Night OH in the Mesosphere of Venus and Earth

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Motivation

- Airglow emissions, such as NO and O_2, have been observed on Venus
- Airglow emissions provide insight into chemical and dynamical processes that control the composition and energy balance in Venus’ upper atmosphere
- The OH airglow emission has been observed previously only in the Earth’s atmosphere

1-D Photochemical Model: KINETICS

- For a typical planetary atmosphere, the distribution of species as a function of altitude is governed by the Continuity Equation, dependant on the following parameters:
  - Vertical mixing (eddy diffusion and molecular diffusion)
  - Eddy diffusion at the homopause, K_h
  - Temperature profile
  - Initial mixing ratio of key species at the lower boundary

$$\frac{\partial n_i}{\partial t} + \frac{\partial \phi_i}{\partial z} = P_i - L_i n_i$$

For the Earth...

- Satellite measurements of the terrestrial nightside mesosphere from the Aura MLS instrument show a layer of OH near 82 km.
- These 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 KINETICS model has been extended to include vibrational dependence of OH reactions for the Earth showing good agreement with MLS OH data and with observations of the Meinel bands (Pickett et al, 2006).
- The model shows a chemical lifetime of HO_x 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_x chemistry.
- The model predicts that ground state OH represents 99% of the total OH up to 84 km.

- An important change is to treat the vibrationally excited states of OH for $v = 0 \ldots 9$ 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.

- 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_2 to form HO_2 rather than reacting with O_3.
- In the region of 80 - 85 km, three-body formation of HO_2 becomes less important because the rate depends on square of the total pressure.

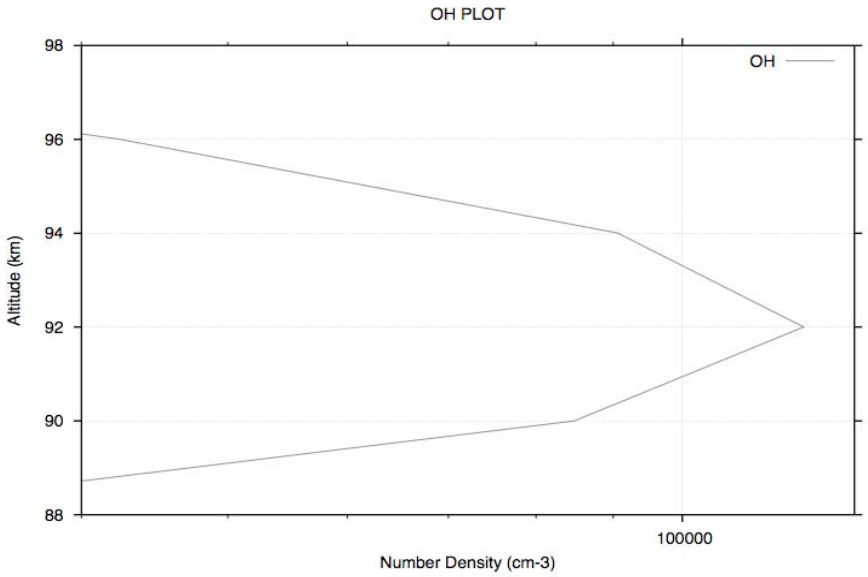
- This increases the [H] fraction and increases the importance of the H + O_3 reaction for Earth.
- At slightly higher altitudes, [O] starts increasing rapidly with height because three-body formation of O_3 from O also depends on the square of pressure.
- The increase in [O] suppresses both [OH] and [HO_2] through the reactions with O.
- The lifetime of HO_x increases with height because the loss depends on [OH] and [HO_2], but not directly on [H].

- Similarly, Venus airglow emissions detected at wavelengths of 1.40−1.49 and 2.6−3.14 μm in limb observations by the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) on the Venus Express spacecraft are attributed to the OH (2−0) and (1−0) Meinel band transitions as well (Piccioni et al., 2008).
- The integrated emission rates for the OH (2−0) and (1−0) bands were measured to be 100±40 and 880±90 kR respectively, both peaking at an altitude of 96±2 km near midnight local time for the considered orbit.

- We begin to use the same Caltech 1-D KINETICS model to model these observations for Venus as was used for the Earth (Pickett et al., 2006) and discuss the conclusions from a comparative planetology perspective, highlighting the similarities and differences between Venus and Earth.
- We have not yet finished the inclusion of higher vibrational excited states of OH as separate species, but can say much...

Key Reactions for OH

- $HO_2 + O \rightarrow OH^* + O_2$ (71% OH) (1)
  - k = 3.00E-11 EXP(200/T)
- $H + O_3 \rightarrow OH^* + O_2$ (<1% OH) (2)
  - k = 1.40E-10 EXP(-470/T)
- $Cl + HO_2 \rightarrow ClO + OH^*$ (22% OH) (3)
  - k = 4.10E-11 EXP(-450/T)
- $SO + HO_2 \rightarrow SO_2 + OH^*$ (6% OH) (4)
  - k = 2.80E-11


OH PLOT
OH
Altitude (km)
98
96
94
92
90
88
100000
Number Density (cm-3)

QuickTime™ and a
decompressor
are needed to see this picture.

- The model shows a chemical lifetime of HO_x that increases from less than 10 minutes at 92 km to about an hour at 100 km and 10 hours at 110 km, MUCH shorter than for the Earth.
- Above this altitude transport processes become a more important part of HO_x chemistry.
- The model predicts that ground state OH represents 99% of the total OH up to these altitudes.
- $H + O_3 \rightarrow OH^* + O_2$ also represents <1% OH concentration, very different from Earth.

Reaction	Venus @ 94km; 162K; ~1mbar	Earth @ 84 km; 220K; ~5mbar
(1) $3x10^{-11}e^{200/T}$	$\sim 1 \times 10^{-10}$	$\sim 7 \times 10^{-11}$
(2) $3x10^{-10}e^{-470/T}$	$\sim 7.7 \times 10^{-12}$	$\sim 1.7 \times 10^{-11}$
(1)/(2)	~13	~4

- For Venus, we have dominance of reaction (1) over (2) above 80 km
- On the Earth, this isn’t true as it is for Venus
- (4) is also a significant source for OH above 80 km, it is small compared to reactions (1) and (3).

- This also allows simplifications in VTGCM modeling since we don’t have to carry H along in the reaction set, nor worry about photolysis H_2O or HCl for production of H, although, photolysis of HCl is required for calculation of distribution of Cl reaction (3) (Please see P4.05 A. Brecht, Thursday May 14)

Conclusions

- Observations of OH in its ground vibrational state show a night layer at ~82 km for the Earth and ~96 km for Venus
- A modified version of the Caltech 1-D model for Earth predicts a very narrow 1.6 km wide layer that is consistent with narrowest widths observed.
- However, the data 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.

- A modified version of the Caltech 1-D model for Venus predicts a wider layer that is consistent with VIRTIS observations.
- Further modeling will elucidate details, but examination of the current model calculations show important H + O_3 --> OH + O_2 reaction for Earth not important for Venus.
- Modeling of OH at altitudes in lower pressure regions require explicit description of longer-term transport as well as explicit inclusion of OH vibrational state dependent chemistry (VTGCM).

- 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 the Earth.
- For altitudes above this pressure, there is an increasing fraction of OH in excited states and the chemical lifetime is longer than a month.