Stratospheric and mesospheric HO\textsubscript{x}: Results from Aura MLS and FIRS-2

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Observations of OH and HO\textsubscript{2} from Aura MLS for four seasons and diurnal profiles from the FIRS-2 balloon instrument for Fall 2004 are compared with photochemical model simulations testing three sets of kinetics parameters. MLS and FIRS-2 OH profiles, between 25–60 km, are lower than model results using standard kinetics. Use of a faster, previously published rate constant for O+OH leads to better agreement with MLS and FIRS-2 profiles of OH. A 20% increase in the rate of HO\textsubscript{2}+OH and the faster rate for O+OH results in improved overall agreement with observations of OH, HO\textsubscript{2}, HO\textsubscript{x}, and HO\textsubscript{2}/OH. Since the MLS and FIRS-2 observations of HO\textsubscript{x} are reasonably well described by these models, they are therefore not consistent with the previously reported HO\textsubscript{x} dilemma. However, all models considered here result in calculated odd oxygen loss exceeding production, consistent with the long standing ozone deficit problem. Citation: Canty, T., H. M. Pickett, R. J. Salawitch, K. W. Jucks, W. A. Traub, and J. W. Waters (2006), Stratospheric and mesospheric HO\textsubscript{x}: Results from Aura MLS and FIRS-2, Geophys. Res. Lett., 33, L12802, doi:10.1029/2006GL025964.

1. Introduction

Simultaneous observations of OH and HO\textsubscript{2} from the Microwave Limb Sounder (MLS) instrument on board the Aura satellite, launched July 15, 2004, provide a unique opportunity to test our understanding of stratospheric HO\textsubscript{x}, (OH+HO\textsubscript{2}). We present an analysis of daytime zonally averaged profiles of OH and HO\textsubscript{2} for four seasons using a photochemical model constrained by MLS observations of HO\textsubscript{x} precursors. Measurements of OH and HO\textsubscript{2} acquired by the Far-Infrared Spectrometer (FIRS-2) instrument during an Aura validation balloon campaign in September 2004 are also examined.

In the stratosphere, OH is primarily produced through the reaction of water with metastable oxygen, O(1D), and by water photolysis above 60 km. HO\textsubscript{x} is lost primarily through the reaction

\[
\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2. \tag{1}
\]

Previous observations of either OH or HO\textsubscript{2} alone have shown poor agreement with model simulations. As a result, two studies have suggested modifications to the rate constants of HO\textsubscript{x} partitioning reactions to reach better agreement between measurements and model calculations (see auxiliary material\textsuperscript{1} for further discussion). Ground based microwave observations of HO\textsubscript{2} were used to suggest a 60–80% decrease in the rate of

\[
\text{HO}_2 + \text{O} \rightarrow \text{HO}_2 + \text{O}_2 \tag{2}
\]

[Clancy et al., 1994]. Mesospheric OH observations by the Middle Atmospheric High Resolution Spectrograph Investigation (MAHRSI) instrument in November 1994 led to the suggestion of either a 50% reduction in the rate of reaction (2) or both a 20% reduction of rate (2) and a 30% increase in rate (1) [Summers et al., 1997]. However, without simultaneous observations of OH and HO\textsubscript{2}, it is difficult to attribute the above discrepancies to HO\textsubscript{x} loss, production, or partitioning.

These suggested changes were tested against an OH profile measured by MAHRSI in August 1997 [Conway et al., 2000]. Their results showed that the kinetic changes needed to match the MAHRSI OH profile above 50 km led to poorer agreement between modeled and measured OH from 35–45 km. No particular kinetic change allows models to reproduce MAHRSI OH in both the mesosphere and the upper stratosphere. This is known as the “HO\textsubscript{x} dilemma” [Conway et al., 2000].

Loss of odd-oxygen (O\textsubscript{x} = O\textsubscript{3} + O) is dominated by HO\textsubscript{2} catalytic processes above 45 km. Ozone, the main component of O\textsubscript{x} at these altitudes, should be in photochemical steady state. However, calculated loss of O\textsubscript{3} generally exceeds production by ~35% [e.g., Jucks et al., 1996, Osterman et al., 1997]. This leads to an underprediction of upper stratospheric O\textsubscript{3}, commonly known as the “ozone deficit problem”.

The kinetics changes suggested by Clancy et al. [1994] and Summers et al. [1997] lead to good agreement with measured mesospheric HO\textsubscript{2} and OH, respectively, and also largely resolve the ozone deficit problem. These results are driven by a reduction in the rate of (2), resulting in more HO\textsubscript{2}, less OH, and slower O\textsubscript{3} removal compared to a standard model. In contrast, Jucks et al. [1998] suggested the rates of reactions (1) and (2) must both be reduced by 25% to best explain FIRS-2 observations of OH and HO\textsubscript{2}. The Jucks et al. [1998] kinetics change has a negligible effect on the ozone deficit problem. Below, we investigate...
the implications of recent Aura MLS and FIRS-2 observations for the HO$_x$ dilemma and ozone deficit problem.

2. Measurements and Model

The Aura MLS instrument measures OH at 2.5 THz and HO$_2$ at 643 GHz [Pickett, 2006]. Validation of MLS OH and HO$_2$ by comparison with balloon-borne remote sensing measurements of these species is described by Pickett et al. [2006].

The MLS profiles presented here are 15 day zonal averages, spanning 34 ± 10°N, centered on September 23 (fall) and December 23, 2004 (winter) as well as March 15 (spring) and June 15, 2005 (summer), based on version 1.51 of the retrieval software. The local solar time (LST) of the observations is ~13:30 hr. MLS observations of OH, HO$_2$, HO$_x$, and HO$_2$/OH are shown in Figure 1. Here, we only consider data below 60 km, because above 60 km only observations of OH are available [Pickett et al., 2006]. Precision in the 15 day averages for OH and HO$_x$ is good with negligible uncertainty. The error bars in Figures 1a and 1b are equal to 10%, which represents our estimate of the uncertainty in instrument calibration (i.e., measurement accuracy) [Pickett et al., 2006]. Raw MLS HO$_2$ profiles (not shown) exhibit oscillatory behavior that is likely a retrieval artifact [Pickett et al., 2006]. This behavior will result in

![Figure 1.](image1.png)

**Figure 1.** (a) MLS OH profiles (red curve) for four seasons and model results for JPL02 kinetics, “MdlJPL02” (solid black line), Smith and Stewart [1994] rate for O+OH, “MdlSmSt” (dash-dotted blue line), Smith and Stewart [1994] rate for O+OH and a 20% increase to OH+HO$_2$, “MdlC” (see text) (dashed black line), FIRS-2 observations from Sept 23, 2004 (green curve, data fit to assumed profile shape above float altitude indicated by green dotted curve) are also shown. (b) Same as Figure 1a except for HO$_2$; (c) same as Figure 1a except for HO$_x$; (d) same as Figure 1a except for HO$_2$/OH.

![Figure 2.](image2.png)

**Figure 2.** O+OH reaction rate from JPL02 (black line) and from Smith and Stewart [1994] (blue line). Black dotted curves denote uncertainties from JPL02.
Reduced chi-square ($\chi^2_r$) values significantly greater than 1 even for a model that simulates quite well the overall shape and magnitude of HO$_x$ species. To avoid this situation, we have smoothed the raw MLS profiles of HO$_2$ using a boxcar average (see auxiliary material) to arrive at the HO$_2$ profiles used throughout.

Observations from FIRS-2 were taken by a thermal emission far-infrared Fourier transform spectrometer [Jucks et al., 1998] on board a balloon gondola launched from Ft. Sumner, NM (34.5°N, 104°W) on September 23, 2004. These profiles are from $\sim$1 hour limb scans. Seven profiles, taken over the course of the day (7:30–17:00 LST), are used for statistical comparison. We consider all data below the balloon float altitude (38 km) and three points above (42, 44 and 48 km) to account for the poorer vertical resolution above float. The OH and HO$_2$ error bars are the root sum squared (RSS) combination of 1σ estimates of accuracy and precision. Error bars for both HO$_2$ and HO$_2$/OH shown in Figures 1c and 1d are the RSS propagation of the errors in OH and HO$_2$ from the respective instruments.

The photochemical model is constrained by MLS measurements of H$_2$O, O$_3$, N$_2$O, CO, and temperature for each season. The model assumes a balance of production and loss for each species integrated over 24 hrs and has been used in previous studies to analyze observations from balloon, satellite, and aircraft platforms [e.g., Pickett et al., 2006, Jucks et al., 1998]. Profiles of Cl$_3$, NO$_3$, and CH$_4$ are specified using well established tracer-tracer relations [Jucks et al., 1998]. The model includes mesospheric chemistry and solar cycle effects, a new feature described in the auxiliary material of Pickett et al. [2006].

We show model results for several sets of kinetic parameters: those for JPL02 kinetics [Sander et al., 2003] (hereinafter referred to as MDL$_\text{JPL02}$); those similar to JPL02 except the Smith and Stewart [1994] (hereinafter referred to as SMST94) rate constant for O+OH (MDL$_\text{SMST}$); those similar to MDL$_\text{SMST}$, except a 20% increase in the rate of HO$_2$+OH (MDLC). The SMST94 rate constant for O+OH is $\sim$20% faster than the JPL02 rate and is within the JPL02 uncertainty (Figure 2). The suggested increase in the rate of O+OH is consistent with Jucks et al. [1998], who suggested a reduction in k(O+OH)/k(O+OH). Two recent laboratory studies of the O+OH rate constant that report contrasting results, published as our work was being completed, are discussed in the auxiliary material.

### 3. Results and Discussion

The MLS OH profiles (Figure 1a) all peak near 45 km. Differences in peak values are due to seasonal changes in solar declination. The MLS OH observations and MDL$_\text{JPL02}$ calculations result in $\chi^2_r = 12.3$, between 25–60 km and considering all seasons (see auxiliary material for description of $\chi^2_r$; a value of 1 indicates that model profiles generally lie within measurement uncertainty). MDL$_\text{JPL02}$ overestimates observed OH between 40–60 km, often outside of the measurement uncertainty. Better agreement between modeled and measured OH is achieved for MDL$_\text{SMST}$. This comparison results in a $\chi^2_r = 3.1$ for OH. Results for MDLc, described below, lead to a $\chi^2_r = 1.6$ (Figure 3). The good agreement between measured OH profiles and the MDLc simulation at all altitudes and seasons indicates that MLS observations do not exhibit a “HO$_x$ dilemma” as reported by Conway et al. [2000] for MAHRSI observations of OH.

The closest FIRS-2 observations in time (LST = 13.6 h) to the MLS overpass are shown in Figure 1a. The $\chi^2$ between FIRS-2 observations of OH and the three model cases are larger than for the MLS comparison. The $\chi^2$ values for FIRS-2 are 16.7 for MDL$_\text{JPL02}$, 11.8 for MDL$_\text{SMST}$, and 10.7 for MDLc (Figure 4; profiles at seven times have been used to calculate $\chi^2$, as described above). These larger values are due to the influence of the higher altitude measurements of OH, which are much smaller than model values. The sense of the discrepancies between FIRS-2 OH and the MDLc calculation for September 2004 at various altitudes is the same as noted by Conway et al. [2000]. However, the FIRS-2 discrepancies are smaller, particularly near 40 km. The MDLc simulation provides a reasonably good description of the shape and abundance of the FIRS-2 OH profile. Hence, the FIRS-2 observations are also not consistent with a HO$_x$ dilemma.

Figure 1b shows comparisons of measured and modeled HO$_2$. MDL$_\text{JPL02}$ overestimates MLS OH$_2$ mainly below 40 km, resulting in a $\chi^2_r = 2.9$. In contrast to the comparison for OH, MDL$_\text{SMST}$ results in a slightly higher value of $\chi^2_r$ (4.1) than MDL$_\text{JPL02}$. Best agreement with MLS OH$_2$ is achieved by MDLc, with $\chi^2_r = 1.7$. The HO$_2$ profile
measured by FIRS-2 is generally higher than observed by MLS (Figure 1b). All three models give excellent agreement with FIRS-2 HOx (Figure 4).

[16] We have determined, through a series of sensitivity studies, that a reasonably good overall description of measured OH, HO2, HOx, and HOx/OH is achieved using MdlC, which includes a 20% increase in (1) and the SmSt94 rate for O+OH. Profiles of total HOx and HOx partitioning from MLS and FIRS-2 are shown in Figures 1c and 1d. Best agreement between measured and modeled MLS HOx is found for MdlC, with a $\chi^2 = 3.0$ (Figure 3). For HOx partitioning (e.g., HO2/OH) measured by MLS and FIRS-2, the two simulations using the SmSt94 rate for O+OH result in slightly better agreement compared to MdlJPL02 (Figures 3 and 4). Considering the suite of model and measured OH, HO2, HOx, and HOx partitioning, represented by “Total” in Figures 3 and 4, MdlC kinetics leads to the best overall simulations for both the MLS ($\chi^2 = 2.3$) and FIRS-2 ($\chi^2 = 7.5$) data sets.

[17] If we use the JPL02 rate for O+OH, no simple change to the rate of HO2+OH improves the simulation of both MLS OH and HOx in a manner comparable to MdlC kinetics. Likewise, it is difficult to reconcile the observations and model results considering only uncertainty in the O+OH rate. The range of model calculations based on the JPL02 uncertainty in O+OH is given in the auxiliary material.

4. Ozone Deficit Problem

[18] Calculated (O3) production (P) and loss (L) rates during Fall 2004, for the three model runs, are shown in Figure 5. Production is the same for all cases because model O3 has been constrained to the daytime MLS profile. Calculated L exceeds P throughout the upper stratosphere and lower mesosphere, consistent with an ozone deficit problem.

[19] Introduction of the SmSt94 rate for O+OH leads to an increase in calculated HO2 compared to MdlJPL02. This increased HO2 results in larger L-P compared to MdlJPL02 because O+HO2 is a rate determining step of Ox loss. The MdlC simulation results in a value of L-P that is intermediate between the other two simulations above 50 km: the increase in HO2+OH results in lower HOx and hence slower O3 loss by all HOx cycles compared to the MdlSmSt simulation. A 50% reduction in the rate of O+HO2 results in balance of P and L near 40 km, as suggested by Summers et al. [1997], but leads to poorer agreement with MLS and FIRS-2 HOx profiles compared to the other simulations shown above (see auxiliary material).

[20] There have been many suggestions in the literature regarding possible resolutions to the HOx dilemma and the O3 deficit problem. It has been suggested that reactions involving vibrationally excited O2 (v > 26) + O2 could solve the ozone deficit problem by providing an autocatalytic source of O3 [Miller et al., 1994]. However, Slainger and Copeland [2003] question the existence of this reactive pathway. Varandas [2004] suggested reactions involving vibrationally excited O2 and OH could be important for both the HOx dilemma and the O3 deficit problem. However, Smith and Copeland [2005] have raised doubts regarding the suggestion of Varandas [2004]. Our observations and simulations, taken at face value, suggest a continued need to resolve the ozone deficit problem without recourse to major perturbations in the kinetic parameters that regulate HOx.

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References

Smith, I. W. M., and D. W. A. Stewart (1994), Low temperature kinetics of reactions between neutral free radicals: Rate constants for the reactions of OH radicals with N atoms (103 $\leq$ T/K $\leq$ 294) and with O atoms (158 $\leq$ T/K $\leq$ 294), J. Chem. Soc. Faraday Trans., 90(21), 3221 – 3227.


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