Satellite observations of high nighttime ozone at the equatorial mesopause

Anne K. Smith,1 Daniel R. Marsh,1 James M. Russell III,2 Martin G. Mlynczak,3 F. Javier Martin-Torres,4,5 and Erkki Kyrolä6

Received 4 March 2008; revised 11 June 2008; accepted 20 June 2008; published 10 September 2008.

1. Introduction

[2] Measurements by the Sounding of the Atmosphere using Broadband Emission Radiometry instrument enable the characterization of the seasonal variation of ozone and temperature in the upper mesosphere. These are the first global measurements that resolve both the structure of the secondary ozone maximum at night and the temperature over all seasons of the year. The average nighttime mixing ratios at the altitude of the maximum vary with latitude and season. Analysis shows that the highest mixing ratios are clustered near the equator during equinoxes. The high ozone mixing ratios are observed in exactly the place and time at which the diurnal tide is largest. The diurnal tidal phase is such that coldest temperatures at 95 km occur near midnight. The high ozone is coincident with regions that have both low temperature and low amounts of atomic hydrogen. We focus particularly on ozone mixing ratios in the range of 18–50 ppmv; these occur intermittently in the equinoctial tropics on days when the night temperature is particularly cold. The occurrence of ozone maxima over 20 ppmv was unexpected but is shown in this paper to be consistent with theory and is a result of large-amplitude diurnal tides. The same seasonal and latitudinal characteristics are seen in ozone density measured by Global Ozone Monitoring by Occultation of Stars.

and Dynamics (TIMED) satellite. SABER ozone profiles for day and night often extend into the lower thermosphere (over 100 km). The SABER data record begins on 25 January 2002; data collection is ongoing as of 2008. TIMED is in a precessing orbit so makes measurements spanning nearly all local times every 60 days. Version 1.07 of the SABER retrieval and processing is used.

There are few other measurements for comparison and validation of nighttime ozone above 90–95 km. This paper includes comparisons of nighttime densities with those from GOMOS. In addition to validation by comparison with these measurements, self-consistency tests can be used to determine whether the data fit with other measurements from SABER and with our understanding of ozone chemistry. Three other SABER measurements are particularly useful: the temperature, which is very important in the photochemistry; the Meinel emissions from vibrationally excited hydroxyl, which depend ultimately on the production rate of ozone; and daytime ozone determined using an independent radiance measurement and different retrieval algorithm.

In this paper we look at one aspect of the SABER ozone: the occurrence of profiles with relatively high mixing ratios in the tropics at certain times of year. As inferred from the comparisons and from uncertainties in some of the physical parameters needed in the retrieval, there is still some uncertainty about the absolute magnitude of the ozone at the mesopause. The temporal and spatial distribution of high nighttime ozone is quite similar in GOMOS densities even though the magnitudes are different. We argue that the existence of high values is plausible and that the variation in ozone mixing ratio at the mesopause is consistent with other SABER measurements and with current theory.

2. Data and Processing

2.1. SABER Data

SABER uses two independent techniques, emission from molecular oxygen and emission from ozone itself, for determining ozone profiles in the mesosphere and lower thermosphere. The 1.27 µm emission from O\(_2\)(\(^{1}\Delta\)) is used for the determination of daytime ozone since the primary source of this emission feature is the photolysis in the Hartley band of ozone. Measurements of this emission during a rocket experiment were used by Evans and Llewellyn [1972] to determine mesospheric ozone. Measurements of O\(_2\)(\(^{1}\Delta\)) by the Solar-Mesosphere Explorer (SME) satellite were used to determine global ozone distributions in the mesosphere [Thomas et al., 1984]. Due to the SME orbit, these observations were made at a fixed local time in the afternoon. The retrieval of ozone from 1.27 µm emission relies on the assumption of photochemical equilibrium between the O\(_2\)(\(^{1}\Delta\)) molecule and the ozone abundance. However, the radiative lifetime of O\(_2\)(\(^{1}\Delta\)) is about 75 minutes. Ozone profiles retrieved from measurements of O\(_2\)(\(^{1}\Delta\)) 2–3 hours after sunrise, or in the presence of strong dynamical events, may contain systematic errors because of the lag time between the O\(_2\) emission and the changing ozone abundance [e.g., Zhu et al., 2007].

Mlynczak et al. [2007] describe the algorithm used to derive ozone from O\(_2\)(\(^{1}\Delta\)) for the SABER data.

The emission from ozone itself in the strong 9.6 µm bands provides a method for observing ozone both day and night as the origin of this emission is thermal in nature. As with the 1.27 µm emission, the 9.6 µm bands depart from local thermodynamic equilibrium (LTE) in the mesosphere and lower thermosphere. The SABER v1.07 ozone 9.6 µm retrieval incorporates a detailed non-LTE model originally developed by Mlynczak and Drayson [1990a, 1990b], updated with collisional rates from Martin-Torres [1999]. Rate coefficients for the quenching of ozone vibrations and molecular oxygen and molecular nitrogen for all temperatures are used in the formula for temperature dependence deduced from measurements by Doyennette et al. [1992] and Menard et al. [1992]. Quenching of ozone vibrations by atomic oxygen incorporates the only extant measures of this rate from West et al. [1976]. In version 1.07, the atomic oxygen profiles used in the ozone retrieval are taken from the NRL-MSIS model [Picone et al., 2002] for the appropriate conditions. Note that this will not include the variations of atomic oxygen with large-amplitude diurnal tides, which, as shown in section 5, can be appreciable. A total of 133 vibrational states are included in the non-LTE model. Chemical pumping, quenching and excitation by collisions, radiative emission, radiative absorption, photolysis, and chemical reaction of ozone vibrations are included. A paper on the validation of SABER ozone in the non-LTE region (Martin-Torres et al., manuscript in preparation, 2008) will be submitted shortly. Rong et al. (E. E. Rong et al., Validation of TIMED/SABER v1.07 ozone at 9.6 µm in altitude range 15–70 km, submitted to Journal of Geophysical Research, 2008) describe the LTE determination of SABER ozone in the stratosphere and lower mesosphere (below 65 km).

In the SABER v1.07 data set the offset between the mean mixing ratios of ozone derived in the daytime from the 1.27 µm and 9.6 µm radiances are smaller than in previous versions of the data and are usually within the error bars of the two retrievals. The differences vary with altitude, latitude, season, and local time; details are given in Martin-Torres et al. (manuscript in preparation, 2008).

The vertical resolution of SABER 9.6 µm ozone is about 2 km. Radiance measurements are made at higher resolution so that the full vertical resolution can be achieved.

At the altitudes under consideration in this paper, signal-to-noise is an issue. For the 9.6 µm emission the general decrease in ozone with altitude results in a lower radiance signal. For the 1.27 µm emission, photolysis of O\(_2\) becomes competitive with ozone photolysis at about 92 km, and rapidly becomes the dominant source of O\(_2\)(\(^{1}\Delta\)) at higher altitudes. There is also substantial geophysical variability in this region over time. In particular, the diurnal tides at the equator may contribute to alternating positive and negative biases [Zhu et al., 2007] that cause a vertical offset between the equilibrium ozone and the true ozone. Although averaging large amounts of data is a standard practice for increasing confidence when the signal to noise is low, that is not the approach used in this paper. Instead, we consider individual profiles but look for common patterns in the ozone concentration and we use physical arguments to support our contentions that the patterns we see are real. We note that the signals in ozone that we focus
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Figure 1. Histogram showing mixing ratios of SABER ozone from the version 1.07 data archives. The bottom axis is the mixing ratio in 1 ppmv bins. The color indicates how many times the mixing ratio fell into a particular bin during the years 2002–2007. One percent of the values fall above the dashed line and 0.1% fall above the solid black line.

2.2. Screening SABER Data to Remove Outliers

We also use SABER temperature and OH emissions at 2.0 μm from version 1.07, Level 2A of the operational SABER data set. The non-LTE inversion of the CO$_2$ infrared emissions to obtain temperature and comparisons with other data are given by Remsberg et al. [2004, 2008], Kutepov et al. [2006], Oberheide et al. [2006a], and Remsberg et al. [2008]. Validation of the OH volume emission rate (VER) through comparisons with other data is pending.

2.3. Comparison of SABER and GOMOS Nighttime Ozone Density in the Upper Mesosphere

This comparison uses GOMOS data from August 2002 to early 2005, spanning more than 2 years. In February 2005, a technical problem led to a shut down for several months; data collection then resumed but with fewer profiles per day. Since GOMOS does not measure temperature, it is not possible to determine the background atmospheric density needed to convert the profiles to units of mixing ratio. This also means that it is not possible to determine the pressure as a function of altitude. Therefore the comparisons of SABER and GOMOS data use ozone density on altitude levels. The geometric altitudes of data points along the SABER profiles are known to within a few hundred meters. The altitude determination makes use of the simultaneous temperature profiles and the hydrostatic approximation, along with a tie-on to National Center for Environmental Prediction (NCEP) height data in the stratosphere. The ozone can be expressed in either mixing ratio or density through application of the ideal gas law. Screening of the SABER densities to remove outliers uses a similar criterion to that used for mixing ratio, that is, discarding the highest 0.1% of the data. The density screening is applied to both the top 0.1% and the bottom 0.1%. The limits determined in this way from SABER are applied to both the SABER and the GOMOS density profiles. Tests indicate that determining the screening limits for GOMOS from the GOMOS profiles rather than those of SABER has virtually no impact on the comparisons.

In addition to the screening described above, data from the occultation of stars that are not suitable for ozone determination are eliminated. To avoid possible problems with scattered light, data near the dawn/dusk terminator are discarded by applying a solar zenith angle cutoff of 108°. Following Kyrölä et al. [2006], we eliminate profiles from stars that have both a temperature of less than 7000 K and a magnitude greater than 1.9 (i.e., stars that are both cool and have low magnitude). In addition, based on the “GOMOS Product Handbook” (http://envisat.esa.int/handbooks/gomos/CNTR.htm), we eliminate data from all stars with temperature less than 6000 K and with occultation obliquity greater than 10°. Noise in the GOMOS inversion can give rise to negative ozone densities. To avoid biasing the averages toward higher values, we consider negative as well as positive densities. The negative outliers are screened...
in a similar way to the positive ones. The SABER retrieval does not produce negative values, which may account for some part of the offset between SABER and GOMOS above 95 km where the signal to noise ratio of SABER radiance is low. The lack of negative values in SABER may affect the averages and calculations of climatology but has no impact on the occurrence of the high ozone mixing ratios that are the subject of this paper.

[17] Because of the variable path that the stars make along the horizon, the vertical resolution of GOMOS profiles is variable. In addition, some profiles span a geographical area of more than 5° latitude and/or longitude. Therefore the data are collected into altitude bins but are not treated as a single profile. In other words, at each altitude the comparison could use a different SABER profile, based on the closest coincidence. The number of points to be compared with SABER will vary with altitude.

[18] At each altitude bin of a GOMOS profile, the SABER data for the same day are examined to see which, if any, SABER profiles satisfy the coincidence criteria of 5° latitude, 10° longitude and 0.5 hour local time. If there is more than one profile that satisfies this limit, the closest in geographical distance is chosen and comparisons made.

[19] Figure 2 shows the GOMOS versus SABER differences. More than 10,000 coincident profiles over a span of more than 28 months were used to make this figure. Above 85 km, the SABER inversion gives more ozone than does that of GOMOS. The differences are consistent when the data is subdivided into years or into latitude bands. Note in particular that the GOMOS average ozone density is lower than that from SABER by about 20% at 95 km, which is approximately the location of the nighttime secondary maximum in ozone mixing ratio. The GOMOS minimum density at 80 km is similar to but slightly shallower than that from SABER. These differences could be a result of the higher vertical resolution of the SABER data and/or could indicate a greater degree of smoothing in the GOMOS retrievals. Comparisons of GOMOS and MIPAS mesospheric ozone for two days were presented by Verronen et al. [2005]. The comparisons indicate that the MIPAS night ozone (which is, like \( R \), derived from the 9.6 \( \mu m \) ozone thermal emission) is higher than that of GOMOS at the location of the mesopause maximum and lower than that of GOMOS at the location of the minimum around 80 km. In fact, the comparison plots in their Figures 2 and 3 look remarkably similar to the SABER-GOMOS comparisons in Figure 2, even though theirs are given in terms of mixing ratio rather than density. Also note that the MIPAS vertical spacing in the upper mesosphere (5 km) is wider than those of both SABER (2 km) and GOMOS (3 km).

3. Photochemistry of Ozone at the Mesopause

[20] The photochemical equations that are relevant to understanding ozone variations in the upper mesosphere are

\[
\begin{align*}
O + O_2 + M &\rightarrow O_3^* + M & k_1 &= 6.0 \times 10^{-14} (300/T)^{2.4}, \\
H + O_3 &\rightarrow OH^* + O_2 & k_2 &= 1.4 \times 10^{-19} \exp(-470/T), \\
O + O_3 &\rightarrow O_2 + O_2 & k_3 &= 8.0 \times 10^{-12} \exp(-2060/T), \\
O_3 + h\nu &\rightarrow O_2^* + O & J_{O_3} \\
\end{align*}
\]

[21] The asterisks indicate that the product is, or sometimes is, in an excited state. Reaction rates are from (http://jpldataeval.jpl.nasa.gov; Evaluation Number 15). The rate for \( k_2 \) is not well known under mesospheric conditions because of the scarcity of laboratory measurements at the extremely low temperatures characteristic of the upper mesosphere. Ozone is close to photochemical equilibrium throughout the mesosphere. During night, the production through the associative reaction between atomic and molecular oxygen \((k_1)\) is approximately balanced by destruction through reaction with atomic hydrogen \((k_2)\). \( k_3 \) contributes about 10% to the nighttime ozone loss.

[22] In terms of volume mixing ratio [Smith and Marsh, 2005]

\[
\frac{d(O_3)}{dt} = k_1 \cdot O \cdot O_2 \cdot n^3 - (k_2 \cdot H + k_3 \cdot O) \cdot O_3 \cdot n^2 \approx 0
\]  

(1)

where \( n \) is number density. Equation (1) is set equal to zero because ozone is approximately in photochemical equilibrium. Even during night, when reaction times are slower than during the day, the ozone lifetime is normally less than a few 10s of minutes but varies with temperature and the concentration of atomic hydrogen. The ozone mixing ratio is then

\[
O_3 \approx \frac{k_1 \cdot O \cdot O_2 \cdot n}{k_2 \cdot H + k_3 \cdot O}
\]  

(2)

[23] The temperature dependence is such that ozone is produced more quickly \((k_1)\) and destroyed more slowly \((k_2\) and \( k_3 \)) when the temperature is colder. In addition, the number density on a pressure surface increases with decreasing temperature according to the ideal gas law \((n = p/kT)\), where \( p \) is pressure and \( k \) is Boltzmann’s constant. The combined effect of these temperature dependencies causes the well-known anticorrelation of ozone and temperature in the mesosphere.

[24] Atomic oxygen and hydrogen can also be determined from SABER using the measurement of Meinel bands
emission. The product of the reaction of ozone and hydrogen is $\textit{OH}^*$. 

$$P_{\textit{OH}^*} = \frac{k_2}{C_1} \cdot \frac{H}{C_2} \cdot \frac{O_3}{C_3} \cdot n^2$$  \hspace{1cm} (3)$$

where $P_{\textit{OH}^*}$ is the production rate of excited hydroxyl. From equations (1) and (3)

$$P_{\textit{OH}^*} = \frac{k_1}{C_1} \cdot \frac{O}{C_2} \cdot \frac{O_2}{C_3} \cdot n^3 - \frac{k_3}{C_3} \cdot \frac{O_3}{C_1} \cdot n^2$$  \hspace{1cm} (4)$$

$\textit{OH}^*$ gives rise to the $\textit{OH}$ Meinel bands emission also measured by SABER. The oxygen can be determined from equation (4) and the knowledge of the production rate of excited hydroxyl [McDade and Llewellyn, 1988]. With the additional information of the ozone amount, the oxygen determination is more accurate and the hydrogen can also be determined. This method, which is used to determine these species in SABER as a Level 2 product, has been described by Mlynczak et al. [1998] and Mlynczak [1999] and analyzed by Marsh et al. [2006].

$$H \approx \frac{P_{\textit{OH}^*}}{k_2 \cdot O_3 \cdot n^2}$$  \hspace{1cm} (5)$$

4. Observation of High Ozone Mixing Ratios

[25] In this paper, we use nighttime profiles of atomic oxygen and hydrogen calculated from equations (5) and (6). The calculation of $P_{\textit{OH}^*}$ from the observed emission involves iteration to account for the role of quenching of the $\textit{OH}$ vibrational levels by $O$. See Marsh et al. [2006] for details of the calculation.

[26] A scan of SABER ozone data for the upper mesosphere reveals that mixing ratios above 20 ppmv are not uncommon at the secondary maximum (Figure 1). In general, SABER is finding nighttime ozone amounts that are larger than previously believed. However, before SABER data are used to determine the climatology of nighttime ozone, we need to assess whether or not these unexpectedly large ozone concentrations are realistic.

[27] There could be some profiles with high values due to random noise or other inaccuracies. There may also be systematic errors due to inaccuracies in rates used in the retrieval. Since the density measured by SABER is higher.

![Figure 3.](image-url) Percent of all SABER night profiles for which the ozone mixing ratio is greater than 18 ppmv at $5.6 \times 10^{-4}$ hPa (about 96 km) for each year from 2002 to 2007.
than that measured by GOMOS, % and the daytime mixing ratio of the 9.6 μm ozone is higher than the %1.27 μm, it is possible that the 9.6 μm ozone is too high by 10–20% or so. We do not want to put too much emphasis on the overall absolute magnitude but rather to examine the cases with higher ozone for consistency with the other SABER measurements and with our theoretical understanding of ozone chemistry.

Further examination of the data after the outliers have been eliminated from consideration reveals that the profiles with the highest concentrations are clustered in space and time. In particular, they occur near the equator around equinoxes. Figure 3 shows the percentage of occurrence of profiles at 5.6 × 10⁻⁴ hPa (about 96 km) during 2002–2007 that have a vmr greater than 18 ppmv but less than the cap described in section 2.2. A similar plot but using a 99% cutoff for outliers (see Figure 1 and discussion of it) is almost identical. Figure 4 shows a similar distribution of high density values from GOMOS; note that the units are different. The cases are clustered around the equator and are mostly confined to periods near equinoxes. The latitude and seasonal distribution suggests that the large ozone values are associated with the diurnal tide. The magnitude of temperature and vertical velocity variations associated with the dominant mode of the migrating diurnal tide is greatest near the equator. Both ground-based and space observations show a strong enhancement of diurnal tide amplitude around the equinoxes [e.g., Zhang et al., 2006]. Level 1 SABER data of the radiance from the 9.6 μm channel (not shown) also indicates much higher values in the upper mesosphere that coincide with the high retrieved ozone mixing ratios.

Figure 4. Percent of all GOMOS night profiles for which the ozone density is greater than 0.3 × 10⁻⁹/cm³ at 96 km for 2003 and 2004.

The phase of the migrating diurnal tide in SABER temperature at the level shown in Figure 3 is such that the maximum is approximately at noon [e.g., Zhang et al., 2006; Xu et al., 2007] so the coldest temperatures are found near midnight. The temperature minimum occurs roughly 1/4 period (6 hours, for the diurnal tide) after the hour of maximum vertical motion. Diurnal minima in trace species with positive vertical mixing ratio gradients and lifetimes longer than a day will occur simultaneously with the temperature minimum. Since the mixing ratio of atomic oxygen increases with altitude, it will have a diurnal variations similar to that of temperature in areas where tidal dynamics dominate. Atomic hydrogen also has a positive mixing ratio gradient and is affected by transport but its lifetime is shorter and its variation is also influenced by diurnally varying photochemistry and reaction with ozone.

Equation (2) indicates that there will be less ozone where the temperature is higher or the hydrogen concentration is higher and there will be more ozone where the atomic oxygen concentration is higher. However, it is also the case that, under conditions of vertical transport, temperature and atomic oxygen are positively correlated. Higher temperature (implies lower ozone) is expected to be positively correlated with higher atomic oxygen (implies higher ozone). Clearly the ozone variation cannot simultaneously satisfy both of these expectations. We look now at the relationship of ozone with temperature, hydrogen, and atomic oxygen to see which of these variable fields has the dominant effect on ozone.

Figure 5 shows histograms of the relative frequencies of numerical values in four fields against the ozone mixing ratio at 5.6 × 10⁻⁴ hPa (~96 km) based on six years of SABER data (all latitudes). Figure 5a indicates that the high ozone values are associated with low temperatures. Likewise, Figure 5b indicates that the high ozone is associated with low hydrogen. Either temperature or hydrogen individually “predicts” the occurrences of ozone maxima since both low T and low H directly contribute to higher nighttime ozone. From Figure 5c, it is evident that atomic oxygen by itself is not able to predict the occurrence of high ozone values; instead, oxygen is low whenever ozone is high. Figure 5d shows the relationship between the ozone and VER from the Meinel 2 μm emission and has been included to demonstrate that there is a consistent pattern between these two independently measured fields even though, at the altitude of the data shown, the OH Meinel emission is weak compared to its maximum at about 87 km.

Referring to equation (2), but neglecting the loss of ozone due to reaction with atomic oxygen (reaction kₜ), the equilibrium ozone varies according to the ratio of O to H. Since both have similar diurnal variations due to tidal transport, there is some cancellation of their individual impacts on ozone variability. The interpretation of the ozone-atomic oxygen relationship in Figure 5 is that the temperature and density dependence, along with the low atomic hydrogen, are sufficient to give a low equilibrium ozone despite the also low value of atomic oxygen. There are no examples of atmospheric conditions that give low temperature and low H simultaneously with high atomic oxygen. Figure 5 indicates that the air parcels with the highest nighttime ozone are always characterized by low

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temperature and low mixing ratios of hydrogen and atomic oxygen.

Figure 6 shows the average of equatorial night and day temperatures and night ozone profiles from a 10-day period. Temperature and ozone include all profiles within 5 degrees of the equator and include all longitudes. It is evident from Figure 6 that the equatorial temperature has wavelike variations that are out of phase between day and night. The average local times of the profiles at the equator are 0.3 hour and 9 hour. The temperatures are very low at night (\(160\) K). The phase of the diurnal tide is such that the minimum temperature occurs at about this time at this altitude. The cold temperature is therefore associated with the coincidence of the background cold mesopause temperature and the temperature perturbation of the migrating tide. The difference between ascending and descending node temperatures at \(.0005\) hPa is \(45\) K even after averaging over 10 days and all longitudes and even though the separation in local time of about 9 hours would underestimate the diurnal tidal amplitude. Individual profiles can show larger differences due to the superposition of nonmigrating tides and additional migrating modes. The temperature itself is very important in the occurrence of the exceptionally high ozone, as shown in the following section, and is also an indicator of the phase and amplitude of the diurnal tide.

The apparent temperature amplitude of the tide is similar to that predicted by the climatological Global Scale Wave Model (GSWM) of Hagan et al. [1999] (also see http://www.hao.ucar.edu/modeling/gswm/gswm.html) but is somewhat higher than SABER monthly average amplitudes for March [Zhang et al., 2006]. Although it is difficult to determine short-term tidal variability from SABER because of the TIMED satellite’s slow precession in local time sampling, our examination of the data indicates that such large day-night differences can persist for a week or two and can cover a substantial range of longitudes but they do not persist for an entire 60-day yaw cycle and they show significant variation with longitude. Also note that, due to the precession of the TIMED orbit, the periods during which the data sampling coincides with the local time of...
the tidal minimum temperature at a particular level is limited to a few weeks.

5. Mechanism for Enhanced Ozone Associated With Diurnal Tide

[32] The diurnal tide can affect the mesospheric ozone in several ways: transport of trace species through horizontal and vertical winds, temperature perturbations affecting the rates of reactions that produce or destroy ozone, and density perturbations affecting the rates of reactions. Here we present a simple model to show how ozone would respond to a tide with the amplitude inferred from the SABER temperature observations shown in Figure 6.

[36] The model is a simplified representation in which we determine the relationships of quantities on a specified pressure level. The following assumptions are made: temperature varies adiabatically because of vertical displacement; \( O \) varies only because of transport; and \( H \) varies because of transport and reaction with ozone. There are two calculations of ozone: in the first, ozone is in equilibrium according to equation (2) and, in the second, ozone varies because of time-dependent chemical production and loss.

\[
w' = W \cdot \exp \left\{ i \left[ (s\bar{u} - \sigma) t + \phi \right] \right\}
\]

\[
T' = \frac{iS}{(s\bar{u} - \sigma)} w'
\]

\[
O' = \frac{i\bar{Q}_2}{(s\bar{u} - \sigma)} w'
\]

\[
H' = \frac{i\bar{H}_2}{(s\bar{u} - \sigma) - ik_2 \cdot O_3 \cdot n^2} w'
\]

\[
O_3(equil) = \frac{k_1 \cdot (O + O') \cdot O_3 \cdot n}{J_{O_3} + k_2 \cdot (H + H') + k_3 \cdot (O + O')}
\]

\[
O_3(time-dep) = \frac{O_3(t - 1) + \Delta t \cdot k_1 \cdot (O + O') \cdot O_2 \cdot n}{1 + \Delta t \cdot (J_{O_3} + k_2 (H + H') + k_3 \cdot (O + O'))}
\]

where \( s \) is the zonal wavenumber, \( \bar{u} \) is the mean zonal wind, \( \phi \) is the tidal phase, \( \sigma \) is the tidal frequency \( 2\pi/24 \text{ hr} \), \( S \) is the static stability, \( t \) is time (hours), and the static stability and the background vertical gradients of \( \bar{Q}_2 \) and \( \bar{H}_2 \) are calculated from the NRLMSIS-00 model [Picone et al., 2002]. The photolysis rate \( J_{O_3} \) is zero at night. The two calculations of ozone are \( O_3(equil) \) (equilibrium) and \( O_3(time-dep) \) (time dependent). In the time dependent calculation, \( O_3(t - 1) \) is the ozone from the previous model time step and \( \Delta t \) is the time step itself. The amplitude of all variations are determined by that of \( w' \). There are no observations of \( w' \) so we use SABER temperatures to estimate it, with the assumption that the entire difference between ascending and descending temperatures is associated with the diurnal tide. This results in a value of \( w' = 20 \text{ cm s}^{-1} \), which gives the observed temperatures at 0.3 and 9 hours.

[37] Figure 7 shows the variation over 24 hours of \( T, O, H \), and the two calculations of \( O_3 \). The ozone curves from the two calculations are offset by up to two hours, indicating that ozone departs from equilibrium because of the very low loss rate (associated with the low temperature and low concentrations of hydrogen and oxygen). The effective ozone lifetime under these conditions is longer than is usual for the mesopause region. The calculations give an ozone maximum near midnight of 30 ppmv, almost identical to that measured by SABER (Figure 6).

[36] The daily variations in local temperature are made up of the superposition of all tidal modes. The diurnal tide generally has the largest impact on temperature but other modes, such as the semidiurnal tide, also contribute. Observations indicate that the diurnal tide is made up of a migrating tide, whose phase follows the motion of the sun, and various other tidal variations which are collectively known as nonmigrating tides. See Oberheide et al. [2006a] for observations of the nonmigrating wind tides from TIMED. Interference between diurnal and semidiurnal tides at a particular local time and between persistent nonmigrating tides and the migrating modes will lead to longitudes where the temperature amplitude at a given altitude is preferentially larger. This should lead in turn to longitudes where the high nighttime ozone values are preferentially seen. Figure 8 shows the percentage of high ozone nighttime profiles found near the equator (5°S to 5°N) as a function of longitude. The percentage of profiles whose temperature is below 160 K is also shown and is in good agreement with the high ozone variation. The high ozone and low temperature values are least frequent near 180°. Note that other processes, such as the diffusion due to breaking or dissipating gravity waves and variations in the molecular diffusion rate, can also lead to variations in ozone [Smith and Marsh, 2005]. Although variations in these
diffusivities could also contribute to the longitudinal variations seen in Figure 8, the excellent agreement between low temperature and high ozone indicates that local photochemistry is the dominant contributor.

6. Conclusions

This paper documents some large values of ozone found at the nighttime mesopause by SABER and GOMOS satellite measurements. To assess the reliability of the SABER nighttime ozone derived from 9.6 μm radiance, we compare the nighttime ozone densities with those from GOMOS stellar occultation. We also note that there is now (with SABER version 1.07) a good agreement of the 9.6 μm ozone during day with ozone measured simultaneously by SABER using another technique. The comparisons, along with known uncertainties in physical parameters used in the SABER retrievals, indicate that the retrieved 9.6 μm ozone at the mesopause (95–100 km) could be too high, perhaps by 10–20%. Even with this, the concentrations are higher than any previously reported. The occurrences of the highest ozone mixing ratios are not randomly distributed; instead, they are almost exclusively found in low latitudes during equinoctial periods. Simultaneous measurements of temperature and Meinel band airglow give us information about the chemistry taking place during these events. These indicate that the high ozone is always found with low temperature, low atomic hydrogen and low atomic oxygen concentrations. Together these findings suggest that upward motion is responsible since rising air cools adiabatically and transports air low in atomic oxygen and hydrogen from below. Both O and H have positive vertical gradients in mixing ratio throughout the mesosphere and therefore have a response to wave perturbations that is the same sign as that of temperature. Although low O by itself would lead to lower ozone, the effect is countered by the very strong impact on ozone of the lower temperatures; the net effect is a much higher equilibrium ozone at a particular phase of the diurnal tide. The latitude distribution and timing of seasonal appearance of the high ozone events coincide with the location and seasons of the highest amplitude of the migrating diurnal tide.

The important role of the diurnal tide in the nighttime ozone variability is a natural and, for example, was not found in the modeling study of Smith and Marsh [2005]. That particular modeling study simulated diurnal tides that have smaller amplitude and less temporal variability than those measured by SABER. The model diurnal tide was forced at the tropopause using seasonal mean fields and therefore was missing the temporal and longitudinal variability in forcing that occurs in the atmosphere. The reason for smaller amplitude in the model tide is under investigation. The smaller amplitude and variability means that the model did not simulate the cold tropical temperatures that occur for particularly high amplitude tides and therefore did not simulate the resulting peaks in ozone mixing ratio. Not all tidal models give simulated amplitudes that are small compared to SABER; amplitudes from the GSWM [Hagan et al., 1999] at 95–100 km are similar to those estimated from the SABER day-night temperature differences.

Because the validation of SABER ozone is not yet complete, we do not want to focus on the absolute magnitude of the night ozone values reported here. Instead, in this paper we point out that there is a specific and well-contained geographical region and season for which the ozone concentrations are high and that they are completely consistent with the retrieved temperature, atomic oxygen and atomic hydrogen profiles from simultaneous measurements. With the support from our theoretical understanding of ozone, as described in this paper, we believe the current high values are realistic. This means that previously accepted values that are mostly around 10 ppmv [e.g., Bevilacqua et al., 1996; Kaufmann et al., 2003; Gil-López et al., 2005] do not give sufficient indication of the large ozone mixing ratios that can occur in some circumstances.

We would also like to emphasize that care must be taken in screening the SABER ozone data in the upper mesosphere to remove outliers and erroneous profiles since the natural range of ozone is so large. Setting a cap that fits with previous expectation may lead to the underestimation of real variability.

Acknowledgments. Support for this work was provided by the NASA Science Mission Directorate. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation.

References

Doyennette, L., C. Boursier, J. Menard, and F. Menard-Bourcin (1992), \( v_1 \to v_3 \) Coriolis assisted inter-mode transfers in O-M gas mixtures (M = O\(_3\) and N\(_2\)) in the temperature range 200–300 K from IR double-resonance measurements, Chem. Phys. Lett., 197, 157–160.


E. Kyrölä, Finnish Meteorological Institute, Earth Observation, P.O. Box 503, FIN-00101, Helsinki, Finland.

D. R. Marsh and A. K. Smith, Atmospheric Chemistry Division, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307, USA. (aksmith@ucar.edu)

F. J. Martin-Torres, Jet Propulsion Laboratory, 4800 Oak Grove Drive, MS 183-501, Pasadena, CA 91125, USA.

M. G. Mlynczak, NASA Langley Research Center, Hampton, VA 23681, USA.

J. M. Russell III, Center for Atmospheric Sciences, Hampton University, Hampton, VA 23668, USA.