EPSC
European Planetary Science Congress

Disulfur dioxide and its NUV absorption in the photochemical model of Venus atmosphere

Vladimir A. Krasnopolsky
Moscow Institute of Physics and Technology (PhysTech), Moscow, Russia (vlad.krasn@verizon.net)

Please make sure that your pdf conversion results in a document with a page size of 237 x 180 mm!

Abstract

The Venus photochemical model (Krasnopolsky 2012) is updated by the data on S_2O_2 formation and photolysis (Frandsen et al. 2016) and improved densities of H_2O, OCS, and H_2 at 47 km (Krasnopolsky 2013). The basic model and four versions with small deviations in eddy diffusion and SO_2 at 47 km are presented and agree with the observed variations of CO, H_2O, SO_2, SO, and OCS. Three methods are used to evaluate S_2O_2 abundance sufficient for the NUV absorption, and the required S_2O_2 exceeds the model prediction by a factor of 200. The SO profile by Na et al. (1994) with 12 ppb at 64-95 km significantly exceeds the model below 74 km. If SO $\approx$ 12 ppb at 64 km, then S_2O_2 contributes to but does not completely explain the NUV absorption.

1. Introduction

Frandsen et al. (2016) proved that S_2O_2 is formed by SO + SO + M as cis- and trans-OSSO isomers that dissociate to SO and calculated their absorption spectra. Using the SO abundances of 12 ppb at 64-95 km observed by Na et al. (1994), they calculated abundances of OSSO that appear sufficient to explain the NUV absorption of Venus at 320-500 nm. We will implement the findings by Frandsen et al. (2016) into our photochemical model (Krasnopolsky 2012, Paper I), update the model using the chemical kinetic model (Krasnopolsky 2013), and test the hypothesis of OSSO as the NUV absorber.

2. Updated photochemical model

It was assumed in Paper I that S_2O_2 is formed as the lowest energy isomer S=SO_2 that dissociates to S + SO_2. The formation of OSSO and its dissociation to SO + SO significantly affect the sulfur chemistry in the model that also adopts the OSSO formation and dissociation reaction rates from Frandsen et al. (2016). The model is updated using mixing ratios of

H_2O = 26 ppm, OCS =140 ppb, and H_2 = 8.5 ppb at 47 km from the chemical kinetic model (Krasnopolsky 2013) as the lower boundary conditions. Similar to Paper I, a basic model and four versions with minor variations of eddy diffusion and SO_2 at the lower boundary were calculated (Table). Here eddy diffusion is 7300 cm^2 s^{-1} below h_e increasing to 10^7 cm^2 s^{-1} at 100 km above h_e.

Table. Some data from five versions of the model

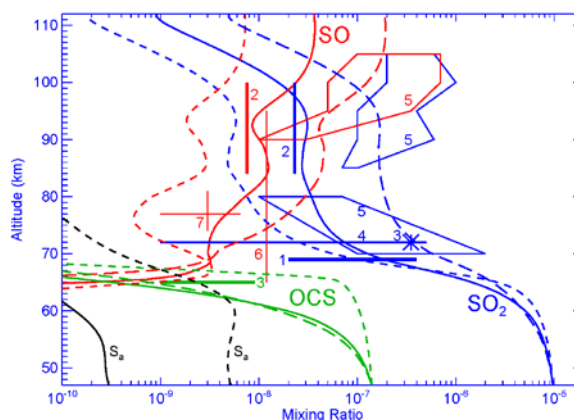| h_e km	SO_2 47 km	H_2O 70 km	SO_2 70 km	SO 90 km	$S_2O_2+h\nu$ cm^{-2} s^{-1}
60	9.7 ppm	3.11 ppm	128 ppb	10.1 ppb	3.91+13
57	9.7	4.38	577	43.4	5.39+13
65	9.7	2.90	57	2.44	5.99+13
60	8.7	5.36	70	6.3	2.77+13
60	10.7	1.48	342	25	5.46+13

Fig. 1. Basic sulfur species: model results (solid, short and long dashes for h_e = 60, 57, and 65 km, respectively) and observations. S_a refers to total number of sulfur atoms in the aerosol. Observations of SO by Na et al. (1994) and Jessup et al. (2015) are (6) and (7).

The model results for the sulfur species SO_2, SO, OCS, and aerosol sulfur S_a are compared with the observations in Fig. 1. Minor variations of eddy diffusion induce variations of the species by a factor

of ≈30 and do not require volcanism. Variations of H_2O in the model and observations are compared in Fig. 2. Again, there is a good agreement between the model and observations.
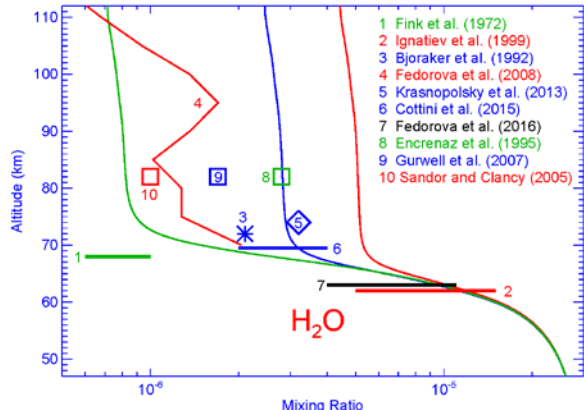

Fig. 2. Vertical profiles of H_2O for SO_2 = 8.7, 9.7, and 10.7 ppm at 47 km (red, blue, and green lines) are compared with the observations.

3. NUV absorption by OSSO

The calculated column photolysis rate of OSSO is 3.9×10^{13} cm^{-2} s^{-1} and peaks at 68 km in a layer of 4 km thick. The NUV absorption at 320-500 nm (Fig. 3) removes 1.9×10^{16} cm^{-2} s^{-1} solar photons and exceeds the OSSO photolysis in the model by a factor of 500. The calculated OSSO column is 2.13×10^{14} cm^{-2} with the cis-to-trans isomer ratio of 0.82/0.18.
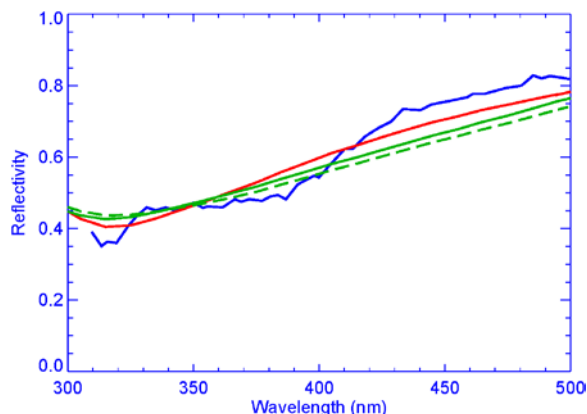

Fig. 3. Observed spectrum of Venus (blue, Barker et al. 1975) is compared with OSSO absorption in a thin layer (red) and for uniformly mixed absorber (green) with the isomer proportion 0.82/0.18 and 0.7/0.3 (solid and dashed curves, respectively). The OSSO abundances in the models are chosen to fit the observation at 350 nm.

The observed spectral reflectivity of Venus is compared with that of OSSO in Fig. 3. The red curve is for a thin absorbing layer above the clouds with OSSO = 2.8×10^{16} cm^{-2} exceeding the model value by a factor of 130. The green curve is for OSSO = 4×10^{16} cm^{-2} uniformly mixed in the upper cloud layer. (The cis-to-trans ratio is 0.7/0.3 in production and 0.82/0.18 in abundances because of the weaker photolysis of cis-OSSO.) This abundance exceeds the model value by a factor of 190. Frandsen et al. (2016) calculated the OSSO densities using SO = 12 ppb at 64-95 km observed by Na et al. (1994). This SO exceeds the recent observations by Jessup et al. (2015, 6.5, 2, and 1 ppb at 74-81 km, Fig. 1) and the model values below 74 km. Even SO from Na et al. (1994) results in an absorption that is weaker than that observed by a factor of 3. The spectral fit by OSSO to the observed NUV absorption is not perfect as well. Even if SO from Na et al. (1994) is valid below 74 km, then OSSO contributes to but does not completely explain the NUV absorption.

Na and Esposito (1997) proposed S_2O as the NUV absorber. They calculated [S_2O] ≈ 5×10^9 cm^{-3} at 64 km, close to that at 47-60 km in our model. However, absorption spectra of gaseous S_2O are lacking.

Strong arguments in favour of $FeCl_3$ diluted to ≈1% in the droplets of sulphuric acid in the upper cloud layer may be found in Krasnopolsky (2017). This species explains the NUV absorption, though contribution of other candidates is not ruled out.

Acknowledgement

References

[1] Barker, E.S., et al., J. Atmos. Sci. 32, 1205-1211, 1975.
[2] Frandsen, B.N., Wennberg, P.O., Kjaergaard, H.G., Geophys. Res. Lett. 43, 11146-11155, 2016.
[3] Jessup, K.L., et al., Icarus 258, 309-336, 2015.
[4] Krasnopolsky, V.A., Icarus 218, 230-246, 2012.
[5] Krasnopolsky, V.A., Icarus 225, 570-580, 2013.
[6] Krasnopolsky, V.A., Icarus 286, 134-137, 2017.
[7] Na, C.Y., et al., Icarus 112, 389-395, 1994.
[8] Na, C.Y., Esposito, L.W., Icarus 364-368, 1997.