = \frac{k_{47}[OH][NO_2][M]}{J_6 + k_{48}[OH]} \qquad (11)$$

The HNO₃ from LIMS data (given in Figure 6) and this HNO₃ (given in Figure 7) are compared and the percent difference is calculated with

$$C = \frac{[HNO_3]_{\text{invert (3) with scheme 2 [OH]}} - [HNO_3]_{\text{LIMS}}}{[HNO_3]_{\text{LIMS}}} \qquad (12)$$

The value C is computed at each point in the 2-D grid and is presented in 2-D form in Figure 8. We derive the 2-D distribution of HNO₃ given in Figure 9 when we (1) compute HNO₃ from the method using scheme 2 for OH with equation (11) only when C is negative and only at altitudes above 5 mbar and (2) use the LIMS HNO₃ data at all other points. The HNO₃ distribution derived in this manner agrees better with other measurements [see Gille et al., 1984b, Figure 12] and model calculations [see Gille et al., 1984b, Figure 14] than that given solely by the LIMS HNO₃ measurements.

Since the OH derived by using scheme 2 has inherent in its calculation the incorrect HNO₃ for pressures above 5 mbar, it is of interest to know if changing HNO₃ makes any difference in the OH derived by using scheme 2. We changed the HNO₃ 2-D distribution to that given in Figure 9 and found differences always less than 7% in this derived OH when compared with the OH derived by using HNO₃ from Figure 6. The HNO₃ distribution affects the OH values via the reactions
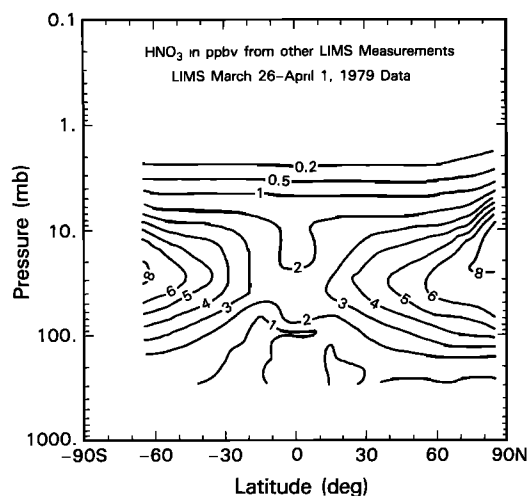
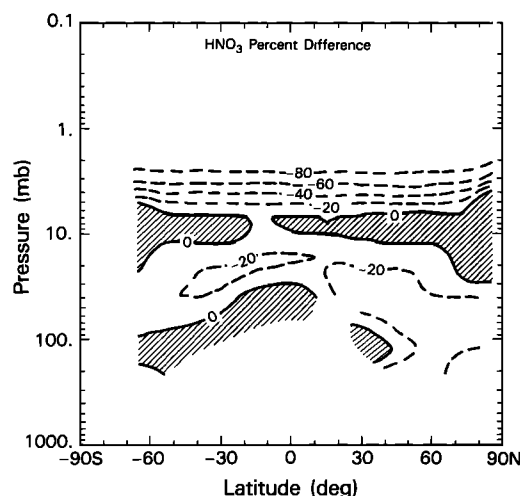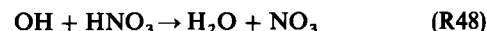$$HNO_3 + h\nu \rightarrow OH + NO_2 \qquad (R6)$$

Fig. 8. Percentage difference between HNO₃ cross sections given in Figures 6 and 7. Use (12) for these values. The hatched areas indicate regions of positive values. Breaks in contour lines indicate lack of data.

and

$$OH + HNO_3 \rightarrow H_2O + NO_3 \qquad (R48)$$

Therefore we conclude that no iteration is necessary in order to compute the correct HNO₃ distribution from the other LIMS measurements (which include the incorrect HNO₃).

CONCLUSIONS

LIMS HNO₃ mixing ratio measurements show values of about 1.5 ppbv to 2 ppbv from 5 mbar to 1 mbar. Gille et al. [1984b] noted that such behavior is contrary to other measurements and model results, which show a rapid decrease in HNO₃ mixing ratio above 5 mbar. The high LIMS HNO₃ results also cannot be supported by any atmospheric chemistry of which we are aware. To support the high HNO₃ measurements, large changes in chemical modeling would lead to substantial changes in other minor species. Differences in other minor species between model predictions and measurements of a magnitude in line with the HNO₃ differences do not exist, thus the high HNO₃ results appear to be unlikely.

We have used other LIMS data to derive HNO₃ above 5 mbar through the intermediate species OH. Until the LIMS

Fig. 7. HNO₃ values calculated by using LIMS H₂O, O₃, NO₂, and temperature measurements for the March 26 to April 1, 1979, time period.
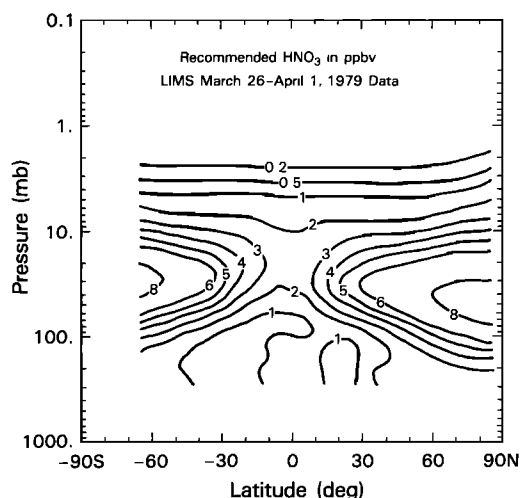

Fig. 9. HNO₃ 2-D cross section constructed by using the HNO₃ values in Figures 6 and 7. Explanation is given in the text.

HNO$_3$ data above 5 mbar have been corrected, we recommend that the method detailed here (using (11)) be used to derive the HNO$_3$ from the other LIMS measurements.

APPENDIX

Effect of Uncertainty of Chemical Reaction Rates

Our conclusion that the only source for the discrepancy in the OH profiles calculated by the two methods is incorrect HNO$_3$ measurement hinges on the assumption that the reaction rates k_{47} and k_{48}, used in deriving [OH] with the method involving HNO$_3$ and NO$_2$, are correct. Clearly, if k_{47} were underestimated and/or k_{48} were overestimated in the upper stratosphere, the effect on the denominator in (3) would be equivalent to that of an overestimate of R.

The uncertainties in k_{47} and k_{48} are sufficiently small [DeMore et al., 1983], however, that it is unlikely that variation of these quantities within their stated error limits would eliminate the problem of extremely large and/or negative values of [OH] determined from (3). In particular, k_{47} is very close to its low-pressure limit in the upper stratosphere, and there the estimated errors are only approximately 20–30% [DeMore et al., 1983]. Similarly, the uncertainty in k_{48} is approximately 45–50% [DeMore et al., 1983]. The latter uncertainty is sufficiently large that it should encompass any systematic errors caused by the assumption of a pressure-independent value for k_{48}. Since the observed (but not unanimously accepted) pressure dependence of k_{48} decreases with increasing temperature [Margitan and Watson, 1982], this neglect should be of roughly the same importance in the warm upper stratosphere as it is in the cooler lower stratosphere. Much larger changes in k_{47} and/or k_{48} would be needed if the observed values of R are correct throughout the upper stratosphere and reasonable values for [OH] (on the order of 3 × 10^{+7} cm^{-3}) are to be inferred. This will be demonstrated in the following section.

Additional Upper Stratosphere HNO$_3$ Sources

Assuming that the high LIMS HNO$_3$ values were correct, just what is required to support such values? It appears that some major changes in our chemical understanding of the atmosphere would be required. We have gone through several schemes, highlighted below, that are possible methods of supporting a higher HNO$_3$. None of these schemes can support HNO$_3$ production of the magnitude needed to give the LIMS HNO$_3$.

Although the evidence presented in the preceding sections argues convincingly that the LIMS HNO$_3$ values obtained above 5 mbar are very high, it is important to reassess HNO$_3$ chemistry in the upper stratosphere to make sure that there are no additional sources of HNO$_3$ we have neglected in (3). We are especially interested in sources of HNO$_3$ that do not directly involve the OH radical. If one hypothesizes some such unknown HNO$_3$ production process with the rate P_x, one may rewrite (3) as

$$[OH] = \frac{J_6 - P_x/[HNO_3]}{k_{47}[M](1/R) - k_{48}} \qquad (A1)$$

Equations (4) and (A1) may be rewritten in terms of [OH] to give

$$P_x = [HNO_3](J_6 + k_{48}[OH]) - P_{47} \qquad (A2)$$

where

$$P_{47} = k_{47}[M][OH][NO_2] \qquad (A3)$$

From (A2) and (A3) we obtain an expression relating the magnitudes of the unknown and known production terms to [OH], R, J_6, k_{47}, and k_{48}:

$$P_x/P_{47} = (R/k_{47}[M])(k_{48} + J_6/[OH]) - 1 \qquad (A4)$$

Although [OH] is unknown, we may approximate the upper stratospheric [OH] by a value of 3 × 10^{+7} cm^{-3} [Pyle et al., 1983]. We will assume k_{47} and k_{48} are given by their tabulated values, J_6 is as determined by the radiation package in the 2-D model of Guthrie et al. [1984], and R is as obtained from the LIMS measurements. This is done for two latitudes in the March 26 to April 1, 1979, time period in Table 2. It is seen that the unknown HNO$_3$ production path(s) must be more important than the OH + NO$_2$ three-body recombination path at altitudes above those where the pressure is approximately 3 mbar and that at altitudes above the 2-mbar pressure level the unknown HNO$_3$ source must be some 10 times greater. Estimates of the HNO$_3$ production rate by (R47), calculated by assuming [OH] = 3 × 10^{+7} cm^{-3}, are also given in Table 2, along with the final estimated values for P_x.

In Table 2 we also list R_a, the value of the ratio R that would be needed if one requires [OH] to be no greater than 3 × 10^{+7} cm^{-3} and assumes no additional HNO$_3$ production mechanism. It is seen clearly that gross changes in the nature of R are required if one is to get reasonable [OH] values.

Known reactions other than R_{47} that lead to HNO$_3$ formation are few, however, and we show here that it seems unreasonable to expect that any of these could even remotely approach the magnitude needed to account for the additional HNO$_3$ production needed to rationalize the LIMS HNO$_3$ profiles.

Besides the OH + NO$_2$ three-body recombination rate, the only HNO$_3$-producing reaction listed in DeMore et al. [1983] is

$$HNO_2 + O_3 \rightarrow HNO_3 + O_2 \qquad (R59)$$
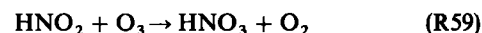
which has been found [Kaiser and Japar, 1977; Streit et al., 1979] to occur very slowly ($k < 5.0 \times 10^{-19}$ cm^{+3}/molecules/s). This reaction is an unlikely source of the additional upper-stratospheric HNO$_3$ for a number of reasons.

TABLE 2. Estimation of Required Missing Production Terms

Level Number	P, mbar	T, °K	M, cm^{-3}	R	P_x/P_{47}	P_{47}	P_x	R_a
				45N				
20	3.96	244.5	1.16(17)*	0.356	0.390	6.07(3)	2.4(3)	0.255
21	2.98	251.6	8.54(16)	0.488	2.33	2.07(3)	4.8(3)	0.147
22	2.24	258.7	6.23(16)	0.771	7.90	7.16(2)	5.7(3)	8.62(−2)
23	1.68	264.1	4.62(16)	1.288	22.9	2.93(2)	6.7(3)	5.38(−2)
24	1.27	267.6	3.43(16)	1.242	33.8	1.50(2)	5.1(3)	3.57(−2)
				35S				
20	3.96	247.8	1.16(17)	0.277	1.75	8.08(3)	1.4(3)	0.236
21	2.98	253.6	8.42(16)	0.377	1.75	2.74(3)	4.8(3)	0.737
22	2.24	259.4	6.17(16)	0.650	6.82	8.56(2)	5.8(3)	8.03(−2)
23	1.68	264.5	4.59(16)	1.055	18.9	3.21(2)	6.1(3)	5.30(−2)
24	1.27	267.4	3.41(16)	1.387	38.2	1.54(2)	5.9(3)	3.54(−2)
25	0.95	267.3	2.56(16)	1.179	45.7	1.03(2)	4.7(3)	2.52(−2)

*1.16(17) means 1.16 × 10^{+17}.

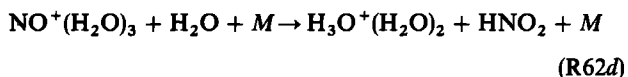First, the dominant path for HNO_2 production is the three-body recombination reaction

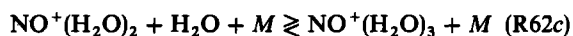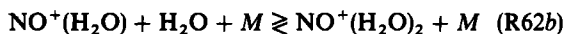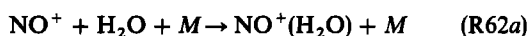$$OH + NO + M \rightarrow HNO_2 + M \qquad (R60)$$

but this would cause $[HNO_2]$ to be proportional to $[OH]$ (since HNO_2 is in photochemical equilibrium in the stratosphere as a result of rapid photolysis), thus making it unsuitable to be the missing HNO_3 source. Second, reactions that produce HNO_2 without direct involvement of OH should not be important in the upper atmosphere. These include

$$CH_3O_2 + NO \rightarrow \begin{array}{ll} CH_3O + NO_2 & (R61a) \\ CH_2O + HNO_2 & (R61b) \end{array}$$
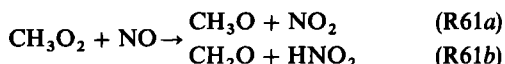
in which (R61b) is, at most, a minor pathway [Ravishankara et al., 1981], and in any case, hydrocarbon oxidation chemistry should be of no importance in the upper stratosphere (recall our sources and sinks method, which neglected CH_4, gave good values for $[OH]$ in the middle and upper stratosphere).

The second [OH]-independent HNO_2 production mechanism involves ion-molecular chemistry by NO^+ by the pathway

$$NO^+ + H_2O + M \rightarrow NO^+(H_2O) + M \qquad (R62a)$$

$$NO^+(H_2O) + H_2O + M \gtrless NO^+(H_2O)_2 + M \qquad (R62b)$$

$$NO^+(H_2O)_2 + H_2O + M \gtrless NO^+(H_2O)_3 + M \qquad (R62c)$$

$$NO^+(H_2O)_3 + H_2O + M \rightarrow H_3O^+(H_2O)_2 + HNO_2 + M \qquad (R62d)$$

NO^+ production in the stratosphere has been found to be "inconsequential" [Ferguson et al., 1979], however, so R62 cannot provide enough HNO_2, and thus HNO_3, to account for the HNO_3 discrepancy.

A second neutral pathway for HNO_3 production is the reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (R63)$$

which has recently been remeasured to have a rate of 1.3×10^{-21} cm^{+3}/molecules/s at room temperatures [Tuazon et al., 1983]. If one assumes this reaction rate to be pressure- and temperature-independent, then mixing ratios of N_2O_5 of from 1 to well over 100 ppm in the upper stratosphere would be needed (and recall that the LIMS data we are working with are for near local noon) if R63 is to provide the missing HNO_3. These are extremely high values for N_2O_5. Recent 2-D calculations of N_2O_5 with the 2-D model described in Guthrie et al. [1984] do not exceed 10 ppbv and agree quite well with the calculations given in Solomon and Garcia [1983]. One recognizes that (R63) cannot be an important source of stratospheric HNO_3. Production of HNO_3 from N_2O_5 by an ionic pathway involving catalysis by hydrated protons has also been suggested [Ferguson et al., 1979]. Recent laboratory experiments [Bohringer et al., 1983] conclusively demonstrate that this pathway should not be important in the stratosphere, however.

A related neutral pathway that could also give rise to HNO_3 production is

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (R64)$$

[Warneck, 1977; Prasad et al., 1978]. This reaction should be fast in heterogeneous systems [Prasad et al., 1978], but it is probably slow in the gas phase, with a rate close to that of
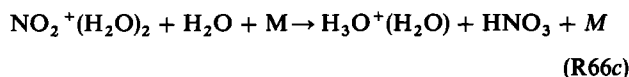
(R63) [Warneck, 1977]. If one assumes $k_{64} = k_{63}$, then in the upper stratosphere, where $[H_2O] = 1-5 \times 10^{+11}$ cm^{-3}, in order to get a production rate of HNO_3 on the order of $4 \times 10^{+3}$ cm^{-3} s^{-1}, one would need $ClONO_2$ in the range from $6 \times 10^{+12}$ to $3 \times 10^{+13}$ cm^{-3}, corresponding to mixing ratios in the vicinity of 100–1000 ppm. These values are orders of magnitude above 2-D predictions [Miller et al., 1981], which suggest that the $ClONO_2$ mixing ratio never exceeds 1 ppb.

An additional possible HNO_3-producing reaction involves the H-atom transfer reaction [Atkinson et al., 1984]:

$$NO_3 + CH_2O \rightarrow HNO_3 + CHO \qquad (R65)$$
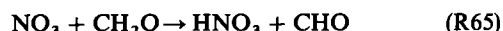
but this can also be shown to be completely negligible because of the low concentrations of both NO_3 and CH_2O in the upper stratosphere, especially at local noon, where photolysis of NO_3 will be very rapid.

Fehsenfeld et al. [1975] has shown that an ion-molecule reaction scheme analogous to (R62) can lead to direct production of HNO_3:

$$NO_2^+ + H_2O + M \gtrless NO_2^+(H_2O) + M \qquad (R66a)$$

$$NO_2^+(H_2O) + H_2O + M \gtrless NO_2^+(H_2O)_2 + M \qquad (R66b)$$

$$NO_2^+(H_2O)_2 + H_2O + M \rightarrow H_3O^+(H_2O) + HNO_3 + M \qquad (R66c)$$

where NO_2^+ is produced by the reaction [Fehsenfeld et al., 1973]

$$O_2^+ + NO_2 \rightarrow NO_2^+ + O_2 \qquad (R67)$$
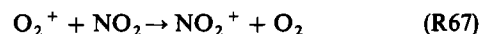
Since the dominant stratospheric positive ion chemistry involves formation of proton hydrate cluster ions following reaction of O_2^+ with O_2 to form O_4^+ [Ferguson et al., 1979], only a small fraction ($10^{-5} \rightarrow 10^{-4}$) of the O_2^+ produced goes on to form NO_2^+. This inefficiency coupled with the low overall rate of cosmic-ray-induced ion-pair production in the stratosphere [Heaps, 1978] will definitely prevent (R66) and (R67) from being the missing HNO_3 source.

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