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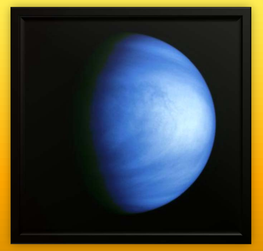

Distribution of H_2O and SO_2 in the upper atmosphere of Venus

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Abstract

The large variability of H_2O and SO_2 in the atmosphere of Venus above the cloud tops (Fig. 1 and 2) is puzzling, especially since there is little evidence for their variability in the lower atmosphere. We note three important related facts: (1) The abundances of H_2O and SO_2 in the deep atmosphere are of the same order of magnitude ~100 ppm, (2) there is a rapid decrease in H_2O and SO_2 just above the cloud tops, resulting in sharp vertical gradients in their vertical profiles, and (3) the primary removal mechanism for H_2O and SO_2 above the cloud tops is formation of H_2SO_4 aerosols. In this work we examine the possibilities that H_2O and SO_2 could be regulated in a chemistry-transport model and that the photolysis of H_2SO_4 could be the source of SO_2 in the Venus mesosphere.

Observations

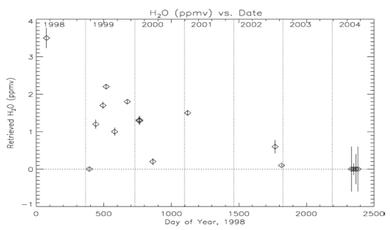


Fig. 1: Disk-average H_2O mixing ratios derived from mm-wave spectra in the Venus mesosphere (65–100 km) (Sandor et al. 2005). The data are shown as a function of measurement date. Error bars indicate 1-sigma s/n uncertainty. Observations show that the Venus mesosphere was drier in December 2002–June 2004 than in March 1998–January 2001.

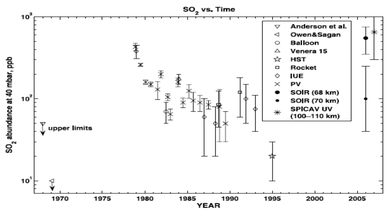
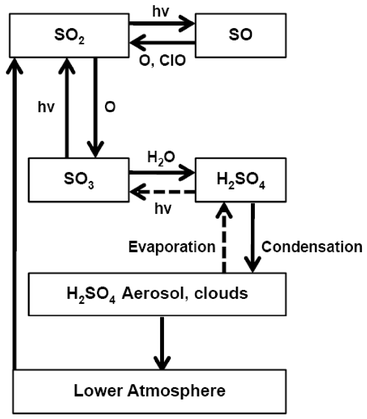


Fig. 2: Measurements of SO_2 on Venus above the clouds, available from 1969 up to now (see Table 2 in Belyaev et al., 2008). The SO_2 content in ppb is at the level of 40 mbar (69 km of altitude).

Chemical Model



The major pathways for the photochemistry of SO_2 above the cloud tops are shown in Fig. 3. SO_2 exchanges rapidly with SO and SO_3. However, formation of H_2SO_4 followed by condensation sequesters SO_2 in aerosol particles and remove it from active chemistry. The reaction that forms H_2SO_4 appears to involve a complex with H_2O:

$$SO_3 + H_2O = SO_3 \cdot H_2O$$

$$SO_3 \cdot H_2O + H_2O = H_2SO_4 + H_2O$$

We adopt the expression for the rate of formation of H_2SO_4 from Lovejoy et al. (1996)

$$R = (2.26 \pm 0.85) \times 10^{-43} Te^{(6544 \pm 106)/T} [SO_2][H_2O]^2$$

Note the extremely large dependence on temperature and the quadratic dependence on the concentration of H_2O. The model we used for this study is based on Yung and DeMore (1982) with updates from Mills (1998) and Yung et al. (2009).

Sensitivity of SO_2

The vertical profile SO_2 has a sharp vertical gradient above the cloud tops due to its rapid loss by conversion to H_2SO_4 aerosols. Hence a change in transport (parameterized by the eddy diffusion coefficient) could result in a large change in the concentration of SO_2 above the cloud tops. The standard model is given by the black curve in Fig. 4. The blue curve is for model in which the eddy diffusion coefficient was multiplied 10 times. Note that at higher altitudes, the changes are on the order of 100, but still not enough to explain the observations above 90 km. Maybe an extra source of SO_2 is needed. We estimated the source from H_2SO_4 photolysis and the result is shown by the red dashed curve.

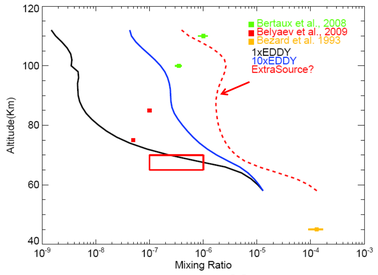


Fig. 4: SO_2 sensitivity to eddy mixing. An extra source for SO_2 (from H_2SO_4 photolysis) is estimated to explain the data. Squares indicate the observations.

Sensitivity of H_2O to the Lower Boundary (at 58 km)

H_2O is removed above the cloud tops by formation of H_2SO_4. As a result, the vertical profile of H_2O falls with height in the standard model (Fig. 5, red curve), where the H_2O at the lower boundary is 100 ppm. As we decrease the H_2O at the lower boundary to 80 and 70 ppm, there is corresponding decrease in the H_2O higher up (green, light blue). As the H_2O concentration at the lower boundary is further lowered to 65 and 60 ppm, there is a sudden falloff of the H_2O above 70 km. The reason is the complete sequestration of H_2O by H_2SO_4 aerosols. Thus, H_2O could exhibit a bifurcation as its value falls below a critical value.

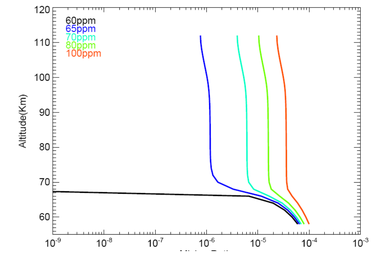


Fig. 5: H_2O sensitivity to lower boundary conditions. Different color refers to different H_2O content at the bottom.

Conclusion

SO_2 and H_2O can regulate each other via formation of H_2SO_4.

Small changes in the transport rates for SO_2 may result in large changes in SO_2 above the cloud tops.

Below a critical value, H_2O could be completely sequestered by H_2SO_4 aerosols.

A combination of the above could explain some of the observed variabilities in SO_2 and H_2O on Venus.

The puzzling observations of SO_2 could be explained if there is a new source of SO_2 in the mesosphere of Venus derived from the photolysis of H_2SO_4.

Reference

Belyaev, D., O. , et al. 2008, First observations of SO_2 above Venus' clouds by means of Solar Occultation in the infrared, J. Geophys. Res., 113, E00B25, doi:10.1029/2008JE003143

Bertaux, J.-L., et al. 2008, SPICAV/SOIR on board Venus Express: An overview of two years of observations, paper presented at 37th COSPAR Scientific Assembly, Montreal, Canada, July 13– 21

Lovejoy E. R., Hanson D. R., and L. G. Huey L. G. 1996, Kinetics and Products of the Gas-Phase Reaction of SO_3 with Water, J. Phys. Chem. 100, 19911

Mills, F.P. 1998, I. observations and photochemical modeling of the Venus middle atmosphere. II. thermal infrared spectroscopy of Europa and Callisto. Ph.D. dissertation, California Institute of Technology, Pasadena, CA, 366pp

Sandor, B. J., and R. T. Clancy 2005, Water vapor variations in the Venus mesosphere from microwave spectra, Icarus, 177, 129– 143

Yung, Y. L., and W. B. DeMore 1982, Photochemistry of the stratosphere of Venus: Implications for atmospheric evolution, Icarus, 51, 199– 247, doi:10.1016/0019-1035(82)90080-X

Yung, Y. L., et al. 2009, Evidence for carbonyl sulfide (OCS) conversion to CO in the lower atmosphere of Venus, J. Geophys. Res., 114, E00B34, doi:10.1029/2008JE003094

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