VSRT MEMO #040

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To: VSRT Group

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Subject: Modeling the diurnal variation of ozone

A detailed model is described by Smith and Marsh in the Journal of Geophysical Research, vol. 110, D23305, 2005. This memo describes a simplified version when should be quite accurate for an altitude of about 90 km.

In the upper mesosphere at about 70 km and higher ozone is created by a 3-body collision between atomic oxygen, molecular oxygen and another "catalytic" molecule like nitrogen or another oxygen molecule this reaction is

$$O + O_2 + M \rightarrow O_3 + M$$

where O = Oxygen
O_2 = Oxygen molecule
M = O_2 or N_2
O_3 = ozone

The rate of this reaction is given by a coefficient k_1 times the product of the densities of O_2 and M. The rate of increase of ozone volume mixing ratio (vmr) is given by

$$k_1 \times O_{-vmr} \times \rho \times O_{2-vmr} \times \rho$$

where ρ is the atmospheric number density or the number of molecules per unit volume and

$$k_1 = 6.0 \times 10^{-34} \left(300/T\right)^{2.5} cm^6 s^{-1}$$

The atmospheric number density is given by

$$\rho = p/\left(KT\right)$$

where K = Boltzmann's constant and p is the pressure. At 1 atmosphere $\left(10^3 hPa\right)$ and 273K

$$\rho = 2.7 \times 10^{19} \text{ molecules per cc}$$

The number density of any particular atom or molecules is just vmr times ρ. At p=0.001 hPa and T=170 K the rate of increase in ozone is 8.7×10^{-9} vmr s^{-1}. In the upper atmosphere ozone is destroyed by uv when illuminated (i.e. in the day) at a rate of 10^{-2} so that any ozone created at night will be destroyed in about 100 seconds (the inverse of the rate). Lower down in the atmosphere ozone is not destroyed by the uv because all the uv has been absorbed by the ozone higher up.

At night ozone is destroyed by 2 reactions:

$$O_3 + O \rightarrow O_2 + O_2$$
and
$$O_3 + H \rightarrow OH + O_2$$

of these the reaction with atomic hydrogen is most important because the rate coefficient k_3 is large and given by

$$k_3 = 1.4 \times 10^{-10} \exp\left(-\left(470 \pm 200\right)/T\right)$$

and the destruction rate is

$$k_3 \times H_{-vmr} \times \rho = 3.9 \times 10^{-4} s^{-1} \text{ for } H_{-vmr} = 10^{-6}, p = 0.001 \text{ and } T = 170K$$

After the ozone has built up following sunset there will be a balance between the creation rate and destruction rate so that

$$3.9 \times 10^{-4} \times O_{3-vmr} = 8.7 \times 10^{-7}$$
$$O_{3-vmr} \sim 22\, ppm$$

You will notice that the rate coefficients are very sensitive to temperature, k_3 is the most sensitive and in addition it has a large quoted error in the laboratory measurements.

This model can be formulated in terms of a differential equation which allows the time dependence of the ozone vmr to be estimated as we go from night to day and back to night as illustrated in figure 1. The red curve is for $T = 180K, p = 0.001\, hPa, O_{-vmr} = 10^{-2}, O_{2-vmr} = 0.21, H_{-vmr} = 10^{-6}$ and the blue curve is for T=170K and the expression for k_3 changed to

$$k_3 = 1.4 \times 10^{-10} \exp\left(-330/T\right)$$

This plot is only a preliminary analysis of the data to be used as a future guide. There are still uncertainties in the calibration of the data, the theoretical line shape and the effects of interference. The ozone spectra were converted to an estimate of ozone assuming 2.88 mK/ppm.

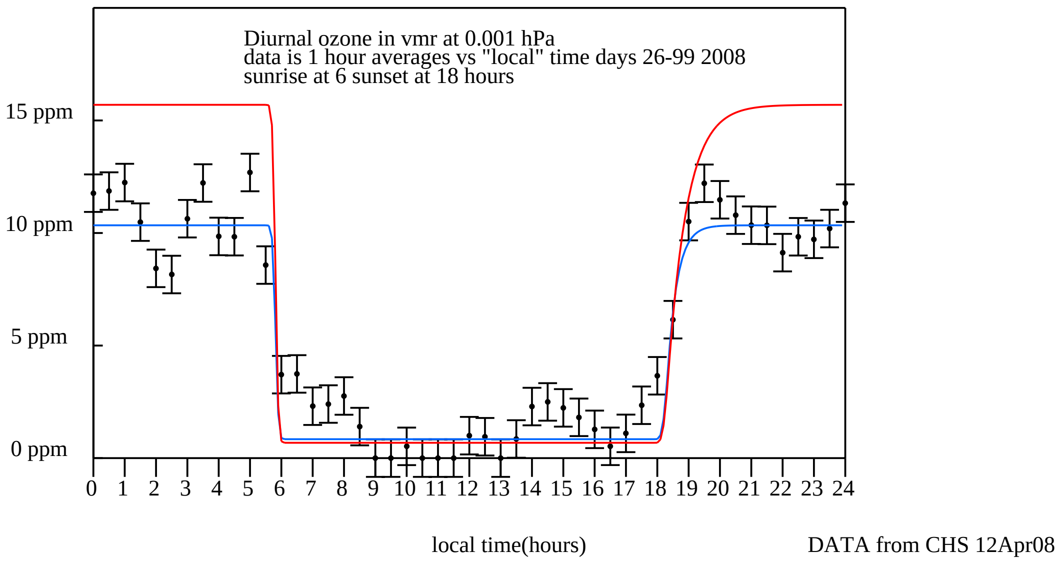

Figure 1. Diurnal variation of mesospheric ozone.