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S_3 and S_4 abundances and improved chemical kinetic model for the lower atmosphere of Venus

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ABSTRACT

Mixing ratios of S_3 and S_4 are obtained from reanalysis of the spectra of true absorption in the visible range retrieved by Maiorov et al. (Maiorov, B.S. et al. [2005]. Solar Syst. Res. 39, 267–282) from the Venera 11 observations. These mixing ratios are $f_{S3} = 11 \pm 3$ ppt at 3–10 km and 18 ± 3 ppt at 10–19 km, $f_{S4} = 4 \pm 4$ ppt at 3–10 km and 6 ± 2 ppt at 10–19 km, and show a steep decrease in both S_3 and S_4 above 19 km. Photolysis rates of S_3 and S_4 at various altitudes are calculated using the Venera 11 spectra and constant photolysis yields as free parameters.

The chemical kinetic model for the Venus lower atmosphere (Krasnopolsky, V.A. [2007]. Icarus 191, 25–37) has been improved by inclusion of the S_4 cycle from Yung et al. (Yung, Y.L. et al. [2009]. J. Geophys. Res. 114, E00B34), reduction of the H_2SO_4 and CO fluxes at the upper boundary of 47 km by a factor of 4 in accord with the recent photochemical models for the middle atmosphere, by using a closed lower boundary for OCS instead of a free parameter for this species at the surface, and some minor updates.

Our model with the S_4 cycle but without the $SO_3 + 2$ OCS reaction suggested by Krasnopolsky and Pollack (Krasnopolsky, V.A., Pollack, J.B. [1994]. Icarus 109, 58–78) disagrees with the observations of OCS, CO, S_3, and S_4. However, inclusion of the S_4 cycle improves the model fit to all observational constraints. The best-fit activation energy of 7800 K for thermolysis of S_4 supports the S_4 enthalpy from Mills (Mills, K.C. [1974]. Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides. Butterworths, London).

Chemistry of the Venus lower atmosphere is initiated by disequilibrium products H_2SO_4 and CO from the middle atmosphere, photolysis of S_3 and S_4, and thermochemistry in the lowest scale height. The chemistry is mostly driven by sulfur that is formed in a slow reaction SO + SO, produces OCS, and results in dramatic changes in abundances of OCS, CO, and free sulfur allotropes. The S_X + OCS fraction is constant and equal to 20 ppm in the lower atmosphere. A source of free sulfur on Venus is in the lower atmosphere, and the calculated S_8 mixing ratio is 2.5 ppm above 40 km and results in condensation and formation of aerosol sulfur near 50 km. Therefore the model does not support sulfur as the NUV absorber that was observed by Venera 14 above 58 km. Sources and sinks of the major chemical products in the model are briefly discussed. The model predicts a significant abundance of 3.5 ppb for SO_2Cl_2 above 25 km. This prediction of SO_2Cl_2 as well as that in the photochemical model for the middle atmosphere (Krasnopolsky, V.A. [2012]. Icarus 218, 230–246) may stimulate search for this species. A modified concept of the fast and slow sulfur cycles in the middle and lower atmospheres, respectively, has been presented and discussed. Some sources of the model uncertainty are briefly discussed.

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1. Introduction

The self-consistent chemical kinetic model of the Venus atmosphere below the cloud layer (Krasnopolsky, 2007; hereafter Kr07) is a convenient tool to analyze chemical structure and basic chemical processes in the lower atmosphere. The model was created to respond to the existing data on the chemical composition of Venus' lower atmosphere from the Venera, Pioneer Venus, Vega, and Magellan missions, ground-based observations of the nightside thermal emission in the near infrared (Bezard et al., 1990, 1993; Pollack et al., 1993; Taylor et al., 1997; Marcq et al., 2006), and detection of NO (Krasnopolsky, 2006). That was the first kinetic model for the Venus lower atmosphere, and a lack of rate coefficients for many reactions in the system presented the greatest problem. The lack was partially compensated using similar reactions with known rate coefficients and thermodynamic calculations of constants for inverse processes.

Another significant problem was related to the observed abundances and vertical gradients of OCS and CO. The observed OCS

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