Using TIMED/SABER nightglow observations to investigate hydroxyl emission mechanisms in the mesopause region

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Received 3 June 2011; revised 31 October 2011; accepted 12 November 2011; published 19 January 2012.

1] Thermosphere, Ionosphere, Mesosphere, Energetics, and Dynamics (TIMED)/Sounding of the Atmosphere Using Broadband Emission Radiometry (SABER) observations of vertical profiles of the OH nightglow emission rates, temperature, and ozone are used along with a theoretical model of the OH nightglow to distinguish the dominant mechanism for the nightglow. From the comparison between the model fit and the observations we conclude that the chemical reaction O3 + H → OH(v ≤ 9) + O2 leads to population distributions of vibrationally excited states that are consistent with the measurements. The contribution of the reaction HO2 + O → OH(v ≤ 6) + O2 to the nightglow is not needed to reproduce the measurements above 80 km, at least for the emissions originating from vibrational transitions with v ≥ 4. The analysis also determines the best fits for quenching of OH(v) by O2 and O. The results show that the quenching rate of OH(v) by O2 is smaller and that the removal by O is larger than currently used for the analysis of SABER data. The rate constant for OH(v) quenching by O2 decreases with temperature in the mesopause region. The vertical profiles of atomic oxygen and hydrogen retrieved using both 2.0 and 1.6 μm channels of Meinel band emission of the OH nightglow and the new quenching rates are slightly smaller than the profiles retrieved using only the 2.0 μm channel and the quenching rate coefficients currently used for the analysis of SABER data. The fits of the model to the observations were also used to evaluate two other assumptions. The assumption of sudden death quenching of OH by O2 and N2 (i.e., quenching to the ground state rather than to intermediate vibrational levels) leads to poorer agreement with the SABER observations. The question of whether the reaction with or quenching by atomic oxygen depends on the OH vibrational level could not be resolved; assumptions of vibrational level dependence and independence both gave good fits to the observed emissions.


1. Introduction

[2] The hydroxyl emissions from the mesopause region, known as the Meinel bands, provide important information about the chemistry and dynamics in this region. The Meinel bands are composed of vibration-rotation emissions in the infrared. The predominant source of the hydroxyl emission is thought to be the ozone–hydrogen reaction,

\[(R1) \quad O_3 + H \rightarrow OH(v ≤ 9) + O_2.\]

However, an additional mechanism of producing the vibrationally excited OH(v) molecules by the reaction between hydroperoxy radical (HO2) and atomic oxygen,

\[(R2) \quad HO_2 + O \rightarrow OH(v ≤ 6) + O_2,\]

has also been proposed [Krassovsky, 1963; Schiff, 1962; Nicolet, 1970; Breig, 1970; Nagy et al., 1976]. Reaction (R2) has sufficient energy to produce vibrationally excited OH(v) up to the sixth vibrational level.

[3] Significant differences of opinion about the potential contribution of reaction (R2) to the OH nightglow still persist. Takahashi and Batista [1981], Turnbull and Lowe [1983], and Sivjee and Hamwey [1987] argue that reaction (R2) could be an important contributor for the OH(v ≤ 6) while Llewellyn et al. [1978] and McDade and Llewellyn [1987] argue that the contribution of reaction (R2) to OH nightglow is very small and can be ignored. Lopez-Moreno et al. [1987] assumed that reaction (R2) produces vibrational levels of 3–6. Kaye [1988] and Makhlouf et al. [1995]
concluded that reaction (R2) probably contributes only to the lower vibrational levels \( v \leq 3 \). As of now, these different proposals have not been resolved. For detailed discussions of the additional OH nightglow source (reaction (R2)), see Le Texier et al. [1987], Kaye [1988], and Makhlof et al. [1995].

The loss of vibrationally excited OH(v) can occur by spontaneous emission of a photon (giving rise to airglow), by quenching through collision with another molecule, or by chemical reaction. Uncertainties in the loss processes affect the interpretation of the Meinel emissions. The most important species involved in collisional quenching are \( \mathrm{O}_2 \), \( \mathrm{N}_2 \), and \( \mathrm{O} \). Because of the difficulty of laboratory measurements, the rate of quenching of high vibrational levels of \( \text{OH}(v) \) by \( \mathrm{O} \) is the least constrained. At this time, there is not sufficient evidence to determine whether the collision between \( \text{OH}(v) \) and \( \mathrm{O} \) is more likely to result in quenching or in chemical reaction or whether the reaction rates between \( \mathrm{O} \) and \( \text{OH}(v) \) depend on the vibrational level.

The quenching process itself can also have several possible outcomes [Adler-Golden, 1997]. One limiting case is “sudden death,” in which \( \text{OH}(v) \) will be chemically removed or will be quenched in a single step to \( \text{OH}(0) \). The other limiting case is a “cascade,” where single-quantum quenching from \( \text{OH}(v) \) to \( \text{OH}(v-1) \) requires a number of steps in the transition from \( \text{OH}(v) \) to \( \text{OH}(0) \). Intermediate between these is a range of possibilities for multiquantum quenching. The sudden death is the simplest model because there is no population of one level from the quenching of a higher level.

There is not agreement on which model is correct. Adler-Golden [1997] cited laboratory studies as the basis for his assumption of single-quantum relaxation for the quenching of \( \text{OH}(v) \) by \( \mathrm{N}_2 \) and a mix of single and multiquantum relaxation for the quenching of \( \text{OH}(v) \) by \( \mathrm{O}_2 \). Makhlof et al. [1995] assumed single-quantum relaxation for the quenching of \( \text{OH}(v) \) by both \( \mathrm{N}_2 \) and \( \mathrm{O}_2 \). Russell and Lowe [2003] and Russell et al. [2005] found that sudden death quenching for \( \text{OH}(v) \) by \( \mathrm{N}_2 \) and \( \mathrm{O}_2 \) gave the best agreement. Smith et al. [2010] allowed single quantum relaxation for quenching by \( \mathrm{N}_2 \) and \( \mathrm{O}_2 \) but assumed sudden death for quenching by \( \mathrm{O} \). Kaufmann et al. [2008] compared the OH nightglow observed by SCIACHMY (The SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY) on the European Space Agency’s Envisat satellite with calculations from an \( \text{OH} \) airglow theoretical model with different collisional relaxation schemes by \( \mathrm{N}_2 \) and \( \mathrm{O}_2 \). They found that a mixture of sudden death and single quantum relaxation gives the best fit to the SCIACHMY measurements.

The Sounding of the Atmosphere using Broadband Emission Radiometry (SABER) instrument is one of the payloads on the TIMED (Thermosphere, Ionosphere, Mesosphere, Energetics and Dynamics) satellite. SABER is a multichannel radiometer for measurement of atmospheric temperature, airglow, and constituent profiles [Kaye et al., 1994; Mlynczak and Russell, 1995]. The TIMED satellite was launched in December 2001 and began making observations of the global distributions of temperature, ozone, and airglows of \( \text{OH} \) and \( \mathrm{O}_2 \) in the stratosphere and mesosphere in late January 2002. TIMED/SABER profiles of the retrieved volume emission rates of two mesospheric hydroxyl airglow emissions are available. The bandpass filters of the two channels are given in the work of Baker et al. [2007, Figure 3]. Channel A measures the 2.0 \( \mu \text{m} \) Meinel band emission, which has contributions from the OH (9–7) and (8–6) vibrational transitions. Channel B measures the 1.6 \( \mu \text{m} \) Meinel band emission, which has contributions from the OH(5–3) and OH(4–2) vibrational transitions. Channel A represents transitions between higher vibrational levels (\( v \geq 6 \)) while Channel B represents transitions between lower vibrational levels (\( v \leq 6 \)). Together, as explained below, these measurements can provide an opportunity to test the role of reaction (R2) as a source of the OH nightglow emission.

The goals of this paper are (1) to determine whether the reaction of \( \text{HO}_2 \) with \( \mathrm{O} \) makes a noticeable contribution to the OH nightglow emission from the low vibrational levels (\( v \leq 6 \)); (2) to determine the magnitudes and temperature dependence of the rates of quenching of \( \text{OH}(v) \) by molecular and atomic oxygen; and (3) to determine whether the sudden death or multiquantum relaxation model of \( \text{OH}(v) \) quenching better fits the hydroxyl nightglow emissions. The paper is organized as follows. Section 2 discusses the data set, the OH nightglow theoretical model, and the analysis method. Section 3 evaluates the dominant chemical source and temperature dependence of OH nightglow emissions in the MLT region by comparing the theoretical model with the SABER observations. A discussion of the impacts of the uncertainties in Einstein coefficients, chemical reaction rates, and observation error on the calculation of quenching rates and the retrieval of \( \text{O} \) and \( \text{H} \) profiles is also given. Section 4 presents the results of tests evaluating the quenching of hydroxyl by molecular oxygen and nitrogen and the quenching or reaction by atomic oxygen. Section 5 gives some comparisons between the theoretical model derived from SABER observation and published ground-based observations. Section 6 summarizes the results and their implications.

2. Data Set and Analysis Method

2.1. Data Set

The TIMED/SABER observations used here are version 1.07 temperature, ozone, and the “unfiltered” 2.0 \( \mu \text{m} \) and 1.6 \( \mu \text{m} \) Meinel airglow emissions. The unfiltering process adjusts the emission magnitude to account for the shape, width, and transmission of the instrument’s broadband filters [Mlynczak et al., 2005]. The filter characteristics were measured in the laboratory before launch. The unfiltering process is applied because the filter is not perfect in two ways (see discussion in the work of Mlynczak et al. [2005]): (1) the filter does not include all lines and (2) the response is not perfect; that is, less than 100% of the radiation passes through. Baker et al. [2007, Figure 3] show the SABER OH filters superimposed on ground-based OH spectra. Baker et al. [2007, Figure 3] indicate the line positions compared with the filter width. What is not apparent from Baker et al. [2007, Figure 3] is that the response of the filter is in the range of 80–100% over most of the band. The unfilter factor is determined by a detailed calculation that takes the ratio of the emission of all lines of (9–7) and (8–6) with no filter to the emission with the
Table 1. Chemistry of the OH Nightglow

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Reaction Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1) $H + O_3 \rightarrow OH(v) + O_2$, $v \leq 9$</td>
<td>$k_1 = 1.4 \times 10^{-10} \exp(-470/kT)$</td>
<td>Sander et al. [2006] and Adler-Golden [1997, Table 1]</td>
</tr>
<tr>
<td>(R2) $HO_2 + O \rightarrow OH(v) + O_2$, $v \leq 6$</td>
<td>$k_2 = 3.1 \times 10^{-11} \exp(-200/kT)$</td>
<td>Sander et al. [2006]</td>
</tr>
<tr>
<td>(R3) $OH(v) + O_2 \rightarrow OH(v') + O_2$, variable rates from equation (11)</td>
<td></td>
<td>Adler-Golden [1997, Table 2]</td>
</tr>
<tr>
<td>(R4) $OH(v) + N_2 \rightarrow OH(v') + N_2$, single-quantum relaxation</td>
<td></td>
<td>Adler-Golden [1997, Table 1]</td>
</tr>
<tr>
<td>(R5) $OH(v) + O \rightarrow OH + O_2$, $5 \times 10^{-11}$; fixed for all $v$</td>
<td></td>
<td>Smith et al. [2010]</td>
</tr>
<tr>
<td>(R6) $OH(v) \rightarrow OH(v-1) + h\nu$, variable rates</td>
<td></td>
<td>Khomich et al. [2008, Table 2.13]</td>
</tr>
<tr>
<td>(R7) $O + O_2 \rightarrow O_3 + M$, $k_7 = 6.0 \times 10^{-10} (100/kT)^{3/4}$</td>
<td></td>
<td>Sander et al. [2006]</td>
</tr>
<tr>
<td>(R8) $O + O_3 \rightarrow O_2 + O_2$, $k_8 = 8.0 \times 10^{-12} \exp(-300/kT)$</td>
<td></td>
<td>Sander et al. [2006]</td>
</tr>
</tbody>
</table>

measured filter characteristics. The contributions of other bands, such as (7–5) and (3–1), to the two channels are very small (few percent level) since the portions are small, and near where the filters are starting to cut off.

[10] The unfilter factors for channels A and B are 1.11 and 1.42, respectively. The main way that the filter factor could introduce error is if there is some unexpected relationship between the bands, for example if emission from $v = 9$ increases while emission from $v = 8$ decreases. SABER cannot distinguish this but we do not have any indication (for example from measured spectra) that this should be a concern. There is no evidence from the in flight monitoring of SABER or from trends in the observed radiances that the detector or filters have changed during the mission.

[11] Owing to the TIMED orbit and the yaw maneuvers every 60–65 days, continuous TIMED/SABER latitudinal coverage is available from 53°S to 53°N. In this paper, we focus on the nightglow of OH. This study uses profiles of volume emission rate from the two OH emission channels and retrieved profiles of temperature and ozone. The daily observations of TIMED/SABER at any latitude are centered at two local times, corresponding to the ascending and descending phases; the observation points are distributed uniformly along longitude circles. For the analysis, nighttime profiles from each day are averaged over all longitudes and over latitude bands 20° wide.

2.2. Hydroxyl Night Airglow Model

[12] The model of OH(v) nightglow follows that of Adler-Golden [1997] and Smith et al. [2010]. The chemical reactions are listed in Table 1. Since measurements of HO2 are not available from TIMED, it is difficult to test the role of reaction (R2) directly. Instead, we apply the following logic. We first assume that reaction (R1) alone is responsible for the OH nightglow emission; then we use SABER observations of the two OH nightglow emissions to test this assumption. If a single source, reaction (R1), can simultaneously reproduce both the 2.0 µm OH nightglow, representing the high vibrational level ($v \geq 6$), and the 1.6 µm OH nightglow, representing the low vibrational levels ($v \leq 6$), the second source (reaction (R2)) is unnecessary. As shown below, the vertical distributions of the two sources are very different.

[13] If reaction (R1) is the only important chemical reaction for producing the OH nightglow, the rate of production of vibrationally excited OH for all vibrational levels is

$$P_{OH^*} = k_1[H][O_3].$$

At night, chemical equilibrium of ozone gives [Smith et al., 2010]

$$k_7[M][O][O_2] = k_1[H][O_3] + k_8[O][O_2].$$

$[M]$ is the atmospheric number density, $[O]$ is the atomic oxygen density, $[O_2]$ is the molecular oxygen density, $[H]$ is the atomic hydrogen density, and $[O_3]$ is the ozone density. Therefore, the rate of production of vibrationally excited OH for all vibrational levels is

$$P_{OH^*} = k_1[H][O_3] = \{k_7[O_2] - k_8[O][O_2]\}[O].$$

The rate of production of vibrational level at $v$ is:

$$P_v = f_v P_{OH^*},$$

$$P_v = f_v P_{OH^*} + \sum_{j=1}^{n_v} \left[ n_{v,j}A_{v,j,v} + n_{v,j}(k_3_{(v,j,v)}[O_2] + k_4_{(v,j,v)}[N_2]) \right].$$

[14] The data for the transition probabilities for various OH bands $A_{v,j,v}$ (Einstein coefficients) are frequently updated and are available in a number of publications. We calculate the Einstein coefficients using the HITRAN-2008 database [Rothman et al., 2009]. The calculation method and coefficients are presented in Appendix A. The new Einstein coefficients are very similar to those in the work of Khomich et al. [2008, Table 2.13], which are from HITRAN-1998 [Goldman et al., 1998]. Here $f_v$ is the branching ratio for reaction (R1), which is given in the work of Adler-Golden [1997], and $[N_2]$ is the molecular nitrogen density. The rate of loss of vibrational level at $v$ is:

$$L_v \cdot n_v = \left\{ \sum_{j=0}^{v-1} A_{v,j} + \sum_{j=0}^{v-1} \left[ k_3_{(v,j,v)}[O_2] + k_4_{(v,j,v)}[N_2] \right] + k_5[O] \right\} \cdot n_v,$$

$$= \left\{ A_v + \sum_{j=0}^{v-1} \left[ k_3_{(v,j,v)}[O_2] + k_4_{(v,j,v)}[N_2] \right] + k_5[O] \right\} \cdot n_v,$$

$$v = 9, 8, 7, \ldots, 1$$

$$A_v = \sum_{j=0}^{v-1} A_{v,j}$$ is the total spontaneous emission rate (Einstein coefficients) for the $v$ vibrational transition.

[15] If the loss time is fast compared to the timescale for OH(v) to change through transport or other processes, then
the vibrational levels are in chemical equilibrium. We calculate the lifetime of OH(v), taking SABER observations near the equator on day 80 in 2003 as an example. The results show that the lifetime of OH(v) at 85 km varies from about 1 ms at v = 9 to about 30 ms at v = 1. To determine the timescale for OH(v) to change due to dynamical variations, we use previous calculations for the sodium layer [Xu and Smith, 2003, Figure 4]. The analysis is the same because the OH(v) and sodium layers both have a Gaussian shape although the peak altitudes are slightly different (the sodium layer is centered at 92 km and OH(v) is centered at 87 km). These calculations show that the timescale for vertical transport with a 1 m/s wind is more than 100 s and the timescale for diffusion is much larger than 1000 s. By this scaling, the hydroxyl states are in chemical equilibrium and we can equate production to loss. Therefore, the number density of the population is:

\[ n_v = \frac{P_v}{E_v}, \]  

(4)

The emission rate for the \( i \rightarrow j \) vibrational transition is:

\[ I_{i\rightarrow j} = E_{ij} A_{ij} n_i, \]  

(5)

where \( E_{ij} \) and \( A_{ij} \) are the photon energy and the Einstein coefficient for the \( i \rightarrow j \) vibrational transition, respectively.

Equations (1)–(5) form a theoretical model for the OH nightglow emission rate under the assumption that reaction (R1) is the only chemical source for the nightglow. It is clear from equations (1)–(5) that, if reaction (R1) is the source of the nightglow, the emission rates at the different vibrational levels are not independent. The relationships among any vibrational transition emissions can be determined from equations (1)–(5).

2.3. Analysis Method

The parameters with the largest uncertainty in the model of the OH nightglow emission given in equations (1)–(5) are the rates for collisional quenching. According to Adler-Golden [1997], the quenching of OH(v) by N\(_2\) is very inefficient; single-quantum relaxation (i.e., cascade) is assumed. Since quenching by N\(_2\) is relatively unimportant, uncertainty in its rate is neglected in our analysis. Adler-Golden [1997] assumes multiquantum relaxation for the quenching of OH(v) by O\(_2\):

\[ k_3(v', v'') = C[\rho_v(v')^{v''}] \text{ cm}^3\text{s}^{-1}. \]  

(6)

\( P_v \) is a probability factor, which is a function of \( v' \); it is given in the work of Adler-Golden [1997, Table 2]. \( C \) is a single constant for the entire system of rate constants for the multiquantum relaxation of OH(v) by O\(_2\). There is an uncertainty in parameter C, which is taken as \( 4.4 \times 10^{-12} \) cm\(^3\) s\(^{-1}\) by Adler-Golden [1997]. We account for this uncertainty by application of a yet unknown correction factor \( \alpha \) that is equal to 1 if \( C \) is correct. The quenching rate can then be expressed as:

\[ k_3(v', v'') = \alpha \times 4.4 \times 10^{-12} \times [\rho_v(v')]^{v''} \text{ cm}^3\text{s}^{-1}. \]  

(7)

A second important parameter with a high degree of uncertainty is \( k_5 \), the rate of quenching of OH(v) by atomic oxygen. Owing to the lack of the knowledge about the \( O + OH(v) \) reaction, including uncertainty about whether the reaction is quenching or kinetic reaction, Adler-Golden [1997] assumed this reaction leads to sudden death loss of OH(v) that is independent of the vibrational level. Smith et al. [2010] used \( k_5 = 5 \times 10^{-13} \) cm\(^3\) s\(^{-1}\); they discuss the impact of this uncertainty on retrievals of atomic oxygen. We use another yet unknown correction factor \( \beta \) to account for the uncertainty in this rate, which gives

\[ k_5 = \beta \times 5 \times 10^{-13} \text{ cm}^3\text{s}^{-1}. \]  

(8)

The densities of atomic oxygen [O] and hydrogen [H] also affect the OH nightglow emission rate profiles. The emission measured by SABER at 2.0 \( \mu \)m \((I^{o}_{2,0})\) has contributions from OH(9–7) and OH(8–6). The emission at 1.6 \( \mu \)m \((I^{o}_{1,6})\) has contributions from OH(5–3) and OH(4–2).

Therefore, the 2.0 \( \mu \)m and 1.6 \( \mu \)m OH nightglow emission rates can be written as:

\[ I^{z, c}_{2,0}(\alpha, \beta, \rho_0(z), \rho_H(z)) = E_{9,7}A_{9,7}n_9 + E_{8,6}A_{8,6}n_8, \]  

(9a)

\[ I^{z, c}_{1,6}(\alpha, \beta, \rho_0(z), \rho_H(z)) = E_{5,3}A_{5,3}n_5 + E_{4,2}A_{4,2}n_4. \]  

(9b)

where \( \rho_0(z) \) and \( \rho_H(z) \) are the vertical profiles of atomic oxygen and hydrogen.

We use a nonlinear least squares fitting method to calculate the values for the parameters \( \alpha, \beta, \rho_0(z), \) and \( \rho_H(z) \) that minimize the deviation of the penalty function \( \epsilon \) between the OH nightglow calculated by the theoretical model and the SABER observations:

\[ \epsilon(\alpha, \beta, \rho_0(z), \rho_H(z)) = \frac{1}{\Delta z} \sum_{z = \text{bottom}}^{z = \text{top}} [(E_{9,7}^{z} - E_{9,7}^{\text{fit}})^2 + (E_{8,6}^{z} - E_{8,6}^{\text{fit}})^2] \Delta z. \]  

(10)

\( \Delta z = 1 \) km is the altitude interval. Details of the calculation are given in Appendix B.

If, after the fitting process, the OH nightglow emission rate vertical profiles from the theoretical model are consistent with those from SABER observations for both channels simultaneously, we can conclude that reaction (R1) is the dominant chemical source for the OH nightglow emission for vibrational levels \( v \geq 4 \). At the same time, we can determine the best fit values for the parameters \( \alpha \) and \( \beta \) and the profiles of \( \rho_0(z) \) and \( \rho_H(z) \).

3. Chemical Reaction Sources of the OH Nightglow

3.1. Case Studies

First we present, as case studies, individual days at equinox and solstice.

For the equinox case, we take the SABER OH nightglow profiles from day 80 of 2003 at three latitude bands: 40°N ± 6°, equator ± 10°, and 40°S ± 10° as examples. Figure 1 gives profiles averaged over the nighttime values for this date. Figure 1a shows the observed profiles of temperature and ozone. Figure 1b shows the OH emission rates from the two OH channels and the model fits to the emissions. Figures 1c, 1d, and 1e show additional
Figure 1. Night averaged profiles of (a) temperature and ozone, (b) observed nightglow from two channels and their model fits, (c) atomic oxygen and hydrogen retrieved by two methods, (d) OH density at each vibrational level, and (e) sources of the OH nightglow emissions from two reactions at day 80 of 2003 for three latitude bands: (left) 40°N/10°, (middle) equator/10°, and (right) 40°S/10°.
profiles from the model fit: atomic oxygen and hydrogen retrieved using two methods (see below), density of each OH(v) vibrational level, and OH(v) sources from the two chemical reaction rates, respectively. The local times of the observations (fixed by the date and the TIMED orbit) are given in Figure 1a. The values for $\alpha$ and $\beta$ determined by the nonlinear least squares fitting are given in Figure 1b.

Figure 1 shows that the model can simultaneously fit the nightglow for the two channels very well when only one source (reaction (R1)) is considered. In the best fit, the values of $\alpha$ and $\beta$ vary between profiles but, in all cases shown, $\alpha$ is less than 1 and $\beta$ is larger than 1. The solid lines in Figure 1c are the retrieved vertical profiles of atomic oxygen $n_O(\text{cm}^{-3})$ and hydrogen $n_H(\text{cm}^{-3})$ derived by minimizing the difference between the OH nightglow observations and the model calculation using emissions from both channels (equation (10)).

We use additional information about the chemical system to further evaluate the possible contribution of reaction (R2) to the nightglow. The loss of HO$_2$ by $\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$ is almost balanced by regeneration from $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$, according to Allen et al. [1984, equation (15)]. Under conditions of chemical equilibrium, this gives

$$k_2 \text{[HO}_2][\text{O}] \approx k^*[\text{H}][\text{O}_2][\text{M}]$$

where $k^*$ is the rate constant for the termolecular reaction [Sander, et al., 2006], [M] is the atmospheric density, and $T$ is the temperature. The rates for OH(v) production $P_{\text{OH}} = k_1[H][\text{O}_3]$ from reaction (R1) and $P_{\text{OH}} = k_2[\text{HO}_2][\text{O}] \approx k^*[\text{H}][\text{O}_2][\text{M}]$ from reaction (R2) are shown in Figure 1e. The vertical distributions of the two sources are very different. The contribution from reaction (R2) is much smaller than reaction (R1) except around 80 km. Figure 1b shows that, near 80 km, the model fit using reaction (R1) as the only source of OH(v) is very consistent with the observations. Therefore, the second OH nightglow source (reaction (R2)) is unnecessary.

Figure 2 gives an example for day 180 of 2003, which represents solstice. As for day 80 (Figure 1), the best fit values for $\alpha$ are less than 1 and those for $\beta$ are larger than 1. The model is again able to fit both emissions using only reaction (R1).
Figure 2. Same as Figure 1 but for day 180 of 2003.
The comparison between the model fit and observations shown in Figures 1 and 2 indicate that reaction (R1) is the dominant chemical source for OH airglow emission for both the high vibrational transition and the low vibrational transition. The analysis indicates that, provided that the parameters $a$ and $b$ are adopted as indicated above, reaction (R2) can be neglected as a source for the OH nightglow above 80 km, at least for vibrational transitions originating at or above $v = 4$.

### 3.2. Sensitivity Analysis of the Correction Factors of Quenching Rates

Here we assess the impact of uncertainties in the Einstein coefficients and chemical reaction rates used in the OH airglow chemical model.

The Einstein coefficients are calculated using HITRAN-2008. Comparison of these with the Einstein coefficients calculated from HITRAN-1998 data [Khomich et al., 2008, Table 2.13], the largest change is in vibration level 9. The Einstein coefficient for the (9, 8) transition calculated from HITRAN-2008 is 18.35, while that calculated from HITRAN-1998 is 20.41, a difference of 10%. The Einstein coefficients for the (9, 7) transition are different by 5% (112.40 from HITRAN-2008 and 117.60 from HITRAN-1998). Khomich et al. [2008, Tables 2.4–2.13] presented several sets of transition probabilities for OH bands, and we can see that there are large differences among these Einstein coefficients.

The most important uncertainties in the reaction rates are those in $k_1$, $k_7$, and $k_8$, because they have the largest impact on the OH airglow. According to Sander et al. [2006], at the temperature of 200 K, the uncertainties of $k_1$, $k_7$, and $k_8$ are about 25%, 20%, and 70%, respectively.

We assess the impact of the uncertainties on the results for a specific case, day 80 of 2003 at the latitude band $\pm 10^\circ$ (see Figure 1 (middle)). To illustrate the impact of differences in the Einstein coefficients we show the calculations with $\pm 20\%$ in the Einstein coefficients for vibration state of $v = 9$. For the impacts of uncertainties in the chemical reaction rates, we take $\pm 25\%$, $\pm 20\%$, and $\pm 70\%$ for $k_1$, $k_7$, and $k_8$, respectively. Figure 3 gives the results. From Figure 3, we can see that, despite these fairly substantial changes in the magnitude of the parameters, the fitting of observations by the theoretical model is very good. (Note that the three lines overlay one another in Figure 3 (left)). Figure 3 (right) also shows that the effects of uncertainties in the Einstein coefficients and chemical reaction rates on the profiles of two sources are very weak. The calculated contribution from reaction (R2) is still much smaller than that from reaction (R1).
Figure 3
[32] However, the uncertainties in the Einstein coefficients and chemical reaction rates change the correction factors for the quenching rates and the profiles of atomic oxygen and hydrogen. When the Einstein coefficient increases by 20%, the correction factor of the quenching rate of OH(v) by O2 increases from 0.57 to 0.71 (Figure 3a). Figure 3b shows that the uncertainty in the chemical reaction rate k1 has strong influence on the calculated profile of atomic hydrogen, but no effects on the correction factors. Figure 3c indicates that the uncertainty in the chemical reaction rate k3+ has large influences on the correction factor of the rate of quenching of OH(v) by O and the profile of atomic oxygen. If the reaction rate k5+ increases by 20%, the correction factor of the quenching rate of OH(v) by O increase from 1.41 to 1.71 and the retrieved atomic oxygen density decreases. From Figure 3d we can see that the uncertainty in the chemical reaction rate k8 also has a large influence on the correction factor of the quenching rate of OH(v) by O.

[33] Figure 3 shows that the uncertainties in the Einstein coefficients and chemical reaction rates have obvious effects on the correction factors that we derive for the quenching rates and also for the retrieved profiles of atomic oxygen and hydrogen. However, even with all the uncertainties, the impact on the evaluation of the role of the two reactions as sources for the OH nightglow is very small. The model fit using reaction (R1) as the only source of OH(v) is very consistent with the observations when the uncertainties of parameters are considered. Therefore, the second OH nightglow source (reaction (R2)) is unnecessary to explain the SABER OH nightglow observations.

[34] Additional sources of uncertainty are systematic errors and noise in the observations of the airglow profiles. We calculate the impact of 5% errors in either or both channels on the test case, day 80 in 2003 at the latitude band of ±10°. Table 2 gives the correction factors of the quenching rates for these errors. Table 2 shows that the correction factors vary with the error assignments. However, for all error permutations, α is less than 1 and β is larger than 1.

### Table 2. Correction Factors for Various Combinations of Error Percentages

<table>
<thead>
<tr>
<th>2.0 μm</th>
<th>1.6 μm</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.57</td>
<td>1.41</td>
</tr>
<tr>
<td>5%</td>
<td>5%</td>
<td>0.57</td>
<td>1.35</td>
</tr>
<tr>
<td>−5%</td>
<td>−5%</td>
<td>0.57</td>
<td>1.49</td>
</tr>
<tr>
<td>5%</td>
<td>−5%</td>
<td>0.37</td>
<td>1.63</td>
</tr>
<tr>
<td>−5%</td>
<td>5%</td>
<td>0.85</td>
<td>1.25</td>
</tr>
<tr>
<td>0</td>
<td>5%</td>
<td>0.7</td>
<td>1.29</td>
</tr>
<tr>
<td>5%</td>
<td>0</td>
<td>0.47</td>
<td>1.47</td>
</tr>
<tr>
<td>−5%</td>
<td>0</td>
<td>0.71</td>
<td>1.36</td>
</tr>
<tr>
<td>0</td>
<td>−5%</td>
<td>0.46</td>
<td>1.56</td>
</tr>
</tbody>
</table>

latitude, although α is in all cases less than 1 and β is in all cases larger than 1. In order to get statistically averaged values of the quenching rates that can be used in theoretical models, we calculate the averaged values of α and β using the SABER observations of the OH nightglow for every day from 2002 to 2008.

[36] In the latitude range 50°S to 50°N, the local time window from −02:30 to 02:30 LT is always in darkness [Gao et al., 2010]. For a uniform selection of nightglow data and in order to eliminate the influence of the transition between the dayglow and the nightglow, we select all profiles in this latitude range whose local time is within 2 h of midnight (from −02:00 to 02:00 h of local time).

[37] The calculations are made for 5 latitude bins: 40°S ± 10°, 20°S ± 10°, equator ± 10°, 20°N ± 10°, and 40°N ± 10°. The averages are calculated for each bin. The averaged correction factors for the quenching rates for the period from 2002 to 2008 are:

$$\begin{align*}
\alpha &= \frac{0.723 \pm 0.152}{1.293 \pm 0.157} \\
\beta &= \end{align*}$$

Therefore, the averaged quenching rate parameters are:

$$\begin{align*}
k_5 &= (6.465 \pm 0.785) \times 10^{-11} \\
\bar{k}_5(v, v') &= (3.181 \pm 0.669) \times 10^{-12} \times |P_1(v-v')| \text{ cm}^3 \text{s}^{-1} \\
\end{align*}$$

The mean value of C in equation (6) for the quenching rate of OH(v) by O2 is 3.18 × 10−12 cm3 s−1 and the mean quenching rate of OH(v) by atomic oxygen is 6.47 × 10−11 cm3 s−1.

[38] There are a few laboratory studies that give some clues of the temperature dependence for the quenching of OH(v) by O2 and atomic oxygen. Lacoursiere et al. [2003, Figure 4] measured a negative temperature dependence of the quenching of OH(v = 10) by O2 between 220 K and 320 K. A theoretical study by Klös et al. [2008, Figures 6–8] showed that the reaction rate between OH(v = 1) and atomic oxygen has a negative temperature dependence when the temperature is larger than 100 K. These results show that, between 200 and 300 K, the two reaction rates have a negative relationship with the temperature that is almost linear. These studies provide the very limited knowledge available about the temperature dependences of OH(v) quenching.

[39] There are very large variations in temperature in the mesopause region, associated with strong tides and temperature inversion layers, especially near the equator [e.g., Xu et al., 2007, 2009]. The tides can also strongly modulate nightglow emission rates [e.g., Shepherd et al., 1998; Yee et al., 1997; Ward, 1999; Zhang and Shepherd, 1999; Xu et al., 2010; Gao et al., 2010]. Therefore, the mesopause region is a natural laboratory to test the temperature dependence of the quenching rates. The widths of airglow layers are about 10 km. Figures 1 and 2 show that the range of temperatures found between 80 and 100 km covers several tens of degrees. Since the quenching rates are determined
for the entire profile, not each individual altitude, we can use variations in the derived quenching rates between different profiles to determine a qualitative relationship between the temperature and the quenching rates within the observed temperature range. The average profile temperature is defined to be the vertically weighted averaged temperature of the two channels:

\[
\bar{T} = \frac{1}{2} \left\{ \frac{\sum_{75\text{ km}}^{100\text{ km}} T(z) f_2^8(z) \cdot \Delta z}{\sum_{75\text{ km}}^{100\text{ km}} f_2^8(z) \cdot \Delta z} + \frac{\sum_{75\text{ km}}^{100\text{ km}} T(z) f_1^6(z) \cdot \Delta z}{\sum_{75\text{ km}}^{100\text{ km}} f_1^6(z) \cdot \Delta z} \right\}
\]

Figure 4 gives scatterplots of \( \alpha \) and \( \beta \) versus the average profile temperature for five latitude bands from 50°S to 50°N.

Figure 4. Scatterplots of (left) \( \alpha \) and (right) \( \beta \) versus the average profile temperature for five latitude windows: 40°S to 40°N, 20°S to 20°N, 20°N to 40°N, 40°N to 60°N, and 60°N to 80°N.

Figure 4 also illustrates the finding that \( T \) is greater than 1. The scatter of \( \alpha \) versus \( T \) and \( \beta \) versus \( T \) is very important for modeling the OH nightglow in the mesosphere and for the retrieval of atomic oxygen vertical profiles. In section 4, we use the TIMED/SABER observations from two OH airglow channels to evaluate several questions related to the quenching or reaction rates of OH(v) by O\(_2\), N\(_2\), and O.

4. Quenching of OH(v) by Molecular and Atomic Oxygen

Knowledge of the rate of removal of OH(v) by quenching or chemical reaction with molecular and atomic oxygen is very important for modeling the OH nightglow in the mesosphere and for the retrieval of atomic oxygen vertical profiles. In section 4, we use the TIMED/SABER observations from two OH airglow channels to evaluate several questions related to the quenching or reaction rates of OH(v) by O\(_2\), N\(_2\), and O.

4.1. Sudden Death or Multiquantum Quenching of OH(v) by O\(_2\) and N\(_2\)?

Two aspects of the quenching of OH(v) by O\(_2\) and N\(_2\) are needed in order to interpret the observed Meinel band emissions. The first is the quenching rate, which, for O\(_2\), was evaluated in section 3. The second is the branching ratio resulting from the quenching, which has an impact on the population of vibrational levels with \( v < 9 \). For single or multiquantum quenching, the quenching of OH(v) from high vibrational levels by O\(_2\) or N\(_2\) will increase the population of OH(v) in the lower vibrational levels. For the sudden death model, the distribution among the different OH vibrational levels is controlled more strongly by the
spontaneous emission rates since quenching does not contribute. The dependence of the quenching rate on the specific vibrational transition also affects the distribution of vibrational levels. Therefore, different models for the quenching will give different relative populations between OH(v) levels and will, in turn, give different predictions for the nightglow. These differences can be used to determine which model gives the best fit with observations.

Russell and Lowe [2003] and Russell et al. [2005] used observations made by WINDII (WIND Imaging Interferometer) on the UARS (Upper Atmospheric Research Satellite) to investigate this question. They calculated atomic oxygen profiles using simultaneous observations of the oxygen green line and the hydroxyl P1(3) line ($\lambda = 734$ nm) from the (8–3) band. They found that a sudden death quenching of the hydroxyl vibrational levels by O$_2$ and N$_2$ gave atomic oxygen profiles that best fit those determined from the green line emissions. In other words, in their best fit there was no population of OH(v = 8) by cascade from OH(v = 9). However, other studies [e.g., Adler-Golden, 1997; Makhlouf et al., 1995] have assumed that quenching of OH(v) by N$_2$ and O$_2$ is a single-quantum or multiquantum

Figure 5. Observed (top) OH airglow profiles and monthly averaged model fits and (bottom) atomic oxygen and hydrogen densities retrieved by two methods near midnight (00:00 to 02:00 LT) of March 2003 for three latitude bands: 40°S ± 10°, equator ± 10°, and 40°N ± 10°.
relaxation. Kaufmann et al. [2008] found that a mixture of sudden death and single quantum relaxations schemes by N$_2$ and O$_2$ gives the best fit to the SCIAMACHY measurements. [46] The removal of OH(v) in quenching by O$_2$ and N$_2$ has been measured in the laboratory [e.g., Rensberger et al., 1989; Dodd et al., 1991; Chalamala and Copeland, 1993; Knutsen et al., 1996; Dyer et al., 1997; Lacoursiere et al., 2003]. Laboratory measurements and modeling studies have shown that O$_2$ is several tens of times more efficient than N$_2$ at deactivating OH(v) [e.g., Chalamala and Copeland, 1993; Lacoursiere et al., 2003; Adler-Golden, 1997]. Table 3 gives the laboratory measured removal rates of OH(v) by O$_2$ and N$_2$ derived by Adler-Golden [1997] for every vibrational level. With multiquantum quenching by O$_2$ and single-quantum relaxation by N$_2$, adapted from Adler-Golden [1997], the total removal rates of OH(v) by O$_2$ and N$_2$ for every vibrational level are as follows:

$$K_{O_2}(v) = \sum_{i=1}^{v} k_3(v, v') = C \sum_{i=1}^{v} |P_i|^{v-v'}$$  \hspace{1cm} (14)

$$K_{N_2}(v) = k_4(v).$$  \hspace{1cm} (15)


\[\text{[47]}\]
calculation (see section 3) shows that the best fit with
SABER observations is to reduce the O$_2$ quenching rates by
a factor of $\alpha = 0.723$. The rates with the 0.723 factor applied
are also given in Table 3; in all cases this factor improves
the agreement between the Adler-Golden [1997] calculation
and the laboratory measurements cited. Figure 7 gives the
laboratory measured removal rates of OH(v) by O$_2$ for
every vibrational level and the results of Adler-Golden [1997] as published and after modification by the 0.723
multiplier. Table 3 and Figure 7 show that the values for the
removal rates of OH(v) by O$_2$ from Adler-Golden [1997]
are consistent with laboratory measurements, especially
after modification.

For the best fit to the TIMED/SABER emissions
discussed in section 3, we used the assumptions of multi-
quantum relaxation for OH(v) quenching by O$_2$ and single-
quantum relaxation for OH(v) quenching by N$_2$. Here, we
recalculate the fit but with the assumption of sudden death
quenching of OH(v) by both O$_2$ and N$_2$. The total removal
rates in the calculation are the modified values from Table 3.
The SABER OH nightglow profiles observed on day 80 of
2003 in the latitude band of the equator $\pm 10^\circ$ are taken as
an example. We calculate the fit for three cases: fitting only
Channel A, fitting only Channel B, and simultaneously fit-
ting both channels.

Figure 8 shows that, if we fit only the Channel A
2.0 $\mu$m Meinel band emission, the calculated OH nightglow
profile of Channel B is much smaller than observed. The
SABER observed peak emission rate of Channel B at 84 km
is $4 \times 10^{-7}$ (ergs/cm$^3$/s) but the calculated peak emission
rate is only $1 \times 10^{-7}$ (ergs/cm$^3$/s). Conversely, if we fit the
Channel B 1.6 $\mu$m Meinel band emission, the calculated OH
nightglow profile of Channel A is much larger than
observed. The SABER observed peak emission rate of

<table>
<thead>
<tr>
<th>Vibrational Quantum Number</th>
<th>Laboratory Measurement of O$_2$ Removal Rate $a$</th>
<th>$O_2^{b}$</th>
<th>$O_2 \times 0.723^b$</th>
<th>Laboratory Measurement of N$_2$ Removal Rate $a$</th>
<th>N$_2^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>2.79 $\pm$ 0.14$^c$</td>
<td>3.09</td>
<td>2.23</td>
<td>0.16 $\pm$ 0.06$^c$</td>
<td>0.048</td>
</tr>
<tr>
<td>10</td>
<td>1.5 $\pm$ 0.12$^c$, 1.92 $\pm$ 0.25$^d$</td>
<td>1.19</td>
<td>0.86</td>
<td>1.02 $\pm$ 0.74$^e$, 0.31 $\pm$ 0.18$^f$</td>
<td>0.07 $\pm$ 0.04$^c$, 0.016</td>
</tr>
<tr>
<td>9</td>
<td>1.7 $\pm$ 1.1$^c$</td>
<td>0.43</td>
<td>0.31</td>
<td>0.43 $\pm$ 0.15$^g$, 0.25 $\pm$ 0.10$^h$</td>
<td>0.0091</td>
</tr>
<tr>
<td>8</td>
<td>0.8 $\pm$ 0.1$^i$</td>
<td>0.13</td>
<td>0.094</td>
<td>0.052 $\pm$ 0.015$^i$, 0.077 $\pm$ 0.056</td>
<td>0.0002</td>
</tr>
<tr>
<td>7</td>
<td>0.7 $\pm$ 0.2$^j$</td>
<td>0.04</td>
<td>0.029</td>
<td>0.027 $\pm$ 0.008$^l$, 0.026 $\pm$ 0.0054$^l$</td>
<td>0.001</td>
</tr>
<tr>
<td>6</td>
<td>0.3 $\pm$ 0.15$^k$</td>
<td>0.019</td>
<td>0.014</td>
<td>0.013 $\pm$ 0.004$^l$</td>
<td>0.0006</td>
</tr>
<tr>
<td>5</td>
<td>0.17 $\pm$ 0.07$^l$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.088 $\pm$ 0.03$^m$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.052 $\pm$ 0.015$^n$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.027 $\pm$ 0.008$^o$, 0.026 $\pm$ 0.0054$^o$</td>
<td></td>
<td></td>
<td>&lt;0.001$^p$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.013 $\pm$ 0.004$^p$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$Removal rate $\times 10^{-11}$ cm$^3$/s$^{-1}$.
$^{b}$From Adler-Golden [1997].
$^{c}$From Dyer et al. [1997].
$^{d}$Temperature at 223 K [Lacoursiere et al., 2003].
$^{e}$From Chalamala and Copeland [1993].
$^{f}$From Knutsen et al. [1996].
$^{g}$From Dodd et al. [1991].
$^{h}$From Rensberger et al. [1989].
Figure 8. Observed (a) nightglow profiles from SABER channels A and B and their model fits, (b) retrieved atomic oxygen and hydrogen by two methods, and (c) OH density profiles of each vibrational level at day 80 of 2003 for the latitude band of equator $\pm 10^\circ$ (left) fitting only channel A, (middle) fitting only channel B, and (right) fitting both channels simultaneously.
Table 4. Reaction Rate of OH(v) + O → O₂ + H From Published Reports Based on Laboratory and Theoretical Investigations and on Estimates From Airglow Observations*  

<table>
<thead>
<tr>
<th>Reaction Rate</th>
<th>Dependence on Vibrational Level</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>v independent</td>
<td>Adler-Golden [1997]</td>
</tr>
<tr>
<td>10.0</td>
<td>for v = 9, 8</td>
<td>Copeland et al. [2006]</td>
</tr>
<tr>
<td>25.0</td>
<td>v = 2–9; v = 0; v = 1</td>
<td>Makhlouf et al. [1995]</td>
</tr>
<tr>
<td>25.0</td>
<td>for v = 9, 8</td>
<td>Russell and Lowe [2003]</td>
</tr>
<tr>
<td>2.2 × exp(120/ν²)</td>
<td>v independent</td>
<td>Sander et al. [2006]</td>
</tr>
<tr>
<td>5.0</td>
<td>for v = 9, 8</td>
<td>Smith et al. [2010]</td>
</tr>
<tr>
<td>20.0 ~ 30.0</td>
<td>v = 7</td>
<td>Thiebaut et al. [2010]</td>
</tr>
<tr>
<td>5.07, 4.52, 3.87, 3.93, 3.22, 3.68, 3.05, 3.19, 3.42, 2.89</td>
<td>for v = 9, 8, 7, 6, ..., 0</td>
<td>Varandas [2004]</td>
</tr>
</tbody>
</table>

*Reaction rate × 10⁻¹¹ cm³ s⁻¹.

Channel A at 85 km is 1.54 × 10⁻⁷(ergs/cm³/s) but the calculated peak emission rate is 1 × 10⁻⁶ (ergs/cm³/s). The calculated atomic oxygen and hydrogen densities are also much larger than the case of fitting only Channel A. If we fit both channels simultaneously, the calculated nightglow at Channel A is stronger than observed and the calculated Channel B nightglow is weaker than observed. The calculations indicate that it is not possible to fit the nightglow from both channels simultaneously when we are constrained by the OH(v) removal rates from laboratory measurements and the assumption of sudden death quenching. Comparison shows that the calculated atomic oxygen and hydrogen profiles using the fit to Channel A under the sudden death assumption (Figure 8b (left)) are close to the results of multiquantum quenching mechanism (Figure 1c (middle)). Conversely, the calculated atomic oxygen and hydrogen profiles using the fit to Channel B under the sudden death assumption (Figure 8b) are quite different. The choice of quenching mechanism for the model fit has a much stronger effect on the OH(v) airglow emission from the lower vibrational levels.

The fits to the SABER OH emissions indicate that the sudden death model for quenching of OH(v) by O₂ and N₂ does not give satisfactory results. Much better results are obtained when the model includes multiquantum relaxation. From this, we conclude that sudden death of OH(v) by O₂ and N₂ is not the appropriate model for the OH quenching.

4.2. Reaction of OH(v) With Atomic Oxygen

The O + OH(v) reaction is one of the largest uncertainties in the determination of the OH(v) populations. A chemical reaction, OH(v) + O → O₂ + H, is assumed in many chemical models of OH nightglow [e.g., Makhlouf, et al., 1995; Adler-Golden, 1997; Russell and Lowe, 2003; Smith et al., 2010]. A theoretical study by Varandas [2004] also supports this by indicating that the reaction of OH + O → O₂ + H is faster than quenching OH(v) + O → OH(v') + O. Therefore, the assumption of the removal of OH(v') by atomic oxygen (i.e., the sudden death model) is also used in our model.

The range of published values for the OH(v) + O reaction rate is large. Table 4 summarizes some of the reaction rates; these values were determined by laboratory measurements or theoretical calculations or were estimated from modeling of the observed OH nightglow. The reaction rates range from 2 × 10⁻¹¹ cm³ s⁻¹ to 30 × 10⁻¹¹ cm³ s⁻¹. Some determinations assume or conclude that the reaction rates vary depending on the vibration level (i.e., v dependent) while others are v independent.

For the calculations in section 3, we used a single v-independent reaction rate for the removal of OH(v) on collision with atomic oxygen. Here, we test the impact of using v-dependent reaction rates. We take the reaction rate set from Varandas [2004], which is given in the last row of Table 4, as an example because this study provides a complete set of reaction rates for vibrational levels from 0 to 9. Similar to equation (8), we account for these uncertainties in the reaction rates by combining them into a single correction factor β* to be multiplied by all rates. The reaction rate of OH(v) + O → O₂ + H is then expressed as follows:

\[ k_5(v) = \beta^* \times k_5^0(v), \quad v = 0, 1, 2, ..., 9. \]

\[ k_5^0(v), \quad v = 0, 1, 2, ..., 9 \]

are the reaction rates for each vibrational level from Varandas [2004] (see the bottom row of Table 4). As before, we simultaneously fit for the parameter α*, which is applied to the quenching of OH(v) by O₂ (equation (7)).

Figure 9 gives the parameters, β*, and the residual, ε*, determined from the fit in the equatorial region (equator ± 10°) for the period from 2002 to 2008. For comparison, the parameters, β and α, and the residual, ε, are also shown. The latter are determined from equations (7) and (8) with the assumptions that the reaction rate of OH(v) with O₃ is v independent and its magnitude is k₅ = β × 5 × 10⁻¹¹ cm⁻³ s⁻¹. Figure 9 shows that the residuals of the fit calculated by equation (10) and the adjustment factors α of the quenching rate of OH(v) by O₂ are almost the same for the two different assumptions about the nature of the OH(v) quenching by or reaction with O. However, the values of β from the two fits are different. The average adjustment factor for Varandas [2004] is larger (1.78) than for Smith et al. [2010] (1.29). The seasonal variations of the two estimates of β are similar even though the magnitudes are different. The similarity occurs in part because the rate of removal of OH(v = 9) is the same in the work of Smith et al. [2010] as in the work of Varandas [2004]. For the lower vibrational levels, the removal rates from Varandas [2004] are smaller than that from Smith et al. [2010].

To investigate the impact of the two sets of OH(v) + O rates, we take the SABER OH nightglow profiles from day 80 of 2003 for the latitude band equator ± 10° as an example. Figure 10 gives vertical profiles of the relative
residuals of the fits of the two channels of OH airglow, the retrieved atomic oxygen and hydrogen profiles, and the OH(v) densities derived for two fits. The relative residuals of the two fits are almost the same. For the atomic oxygen and hydrogen, there are very small differences between the two fits. The OH(v) densities of the lower vibrational levels calculated using the reaction rates of Varandas [2004] are slightly higher than those calculated using the reaction rate from Smith et al. [2010]. The densities of the higher vibrational levels are very similar in the two fits.

**Figure 9.** Time variation of the quenching rates and the vertical averaged residual of the fit near the equator (equator ± 10°) near midnight (from 00:00 to 02:00 LT) from 2002 to 2008.

**Figure 10.** Profiles comparing two different assumptions about the vibrational level dependence of the OH(v) + O reaction rate: (left) relative errors of the model fits of the two nightglow channels, (middle) retrieved atomic oxygen and hydrogen by the two fits, and (right) OH densities of five vibrational levels (v = 1,3,5,7,9) calculated by the two fits at day 80 of 2003 for equator ± 10° latitude band.
The model fits shown in section 4 indicate that the model is able to fit the observed TIMED/SABER emissions from two OH emission channels using either of two models for the reaction rate of OH(v) + O. In one model of the rate, the reaction is independent of the vibrational level whereas in the other, the rate decreases from higher to lower vibrational levels. The observations do not provide any guidance for determining which of these models is correct. The tests shown in Figure 10 also demonstrate that the retrievals of atomic oxygen and atomic hydrogen are not sensitive to which model is chosen for the vibrational level dependence of the reaction rate of OH(v) with O.

5. Comparison With Ground-Based Observations

The SABER observations use broadband filters and provide only two channels for the OH airglow, containing emissions from the (9–7) + (8–6) and (5–3) + (4–2) vibrational transitions. Additional information about the emissions can be obtained from ground-based observations with more details about the OH nightglow emission bands. The parameters in the theoretical model determined by fitting the SABER observations can be compared with existing ground-based observations. For this comparison, we use the correction factors for the quenching rate parameters of equation (13) to calculate the OH nightglow emissions at every vibrational level. The comparisons use the same time period and latitude bins. It should be noted that the comparisons are qualitative because (1) the ground-based observations and the SABER observation do not observe the same time period; (2) the ground-based observations sample entire nights while the satellite observations are from one local time in a daily observation; (3) in order to increase the data for the satellite analysis, the observations from all longitudes in the latitudinal bin centered at ground-based station are used.

On 15–16 December 1971 at Cold Lake, Alberta (56°N), Harrison and Kendall [1973] observed the hydroxyl airglow bands in the spectral range between 0.6 and 2.3 μm, which correspond to the Δν = 2, 3, 4, and 5 sequences. We calculate the averaged OH airglow emissions for December 2003 in the latitude bin 56°N ± 10 by our model using the parameters established from SABER observation. The observations by Harrison and Kendall [1973] are compared with our results in Figure 11. From Figure 11 we can see that two results are quite consistent with each other except for the (2–0) band. Harrison and Kendall [1973] indicated that there may be large errors in some bands, specifically in (8–6), (8–5), (2–0). There are additional small differences between the two results. These may be in part because the calibration by Harrison and Kendall [1973] assumes that the temperature is 220 K and uses specified midlatitude profiles of water vapor and CO2. Another potential reason for the differences is that the two observations are from different years.

Takahashi and Batista [1981] observed several OH nightglow emission bands at Cachoeira Paulista (22.7°S, 45°W) in Brazil for 64 days during the period from June 1977 to August 1978. For comparison, the averaged OH nightglow emissions at those bands using the parameters determined from the SABER observations for the whole of 2003 are calculated. The calculations are for the latitude bin of 22.7°S ± 10°. The comparisons given in Table 5 show that our modeling results are consistent with the ground-based observations of Takahashi and Batista [1981].
Table 5. Comparison Between This Work and the Ground-Based Observations of Takahashi and Batista [1981]

<table>
<thead>
<tr>
<th>Band (v-v')</th>
<th>Takahashi and Batista [1981]</th>
<th>Present Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_{0,4}/1_{4,4}</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1_{0,4}/1_{4,4}</td>
<td>0.62</td>
<td>0.64</td>
</tr>
<tr>
<td>1_{0,4}/1_{4,4}</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>1_{0,4}/1_{4,4}</td>
<td>1.73</td>
<td>1.90</td>
</tr>
<tr>
<td>1_{0,4}/1_{4,4}</td>
<td>1.14</td>
<td>0.99</td>
</tr>
</tbody>
</table>

[60] Table 6 compares calculations made using our parameters to published results from several additional ground-based observations, made by Turnbull and Lowe [1983], Harrison and Kendall [1973], and Llewellyn et al. [1978]. The results show that our theoretical results are within the range of the observations.

[61] Sivjee and Hamwey [1987] made ground-based observation at Longyearbyen, Spitsbergen (78°N), in December 1984. They found the ratio of intensities between the (8–3) band and (6–2) band is 0.31:1. The results of our theoretical model for January 2004 near the latitude of 78°N show that the ratio of these two bands is 0.35:1.

[62] The comparisons of the theoretical model using the parameters established from SABER observations with a number of published ground-based observations indicate that the new parameters agree well with the independent measurements for a range of latitudes and times of year. The new values give good results even for bands that were not observed by SABER. The comparisons provide further evidence for the conclusion that the chemical reaction (R1) is the dominant chemical reaction source for the OH nightglow emission.

6. Summary

[63] In this paper, we use a chemical model of the OH nightglow along with TIMED/SABER observations of the vertical profiles of the OH nightglow emission rates from two channels to distinguish the dominant mechanism for the OH nightglow emission from low vibrational levels. The two channels observed by TIMED/SABER measure mesospheric hydroxyl airglow volume emission rates at 2.0 μm, emitted by the OH (9–7) and (8–6) vibrational transitions, and at 1.6 μm, emitted by the OH(5–3) and OH(4–2) vibrational transitions.

[64] From the comparison between the model fit and the observations, we conclude that the chemical reaction (R1) (O_3 + H → OH(v ≤ 9) + O_2) is the dominant mechanism for the OH nightglow. The contribution of reaction (R2) (HO_2 + O → OH(v ≤ 6) + O_2) to the OH nightglow is not needed to reproduce the measurements above 80 km, at least for v ≥ 4.

[65] Analysis of the quenching rates shows that best fits are obtained if the parameter C in equation (6), which affects the magnitude of the quenching OH(v) by O_2, is smaller than the value of 4.4 × 10^{-12} cm^3 s^{-1} proposed by Adler-Golden [1997]. The best fit for the quenching rate of OH(v) by O is larger than 5 × 10^{-11} cm^3 s^{-1}, currently used for the analysis of SABER data [Smith et al., 2010]. The temperature dependences of the quenching rates are also estimated in this work. The results show that the rate constant for OH(v) quenching by O_2 in the mesopause region decreases with increasing temperature.

[66] The vertical profiles of the atomic oxygen and hydrogen were determined using both channels of the OH nightglow and the new quenching rates. The results show that the retrieved vertical profiles of atomic oxygen ρ_O(z) and hydrogen ρ_H(z) using both channels are slightly smaller than the profiles of atomic oxygen and hydrogen retrieved using only the 2.0 μm channel with the quenching rates used in the SABER O retrieval by Smith et al. [2010]; that is, with α = β = 1.0. Note that, while we need to use data from both of the SABER OH emission channels to determine the best fits for the quenching rates, we can then use the revised quenching rates to derive O and H using data from a single channel. Tests (not shown) indicate that applying the O retrieval method using the 2.0 μm emission described in the work of Smith et al. [2010], but with the quenching rate corrections presented here, gives O profiles that are quite close to those determined with the least squares fit to the two OH emissions.

[67] The assumption of sudden death quenching of OH(v) by O_2 and N_2 does not give satisfactory simultaneous fits to the two SABER channels of OH nightglow emissions. The results indicate that the sudden death model is not the appropriate quenching mechanism for the OH nightglow emission. We also used the model to fit the observed nightglow with two different assumptions about the reaction rate of OH(v) + O → O_2 + H: either a constant independent of vibrational level or a rate that increases with increasing vibrational level. However, the ability of the model to reproduce the TIMED/SABER observations of OH nightglow was equally good under either assumption. Therefore, we cannot use these observations to determine which is the best value and whether the reaction rates are v dependent or v independent. Comparison of the OH nightglow model derived from TIMED/SABER observations with a variety of published ground-based observations support the conclusions of the paper.

[68] The best fit parameters derived in this study rely on the nighttime SABER retrieved profiles of temperature, ozone, and the OH volume emission rates from two regions in the Meinel band system. The model used in the analysis also uses kinetic reaction rates and Einstein coefficients

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</thead>
<tbody>
<tr>
<td>1_{0,4}/1_{4,2}</td>
<td>0.20</td>
<td>0.20</td>
<td>0.63</td>
<td>0.23</td>
</tr>
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<td>1_{6,4}/1_{4,2}</td>
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<td>0.43</td>
<td>0.23</td>
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<tr>
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<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td>1_{4,2}/1_{4,2}</td>
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<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>1_{0,4}/1_{4,2}</td>
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<td>1.05</td>
<td>0.78</td>
<td>0.87</td>
</tr>
<tr>
<td>1_{2,0}/1_{4,2}</td>
<td>0.55</td>
<td>—</td>
<td>0.43</td>
<td>0.54</td>
</tr>
</tbody>
</table>
for the spontaneous emission of radiation. The analysis of quenching rates has been based on the assumption that the uncertainties in these rates are larger than in other inputs to the model. The sensitivity analysis shows that the systematic errors in the observations and in other physical parameters, such as Einstein coefficients and chemical reaction rates, used in the model would affect the precise values derived by this approach.

Appendix A: Calculation of Einstein Coefficients Based on the HITRAN 2008 Database

[60] Einstein coefficients $A_{v'\rightarrow v''}(T_{\text{rot}})(s^{-1})$ for OH molecules $X^2\Pi$ ($v \leq 9$) can be determined by assuming a Boltzmann distribution of rotational quantum states $J$ at rotational temperature $T_{\text{rot}}$. The thermally averaged transition probability for the vibrational band $v' \rightarrow v''$ can be calculated [Turnbull and Lowe, 1989]:

$$A_{v'\rightarrow v''}(T_{\text{rot}})=\sum_{J' J''} \frac{2(2J'+1)}{Q_{v}(T_{\text{rot}})} \exp \left(\frac{-hcE_{v' f}(J')}{kT_{\text{rot}}}\right) A_{v' J' J''}$$

$$+ \sum_{J' J''} \frac{2(2J'+1)}{Q_{v}(T_{\text{rot}})} \exp \left(\frac{-hcE_{v' f}(J')}{kT_{\text{rot}}}\right) A_{v' J' J''}$$

\[\text{(A1)}\]

where $Q_{v}(T_{\text{rot}})=\sum_{J' J''} 2(2J'+1) \exp \left(\frac{-hcE_{v' f}(J')}{kT_{\text{rot}}}\right) + \sum_{J' J''} 2(2J'+1) \exp \left(\frac{-hcE_{v' f}(J')}{kT_{\text{rot}}}\right)$ is the rotational partition function for the $v'$ vibrational level, $A_{v' J' J''}$ and $A_{v' J' J''}$ are Einstein coefficients for the same state $v'$ and $J'$ with different parities signed with $e$ and $f$, respectively, and $E_{v' f}(J')$ and $E_{v' e}(J')$ are rotational term values corresponding to different parities $e$ and $f$. Here $h$ and $c$ are the Planck constant and light speed, respectively. The Einstein coefficients $A_{v' J' J''}$ from HITRAN-2008 [Rothman et al., 2009] and term values $E_{v' e}(J')$ and $E_{v' e}(J')$ from Bernath and Colin [2009] are used for the computation. All the hydroxyl transition lines ($v \leq 9$) in the HITRAN-2008 were considered in the calculation, including lines from $X^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$ states, $X^2\Pi_{3/2} \rightarrow X^2\Pi_{3/2}$ states, $X^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$ states, and $X^2\Pi_{3/2} \rightarrow X^2\Pi_{3/2}$ states. The calculations show that the temperature dependence of the Einstein coefficients is very weak. For instance, the Einstein coefficients for the $(9 \rightarrow 7)$ vibrational transition for the rotational temperature of 150, 200, and 250 K are 112.8, 112.4, and 112.0, respectively. Therefore, we take a temperature of 200 K in the calculation; this is close to the averaged temperature in the mesopause region. The calculated Einstein coefficients are given in Table A1.

### Appendix B: Method for the Retrieval of Vertical Profiles of O and H and the Correction Factors

[70] The profiles of atomic oxygen and the correction factors are calculated by a least squares fitting (equations (1)–(5)) to observations of OH airglow. For each profile, there are $2n$ measurements at $n$ altitudes. We have $n + 2$ unknowns ($n$ values of atomic oxygen and 2 correction factors); the number of unknowns is much less than the number of observations. The profiles of atomic hydrogen can then be calculated from equation (1) using SABER observations of ozone and temperature and the retrieved atomic oxygen.

[71] The method of calculating vertical profiles of O and H and the correction factors $\alpha$ and $\beta$ is an iteration method, which is divided into four steps. The calculation of profiles of O and H and the two correction factors are made alternately in different steps. The method is as follows:

1. **Step 1:** Use the least squares fitting method to retrieve vertical profiles of atomic oxygen using only the 2.0 $\mu$m channel and assuming $\alpha = 1.0$ and $\beta = 1.0$, which is similar to the method of Smith et al. [2010]. The atomic hydrogen is then calculated by equation (1). The vertical profiles of atomic oxygen and hydrogen are taken as the initial profile for the inversion iteration in the next step.

2. **Step 2:** Use the least squares fitting method to calculate the correction factors $\alpha$ and $\beta$ with the fixed vertical profiles of atomic oxygen and hydrogen calculated in the previous step.

3. **Step 3:** Use the least squares fitting method to retrieve vertical profiles of atomic oxygen using the two channels 2.0 $\mu$m and 1.6 $\mu$m with the correction factors $\alpha$ and $\beta$ retrieved in the previous step. The atomic hydrogen is then calculated from equation (1).

4. **Step 4:** Calculate the deviation $\epsilon$ between the OH nightglow calculated by the theoretical model and the SABER observations using equation (10).

5. **Step 5:** If the deviation $\epsilon$ between the modeled OH nightglow and the SABER observations in this iteration is less than in the previous iteration, return to step 2.

### Acknowledgments
We gratefully acknowledge the SABER team for access to the data. This research was supported by the National Science Foundation of China (40890165, 40921063, and 40874080) and the National Important Basic Research Project of China (2011CB811405).
The project is also supported by the Specialized Research Fund for State Key Laboratories. The National Center for Atmospheric Research is sponsored by the National Science Foundation. The authors thank M. G. Mlynczak of NASA Langley Research Center and D. J. Baker of Utah State University for constructive suggestion and comments on the manuscript. We also thank three reviewers for their insightful comments.

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