

# Observation of night OH in the mesosphere

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[1] Satellite measurements from the Aura MLS instrument show a layer of OH near 82 km in the night. This layer confirms earlier measurements by ground-based LIDAR. The MLS and LIDAR observations measure OH in the lowest vibrational state and are distinct, but related chemically, from vibrationally-excited emission from the OH Meinel bands in the near infrared. The Caltech 1-D model has been extended to include vibrational dependence of OH reactions and shows good agreement with MLS OH data and with observations of the Meinel bands. The model shows a chemical lifetime of HO<sub>x</sub> that increases from less than a day at 80 km to over a month at 87 km. Above this altitude transport processes become an important part of HO<sub>x</sub> chemistry. The model predicts that ground state OH represents 99% of the total OH up to 84 km. Citation: Pickett, H. M., W. G. Read, K. K. Lee, and Y. L. Yung (2006), Observation of night OH in the mesosphere, Geophys. Res. Lett., 33, L19808, doi:10.1029/2006GL026910.

## 1. Introduction

[2] The Aura satellite was launched on July 15, 2004 into a sun-synchronous near-polar orbit. The Microwave Limb Sounder (MLS) instrument on the Aura satellite has the capability to measure OH in both day and night [Waters et al., 2006] using thermal emission from 2.5 THz rotational lines in the ground vibrational state. Further details on the THz module and the OH measurement and calibration are given by Pickett [2006]. Validation of MLS stratospheric OH and HO<sub>2</sub> using balloon-based remote sensing are given by Pickett et al. [2006]. MLS observations of OH taken in a 24.6 s limb scan extend over 18-94 km, although measurements below 35 km require averaging of multiple scans. The spatial sampling near the equator is 1.5° in latitude and  $22.5^{\circ}$  in longitude. The local solar time (LST) at the equator is 13.8 hr and 1.8 hr for the ascending and descending parts of the orbit, respectively. The LST is nearly the same for each orbit (±16 min. seasonally) at a given latitude.

[3] With version 1.51 of the MLS production retrieval software, we have consistently observed a layer of OH near 82 km on the night portion of the orbit. Unfortunately, the retrieved OH from this version of this production software is not recommended above 60 km, due to errors that are understood and will be corrected in v2.0 of the software due to be released in 9/2006. The data presented here use the v2.0 calibration and a special retrieval algorithm.

[4] A night layer in mesospheric OH near 82 km was observed previously with ground-based LIDAR measurements from Table Mountain in Wrightwood, CA [*Brinksma et al.*, 1998]. The LIDAR measurements detect resonant fluorescence of OH in the UV and are sensitive to OH in the ground vibrational state. In contrast, OH airglow measurements in the near infrared are due to emission from vibrationally excited OH generated by reaction of atomic H with  $O_3$ . Satellite measurements of Meinel band night-glow has shown that the vibrationally excited OH has a peak altitude of 87 km [*Zhang and Shepherd*, 1999]. The peak emission altitude is inversely correlated with the strength of the emission [*Yee et al.*, 1997] and also has a seasonal dependence [*Liu and Shepherd*, 2006].

## 2. MLS Observations

[5] The first step in use of MLS emission is to calibrate the data using a procedure that is a slight modification from the calibration described by *Pickett* [2006]. The first change is that the gain is now assumed to have a sinusoidal dependence on orbital phase as well as a constant dependence assumed previously. This change is needed to account for small thermal effects on gain observed in the satellite data (1-4%) over the orbit). The second change is that the radiometric zero is derived only from the space view, while before it was derived from both the space view and the calibration target. This change makes small radiances less sensitive to assumptions about the gain. Both changes will be part of v2.0 level 1 processing.

[6] The second step is to take a difference between the signal in the center OH channel and the average signal in the two adjacent channels. These three channels have a width and separation of 6 MHz. The MLS OH line shape is in the Doppler limit for altitudes above the 1 hPa level. Since the Doppler width of the MLS OH lines is ~6 MHz, the radiance difference ( $\Delta R$ ) is sensitive to mesospheric OH while discriminating against baseline and continuum effects.  $\Delta R$  is still a function of limb observation angle and all data for tangent heights above 1 hPa are used.

[7] The model  $\Delta R$  comes from a simulated forward model calculation for a triangular layer of OH that has a width of 1/6 decade in pressure (~2.6 km) and located at 0.681 Pa. The forward model includes field-of-view and frequency smearing and is corrected for the temperature of the layer. Wider layers are synthesized by shifting the radiance from the triangular layer by a multiple of 1/6 decade spacing and summing to give the radiance expected for a trapezoidal-shaped layer. This layer can have arbitrary mean height but has discrete widths. The calculated  $\Delta R$  vs scan angle can then be interpolated to experimental scan angles. The temperature of the layer and mapping of scan angle and tangent height into tangent pressure uses retrieved temperature and geopotential height vs. pressure obtained from

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**Figure 1.** Distribution of the height of the night OH layer on Sept. 23, 2004. Each point represents a single MLS limb scan and its color indicates the measured width.

v1.51 products for the same scan time. This simplified simulation approach works because the radiance responds linearly to OH concentration and because the limb sounding geometry does not depart substantially from the reference case. This special retrieval is different from level 2 production processing that assumes piecewise linear profiles at fixed pressure intervals.

[8] Figure 1 shows the fitted mean height of the OH night profiles as a function of latitude for Sept. 23, 2004 for solar zenith angles (SZA) >100°. This limit assures that no sunlight illuminates the sampled atmosphere below 100 km. The precision in the fitted height is  $\sim$ 1 km. Figure 2 shows the fitted column of OH for the same day as Figure 1. The precision in the fitted column is 10%. In both Figures 1 and 2, the fitted full width at half maximum of OH density widths (FWHM) are designated with different colors. The global mean FWHM is 8.3 km. The model results to be discussed below are located at the intersection of the two red lines. Note that the fitted column is not correlated with the width, indicating that changes in width conserve the column of OH.



**Figure 2.** Distribution of the column of the night OH layer. See Figure 1.



**Figure 3.** Zonal Mean MLS observations of OH density with SZA of  $>100^{\circ}$  on June 22, 2005. The black line is the height of the 1 Pa pressure level. The vertical white line is the latitude where the noon SZA =  $100^{\circ}$ .

[9] Figure 3 shows the zonal mean of fitted night OH for June 22, 2005, a date chosen to maximize the hemispheric differences. The vertical white line near 76S latitude indicates the latitude below which the SZA is  $>100^{\circ}$  throughout the day. The distribution of the night OH seems unaffected by the absence of sunlight. The black line indicates the height of the 1 Pa pressure surface. Its slope is due to the fact that the mesospheric temperature is 100 K colder in the summer pole than in the winter pole. Clearly, pressure is a better coordinate for the night OH layer than is altitude.

### 3. Model Predictions

[10] A simplified version of the one dimensional Caltech/ JPL photochemical model is used in this study. Detailed descriptions of the model are given by *Allen et al.* [1981]. In the current work, the model involves H, O, and N atoms,



**Figure 4.** Comparison between model results (solid lines) and LIDAR measurements (dotted lines) for July 17, 1996 at latitude 34N, LST time 20.9 hr (red), 21.3 hr (blue). Experimental densities are multiplied by 21.



**Figure 5.** Calculated profiles of the (8–3) band emission rate for Sept. 23, 2004 at latitude 34N, LST 2.20 hr (green), 13.5 hr (red) and 20.0 hr (blue).

25 species, and 155 reactions, with updates of kinetics rate coefficients from *Sander et al.* [2002]. Photodissociation rates are evaluated on-line at each time step, although the effect of scattering has not been taken into account. The model atmosphere consists of 89 vertical layers from 0 to 130 km with vertical resolution of 2 km from 0 to 74 km, 90 to 130 km, and a higher resolution of 0.5 km from 75 to 90 km for the night OH peak. The profiles of temperature and eddy diffusion coefficient, solar flux spectrum are originally taken from *Allen et al.* [1981]. The solar irradiance in the Lyman-alpha region near 121.6 nm is increased by 24% to  $2.969 \times 10^{11}$  photons/cm<sup>2</sup>s in order to correct the variations in the 11 year solar cycle.

[11] An important change is to treat the vibrationally excited states of OH for  $v = 0 \dots 9$  as separate chemical species. The primary source of excitation is the reaction  $H + O_3$  [Nelson et al., 1990]. Quenching of OH vibrational excitation occurs by spontaneous emission in the Meinel bands as well as by collisional relaxation. The model uses recommendations of Adler-Golden [1997] for both quenching mechanisms (see auxiliary material<sup>1</sup>).

[12] The model predictions shown in Figures 1 and 2 show excellent agreement with MLS measurements. Figure 4 shows a comparison with the LIDAR measurements using temperatures and concentrations from MLS for July 17, 2005. Both show a layer at 81 km that is only 1.6 km wide. Other LIDAR measurements show larger widths of the layer consistent with the MLS widths. The model shows less variation of amplitude with time than do the LIDAR measurements. The peak absolute concentration derived from LIDAR is 21 times smaller than the model, but calibration of the absolute value of the return signal is very difficult.

[13] Satellite measurements of this band shows that the OH emission from the (8–3) Meinel band has a peak altitude of 87–89 km and a width of 10 km [*Zhang and Shepherd*, 1999; *Yee et al.*, 1997; *Liu and Shepherd*, 2006]. Figure 5 shows the predicted profile of this band for 3 values of LST. These predictions are in general agreement





**Figure 6.** Calculated chemical lifetime of HOx for Sept. 23, 2004 at latitude 34N.

with the satellite observation as well as previous calculations of *Adler-Golden* [1997].

[14] A key property of hydrogen chemistry is the chemical lifetime since it sets the timescale for influence of dynamics. If we define the HO<sub>x</sub> density to be  $[HO_x] =$  $[OH] + [HO_2] + [H]$ , then the HO<sub>x</sub> lifetime is  $[HO_x]$  divided by the loss rate of HO<sub>x</sub>. Below 60 km the lifetime is less than 600 s and [OH] can be calculated using photochemical equilibrium [*Pickett and Peterson*, 1996]. Figure 6 shows the chemical lifetime at higher altitudes. The striking feature is that lifetime varies dramatically with height. By 85 km (0.42 Pa) the lifetime is 30 days. The explanation for the behavior in Figure 3 near the south pole is that (1) HO<sub>x</sub> (principally H) is generated at sunlit latitudes, (2) is transported poleward above 85 km, and (3) descends to 80 km where H reacts with O<sub>3</sub> at night.

[15] With the importance of vibrationally excited OH established for the studies of airglow, it is reasonable to inquire whether MLS measurements of OH need to be corrected for presence of vibrationally excited OH. Figure 7 shows the concentrations of OH as a function of vibrational level as calculated by the model. From this it is clear that



**Figure 7.** Calculated night profiles of vibrationally excited OH densities for Sept. 23, 2004 at latitude 34N, LST 2.20 hr.

the correction to night OH below 84 km (0.5 Pa) is <1% rising to 20% at 90 km (0.2 Pa). In the day vibrationally excited OH is much lower because  $O_3$  is photo-dissociated. On the other hand, ground state OH is present in significant amounts below 80 km because of other reactions that compete with H +  $O_3$ .

[16] The model also provides insight into the cause of the narrow OH night layer. In the stratosphere and lower mesosphere, [H] is a minor fraction of  $[HO_x]$  and >95% of H combines with O<sub>2</sub> to form HO<sub>2</sub> rather than reacting with O<sub>3</sub>. In the region of 80–85 km, three-body formation of HO<sub>2</sub> becomes less important because the rate depends on square of the total pressure. This increases the [H] fraction and increases the importance of the H + O<sub>3</sub> reaction. At slightly higher altitudes, [O] starts increasing rapidly with height because three-body formation of O<sub>3</sub> from O also depends on the square of pressure. The increase in [O] suppresses both [OH] and [HO<sub>2</sub>] through the reactions with O. The lifetime of HO<sub>x</sub> increases with height because the loss depends on [OH] and [HO<sub>2</sub>], but not directly on [H].

## 4. Conclusions

[17] Observations from Aura MLS of OH in its ground vibrational state show a night layer at 82 km, confirming earlier ground-based LIDAR measurements. A modified version of the Caltech 1-D model predicts a very narrow 1.6 km wide layer that is consistent with narrowest widths observed by LIDAR. However, MLS retrievals show a distribution of widths from 1.6 km to 10.8 km with a global mean of 8.3 km that is most likely due to transport. The model does not include transport (other than vertical eddy diffusion). In future studies, it would be useful to measure the OH LIDAR returns at the same date and time as MLS.

[18] The layer observed by MLS is distinct from Meinelband night-glow emission from vibrationally excited OH. However, examination of the model calculations show that both originate from the  $H + O_3$  reaction. The difference in the altitude of the two layers is due to the effect of pressure on collisional quenching of the vibrational excitation. The Meinel emission is inhibited by collisional quenching while both the emission and quenching favor observation of ground state OH.

[19] The pressure level of 0.42 Pa (85 km) is a critical pressure for OH. For altitudes below this pressure, more than 99% of the OH is in the ground vibrational state and chemistry is local. For altitudes above this pressure, there is an increasing fraction of OH in excited states and the

chemical lifetime is longer than a month. Therefore, modeling of OH at altitudes above this critical pressure requires explicit description of long-term transport as well as explicit inclusion of OH vibrational state dependent chemistry.

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#### References

- Adler-Golden, S. (1997), Kinetic parameters for OH nightglow modeling consistent with recent laboratory measurements, J. Geophys. Res., 102, 19,969–19,976.
- Allen, M., Y. L. Yung, and J. W. Waters (1981), Vertical transport and photochemistry in the terrestrial mesosphere and lower thermosphere (50–120 km), *J. Geophys. Res.*, *86*, 3617–3627.
- Brinksma, E. J., et al. (1998), First lidar observations of mesospheric hydroxyl, *Geophys. Res. Lett.*, 25, 51–54, (Erratum, Geophys. Res. Lett., 25, 521, 1998.).
- Liu, G., and G. G. Shepherd (2006), An empirical model for the altitude of the OH nightglow emission, *Geophys. Res. Lett.*, 33, L09805, doi:10.1029/2005GL025297.
- Nelson, D. D., A. Schiffman, D. J. Nesbit, J. J. Orlando, and J. B. Burkholder (1990), H + O3 Fourier-transform infrared-emission and laser-absorption studies of OH (X<sup>2</sup>Π) radical—An experimental dipolemoment function and state-to-state Einstein-A coefficients, *J. Chem. Phys.*, 93, 7003-7019.
- Pickett, H. M. (2006), Microwave limb Sounder THz module on Aura, IEEE Trans. Geosci. Remote Sens., 44, 1122-1130.
- Pickett, H. M., and D. B. Peterson (1996), Comparison of measured stratospheric OH with prediction, J. Geophys. Res., 101, 16,789–16,796.
- Pickett, H. M., B. J. Drouin, T. Canty, L. J. Kovalenko, R. J. Salawitch, N. J. Livesey, W. G. Read, J. W. Waters, K. W. Jucks, and W. A. Traub (2006), Validation of Aura MLS HOx measurements with remotesensing balloon instruments, *Geophys. Res. Lett.*, 33, L01808, doi:10.1029/2005GL024048.
- Sander, S. P., et al. (2002), Chemical kinetics and photochemical data for use in atmospheric studies: Evaluation 14, *JPL Publ. 02–25*, NASA Jet Propul. Lab., Pasadena, Calif.
- Waters, J. W., et al. (2006), The Earth Observing System Microwave Limb Sounder (EOS MLS) on the Aura satellite, *IEEE Trans. Geosci. Remote* Sens., 44, 1075–1092.
- Yee, J. H., G. Crowley, R. G. Roble, W. B. Skinner, M. D. Burrge, and P. B. Hays (1997), Global simulations and observations of  $O(^{1}S)$ ,  $O_{2}(^{1}\Sigma)$  and OH mesospheric nightglow emissions, *J. Geophys. Res.*, 102(A9), 19,949–19,968.
- Zhang, S. P., and G. S. Shepherd (1999), The influence of the diurnal tide on the O(1S) and OH emission rates observed by WINDII on UARS, *Geophys. Res. Lett.*, 26, 529–532.

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