Satellite measurements of OH and HO$_2$ obtained by the Aura MLS instrument are compared to the balloon-borne BOH and FIRS-2 instruments. All measurements are also compared with constrained photochemical model calculations. On average, both balloon measurements of OH agree with MLS within 17% over 25–40 km and the measurements agree with the model within 12%. The three measurements for column of OH above 40 km agree within 8% and the mean is 12% below the model. Measurements of HO$_2$ from FIRS-2 and MLS agree on average within 23% over 25–40 km and the differences are generally within the experimental precision. The HO$_2$ measurements agree with the model within 14%. Measurements of HO$_2$ for the column over 40–60 km agree within 16% and the mean measured column agrees with the model within the experimental precision. Our observations do not appear to indicate a “HO$_x$ dilemma.”

1. Introduction

The Aura satellite was launched on July 15, 2004 into a sun-synchronous near-polar orbit. The Microwave Limb Sounder (MLS) instrument on the Aura satellite has the capability to measure OH and HO$_2$ in both day and night [Waters et al., submitted]. Further details on the THz module and the OH measurement and calibration are given in Pickett [submitted]. Early validation of other molecules measured by MLS are given in Froidevaux et al. [submitted]. Version 1.51 of the retrieval software was used in this paper.

The Balloon OH instrument (BOH) and Far Infrared Spectrometer (FIRS-2) instrument were launched on a common balloon gondola on September 23, 2004, from Ft. Sumner, NM (latitude = 34.5° and longitude = −104°) and stayed aloft at ~38 km for nearly 24 hours. The BOH instrument is a heterodyne limb-viewing thermal emission instrument that is functionally identical to the THz module on MLS [Pickett, submitted] and only measures OH. The FIRS-2 instrument is a thermal emission far-infrared Fourier transform spectrometer developed at the Smithsonian Astrophysical Observatory [Jucks et al., 1998]. It measures OH and HO$_2$ in the far infrared using multiple lines.

Odd hydrogen (HO$_x$=OH+HO$_2$+H) chemistry domi-
nates ozone destruction above 40 km and below 25 km. Previous observations of OH over 40–80 km from MAHRSI [Conway et al., 2000] are not consistent with current chemical models, leading to the designation “HOx dilemma.” However, previous FIRS-2 observations that are mostly sensitive to HOx below 40 km agree better with standard photochemistry [Jucks et al., 1998].

2. Measurements and Model

Since the Aura orbit is sun-synchronous, the local solar time (LST) and solar zenith angle (SZA) are nearly the same for each orbit on a given day. However, successive overpasses have a change in longitude of −24.7°. The MLS retrieval position at 34°N latitude on Sept. 23, 2004 had LST = 13.46 hr and SZA = 38.92° for the daytime ascending overpass. The night descending overpass has LST = 2.20 hr and SZA = 135.1°. MLS OH profiles are available at 1.5° intervals along each orbit for altitudes of 22-90 km. The MLS precision for HO2 and for OH below 35 km is poorer. To obtain better precision, MLS HO2 and OH profiles were zonally averaged over a latitude interval of 20° for a period of 15 days centered on the balloon-flight day.

The BOH and FIRS-2 instruments can spend more time acquiring data because they are localized in latitude and longitude. The BOH instrument scans the limb in 15 seconds, and calibrated radiances averaged for 20–30 minutes are used for the retrieval. The FIRS-2 instrument takes 70 minutes to scan the limb. For direct comparisons with MLS, we use the scans closest to the overpass in LST. For altitudes less than that of the balloon, both balloon-borne instruments obtain profiles in limb-sounding mode with a height resolution of 3–6 km. Above the balloon altitude, both instruments lose the limb sounding path-length advantage. In addition, there is little spectral information in the radiance because the line shape is essentially Doppler-limited above 45 km. In addition, the OH lines are optically thick at noon and the foreground OH tends to mask the OH above 60 km. For both instruments we assume a profile for OH or HO2 above the balloon and then scale it to bring the calculated radiance into agreement with observation. The FIRS-2 instrument uses a diurnally-varying model calculation and the BOH instrument uses a noon MLS OH profile. Despite these differences, both instruments are sensitive to the column density above the balloon.

The MLS and balloon-borne vertical resolution is approximately equal but there are significant differences in the horizontal footprint. In all three instruments, the horizontal resolution perpendicular to the boresight is comparable to the vertical resolution (≈3 km). The horizontal footprint along the line of sight is based on the limb sounding geometry (400 km for 3 km height resolution). For MLS, the boresight at 34°N latitude has a horizontal heading of 350° for the ascending overpass. The balloon-borne instruments look out at a common azimuth angle (east at the time of the Aura daytime overpass). Therefore, the footprint is comparable in size, but the orientation can be quite different. In addition, the MLS footprint position does not change with altitude, while the balloon-instrument footprint position varies with height by as much as 470 km.

The photochemical model employed here has been used previously to interpret data from aircraft, satellite, and balloon platforms [Jucks et al., 1998 and references therein]. In the present analysis, the model is constrained
by MLS measurements of $[O_3]$, $[H_2O]$, $[Cl_2]$, $[NOy]$, $[N_2O]$ (to infer $[CH_4]$), and temperature in the stratosphere and lower mesosphere (see auxiliary material\(^1\)). Currently, MLS $H_2O$ profiles gradually revert to climatology above 60 km. Since there is diurnal variability of ozone, either daytime averages of $[O_3]$ were used or $[O_3]$ is unconstrained (see Figure 3). To improve the mesospheric capabilities of the model, Lyman-\(\alpha\) photochemistry is sampled at 16 wavelengths over the solar Doppler profile \([Chabrillat and Kockarts, 1997]\) using the $O^1D$ yields of \textit{Lacoursiere et al.} \textit{[1999]}. All other kinetics are from \textit{Sander et al.} \textit{[2002]}. During the 15-day averaging period needed for HO$_2$ and low-altitude OH, the $H_2O$ and $O_3$ concentrations were remarkably stable. The model was constrained to the average MLS values. The grey shading in Figures 1, 4, and 5 shows the range of concentrations that correspond to the 20° range of latitudes (and corresponding SZA values) used in the average.

In Figures 1–5, the error bars for all measurements are 1σ estimates of precision for the average displayed. In the lower panel of Figure 1, we inflate the MLS errors to 10% to account for uncertainties in instrument calibration (since the precision in the 15-day average above 35 km is very small). In Figures 1 and 4, the right panels are the percent difference of measurement minus model divided by the model. The balloon-borne instruments are only sensitive to a single column-like quantity above 40 km. Accordingly, the assumed profiles are shown as a dotted line without error bars.

Figure 1 shows the OH altitude profiles in number density near 13.5 hr LST. The nearest FIRS-2 averages were at 13.6 hr LST. The nearest BOH profile had a mean LST = 13.7 hr for altitudes above the balloon, decreasing to 13.4 hr at a tangent of 22 km. The averaging time for this BOH profile is 29 minutes. In the upper panel, MLS OH profiles were averaged over a 5° interval centered on 34N latitude and a longitude range of −122° to −72°. This average represents only 2 minutes of satellite observation time. The lower panel shows the effect of averaging for 15 days centered on the balloon day. The MLS OH values for the 15-day average are daytime values above 32 km and day–night differences below.

The two panels in Figure 1 show the same balloon-borne data compared with a MLS local 1-day average (upper) and the 15-day average (lower). For the 1-day average, the overlap with the balloon instrument profiles is useful over 35–40 km and the differences between the balloon-borne instruments and MLS have an average absolute deviation (AAD) of 15%. Between 25–35 km, where MLS profiles must be zonally averaged over 15 days, the differences have an AAD of 19%. Combining the two ranges, the AAD over 25–40 km is 17%. The AAD between the measurement and the model over 25–40 km is 12%, and deviations are within measurement precision. The sharp dip at 65 km in the MLS data may be a retrieval artifact due to a change in scan speeds at this altitude. In addition, the MLS OH becomes negative above 80 km. The line marked ‘MLS’ in Figure 1 is changed to a dashed line above 64 km to highlight these potential systematic errors. We intend to have these retrieval issues resolved in the next version of the software, but the OH column above 60 km is not likely to change.

Figure 2 shows the diurnal variability of OH density. The altitudes shown are MLS sample points near the mean balloon altitude and one scale height below. The plots show good agreement between model and experiment in the afternoon and night. On this balloon flight, the gondola azimuth pointing system suffered an elec-
tronics failure at 2.5 hr LST on 24 Sept. 2004 and there-
after the gondola rotated freely until flight termination at
10 hr LST. The data for this time period are indicated by
open symbols and should be viewed with some caution.

Figure 3 shows the diurnal variability of the column
over 40–80 km. This column is an approximate measure
of OH observed by FIRS-2 and BOH above the balloon
altitude. The column near 13.5 hr LST shows a differ-
ence of 12% between BOH and MLS and a difference of
4.5% between FIRS-2 and MLS. These columns are an
independent validation of MLS OH measurements above
40 km. The dashed line in Figure 3 indicates the standard
model run in which O$_3$ is constrained to MLS daytime
values (MODEL MLS), while the solid line indicates a
model run in which O$_3$ is unconstrained (MODEL CALC.
O$_3$). The difference between these curves indicates the
sensitivity to O$_3$ above 40 km. The constrained model
is 12% higher than the mean column for the three mea-
surements.

Figure 4 shows the HO$_2$ density profiles near 13.5 hr
LST. Figure 5 shows HO$_2$ diurnal variability at two alti-
tudes. As described above, the MLS data are an average
of 15 days centered on the flight day. The MLS data
shown in both figures are a day–night difference. The
dashed line indicates a model run constrained by FIRS-2
SZA and concentrations of O$_3$, H$_2$O, etc. (see auxiliary
material), and the grey area indicates the range of model
runs for the MLS latitude average. The plots show an
AAD of 23% over 25–40 km for the differences between
FIRS-2 and MLS, well within the combined experimental
uncertainties. We are investigating whether the altitude
oscillation seen in Figure 4 for MLS HO$_2$ is a retrieval
artifact.

The HO$_2$ columns over 40–60 km are shown in Table
1. Column HO$_2$ measured by MLS is 16±12% (1 σ pre-
cision) smaller than that measured by FIRS-2. The MLS
column is 4±7% larger than its model, and the FIRS-2
column is 19±10% larger than its model, a difference of
less than 2σ.

3. Conclusions

Densities of OH obtained from the balloon-borne BOH
and FIRS-2 instruments agree with MLS on average with
an AAD of 17% over 25–40 km and agree with the model
with an AAD 12%. Columns of OH above 40 km agree
among themselves within 8% and are less than the model
by 12%. Measurements of HO$_2$ below 40 km from FIRS-2
and MLS agree with an AAD of 23%. Agreement between
model and measured HO$_2$ is 18% over 25–40 km and is
limited by the experimental precision. The HO$_2$ column
measurements over 40–60 km agree within 15%. MLS
and FIRS-2 HO$_2$ columns agree with the model within
experimental precision.

Earlier measurements of OH from MAHRSI were
shown to be 20% higher than calculated values near the
OH peak at 45 km and about 25–35% lower than calcu-
lated values over 50–70 km [Conway et al., 2000]. These
differences were termed the “HO$_x$ dilemma” because cer-
tain changes in model kinetics, such as variations to the
rate constants of the reactions O+OH, O+HO$_2$, and
OH+HO$_2$ (within laboratory uncertainties), will lead to
better agreement between measured and modeled OH for
one altitude region (e.g., 50–75 km) but will worsen the
agreement in the other height region (e.g., near 45 km)
[Conway et al., 2000]. Our calculations of OH are close
to those reported by the MAHRSI group, for the same
model constraints [Jucks et al., 1998].

In contrast to the MAHRSI measurements, MLS measurements of OH are about 10% lower than model values at the 45 km OH peak. The OH profile measured by MLS for 50–60 km is in better agreement with the model than found for similar comparisons using MAHRSI OH, but nonetheless MLS OH is systematically lower than model OH by 10–25%. The differences between MLS measured and modeled mesospheric OH below 64 km could likely be explained by variations in the rate constants for O+OH, O+HO₂, and/or OH+HO₂ that are well within the laboratory uncertainties [Sander et al., 2002]. The differences between observed and modeled HO₂ place important additional constraints on such perturbations. Regardless, the MLS measurements of OH for Sept. 2004 at mid-latitudes do not present a “dilemma” in the sense of the MAHRSI OH observations because kinetics changes required to bring measured and modeled OH into closer agreement for the mesosphere will not prevent agreement, within measurement uncertainties, from also being obtained near 40 km altitude.

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Notes

References

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Table 1. \( \text{HO}_2 \) Column over 40–60 km near 13.5 hr LST.

<table>
<thead>
<tr>
<th>Source</th>
<th>Column ( (10^{13} \text{cm}^{-2}) )</th>
</tr>
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<tr>
<td>MLS</td>
<td>1.86 ± 0.13</td>
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<td>MLS model</td>
<td>1.79</td>
</tr>
<tr>
<td>FIRS-2</td>
<td>2.21 ± 0.18</td>
</tr>
<tr>
<td>FIRS-2 model</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Figure 1. OH altitude profiles near 13.5 hr LST. The lower panel displays an average of MLS OH for 15 days centered on the balloon-flight day, over a 20° latitude range. For reference, balloon-borne measurements are duplicated in the lower panel. The model denoted by the dashed line uses MLS constraints for 23 Sept. 2004, while the shaded region denotes a model range for the MLS 15-day average.
Figure 2. OH diurnal behavior: upper panel is number density for 37 km and lower panel is for 31.6 km. Data collected after the azimuth pointing system failure is indicated by open symbols.

Figure 3. Same as Figure 2, for column from 40 to 80 km. Two model values are shown, as described in the text.
Figure 4. HO₂ profile near 13.5 hr LST. MLS data is an average of 15 days centered on the balloon-flight day. The model denoted by the dashed line uses FIRS-2 constraints and conditions, while the shaded region denotes a model range for the MLS 15-day average.

Figure 5. HO₂ diurnal behavior: See Figure 2.