

Vertical profile of H₂SO₄ vapor at 70–110 km on Venus and some related problems

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ABSTRACT

The vertical profile of H₂SO₄ vapor is calculated using current atmospheric and thermodynamic data. The atmospheric data include the H₂O profiles observed at 70–112 km by the SOIR solar occultations, the SPICAV-UV profiles of the haze extinction at 220 nm, the VeRa temperature profiles, and a typical profile of eddy diffusion. The thermodynamic data are the saturated vapor pressures of H₂O and H₂SO₄ and chemical potentials of these species in sulfuric acid solutions. The calculated concentration of sulfuric acid in the cloud droplets varies from 85% at 70 km to a minimum of 70% at 90 km and then gradually increasing to 90–100% at 110 km. The H₂SO₄ vapor mixing ratio is $\sim 10^{-12}$ at 70 and 110 km with a deep minimum of 3×10^{-18} at 88 km. The H₂O–H₂SO₄ system matches the local thermodynamic equilibrium conditions up to 87 km. The column photolysis rate of H₂SO₄ is $1.6 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ at 70 km and $23 \text{ cm}^{-2} \text{ s}^{-1}$ at 90 km. The calculated abundance of H₂SO₄ vapor at 90–110 km and its photolysis rate are smaller than those presented in the recent model by Zhang et al. (Zhang, X., Liang, M.C., Montmessin, F., Bertaux, J.L., Parkinson, C., Yung, Y.L. [2010]. *Nat. Geosci.* 3, 834–837) by factors of 10^6 and 10^9 , respectively. Assumptions of 100% sulfuric acid, local thermodynamic equilibrium, too warm atmosphere, supersaturation of H₂SO₄ (impossible for a source of SO_x), and cross sections for H₂SO₄–H₂O (impossible above the pure H₂SO₄) are the main reasons of this huge difference. Significant differences and contradictions between the SPICAV-UV, SOIR, and ground-based submillimeter observations of SO_x at 70–110 km are briefly discussed and some weaknesses are outlined. The possible source of high altitude SO_x on Venus remains unclear and probably does not exist.

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1. Introduction

Ground-based submillimeter observations of the SO₂ and SO lines (Sandor et al., 2010) in 2004–2008 revealed significant abundances of these species on Venus at 84–100 km. SO₂ varied in 21 observations at different local times at the Venus disk center from 0 to 76 ppb with a mean value of 23 ppb, and the abundances of SO were from 0 to 31 ppb with a mean of 7.5 ppb. According to the observations, both SO₂ and SO are much more abundant at 84–100 km than at 70–84 km. This behavior requires a high-altitude source of SO_x on Venus.

Vertical profiles of SO₂ in the mesosphere of Venus were measured by solar occultations from the Venus Express orbiter. Observations of the SO₂ lines near 3.98 μm using the SOIR spectrograph (Belyaev et al., 2008, 2010) show a decrease in the SO₂ mixing ratio from 65 to 80 km by one or two orders of magnitude with typical values of 10–30 ppb at 80 km. The lines become very weak and unobservable above 80 km. Observations of the SO₂ bands near 210 nm using SPICAV-UV gave vertical profiles of SO₂ from 90 to 110 km with typical values of 100–1000 ppb throughout this

altitude range (Belyaev et al., 2010). The SPICAV-UV observations of SO₂ are impossible above 110 km because of the very low number densities of SO₂. These observations are also impossible below 90 km because “the aerosol extinction is too strong below 90 km in the UV to register any solar signal” (Belyaev et al., 2010). Here we do not discuss a history of the nadir observations of SO₂ on Venus and its long-term variations (Esposito et al., 1988). The latest nadir observations using SPICAV-UV (Marcq et al., 2011) show highly variable SO₂ column abundances with typical SO₂ mixing ratios of 100–1000 ppb. Ground-based high-resolution spectroscopy at 4.04 μm gave a mean mixing ratio of 350 ± 50 ppb at 72 km (Krasnopolsky, 2010a). These data agree with the SOIR occultations (Belyaev et al., 2008, 2010).

Though there are significant differences and even contradictions between the observations of vertical profiles of SO₂, both ground-based submillimeter and Venus Express observations indicate a high-altitude source of SO_x. A photochemical model with photolysis of H₂SO₄ vapor as such a source was recently developed by Zhang et al. (2010). To fit the observations of SO₂ and SO, the model requires very large abundances of H₂SO₄ vapor that reach 1–10 ppm near 100 km.

However, there are sufficient data on the composition and properties of the Venus atmosphere to calculate a vertical profile of

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H₂SO₄ vapor with a reasonable accuracy. That will be a subject of this paper, and then we will discuss the results and compare with some data from Zhang et al. (2010).

2. Vertical profile of H₂SO₄ vapor

2.1. Thermodynamic data

For phase equilibrium between liquid or solid sulfuric acid and H₂O and H₂SO₄ vapors, their partial pressures are equal to

$$\ln p_i = \ln p_{si} + \frac{\mu_i - \mu_i^0}{RT}, \quad (*)$$

(see, e.g., Krasnopolsky and Pollack, 1994). Here subscript $i = 0$ and 1 refers to H₂O and H₂SO₄, respectively, subscript s means saturated vapor, R is the gas constant, T is temperature, and $\mu_i - \mu_i^0$ is the difference of chemical potentials of a species in solution and a pure species. Chemical potentials of H₂O and H₂SO₄ in sulfuric acid as functions of its concentration are given in Giauque et al. (1960) and Zeleznik (1991). They are shown in Fig. 1.

Murphy and Koop (2005) describe the saturated vapor pressure of H₂O over ice by the following relationship:

$$\ln p_{s0} \text{ (bar)} = -1.96250 - 5723.265/T + 3.53068 \ln T - 0.00728332T.$$

This function for the temperature range of 150–300 K is shown in Fig. 1.

The saturated pressure of H₂SO₄ vapor was measured by Stull (1947) at 420–580 K, Ayers et al. (1980) at 338–445 K, and Richardson et al. (1986) at 263–303 K. The H₂SO₄ vapor densities at 338 and 263 K are smaller than that at 420 K by factors of 300 and 10⁶, respectively, and the lowering of the temperature range required much more sensitive laboratory methods. There are some differences between the data from those papers. We will use the results of Richardson et al. (1986) because their sensitivity was much better than those in the previous works and their temperature range is closer to that in the Venus mesosphere. Richardson et al. (1986) measured H₂SO₄ vapor pressure above sulfuric acid with weight concentration of 98.479%, which was equal to

$$\ln p_{s1} \text{ (bar)} = 14.07 - 9360/T.$$

Our correction to the pure H₂SO₄ acid using the chemical potentials from Giauque et al. (1960) gives

$$\ln p_{s1} \text{ (bar)} = 14.07 - 9317/T.$$

This function is shown in Fig. 1 in the temperature range of 150–300 K. The vapor pressure of H₂SO₄ is smaller than that of H₂O by a factor of $\sim 10^8$ at 200 K.

2.2. Some data on the atmosphere of Venus

The vertical profiles of H₂O, HDO, and CO₂ in the altitude range of 70–112 km were measured by solar occultations from Venus Express using the SOIR spectrograph (Fedorova et al., 2008). The analyzed profiles were observed at 22 locations at latitudes 63–88°N. A mean of those H₂O profiles is shown in Fig. 2. There are no published H₂O profiles at the middle and low latitudes. However, the observed H₂O profiles do not show any latitude trend within 63–88°N (see Fig. 12 in Fedorova et al. (2008)) and may be rather typical of the Venus atmosphere.

For the conditions of the H₂O observations we choose a mean of four temperature profiles measured by radio occultations from Venus Express (Tellmann et al., 2009) at latitudes 81–88°N. The profile is in the $T(p)$ format, and its conversion to $T(z)$ and $p(z)$ may be made by integration of the barometric formula:

$$\frac{dp}{p} = -\frac{dz}{H} = -\frac{mg_0 dz}{kT(p) \left(1 + \frac{z}{R_0}\right)^2}; \quad x = \frac{z}{1 + \frac{z}{R_0}} = -\frac{k}{mg_0} \int_{p_0}^p T(p) \frac{dp}{p};$$

$$z = \frac{x}{1 - x/R_0},$$

and $k/mg_0 = 2207.5$ cm/K for $z_0 = 70$ km ($R_0 = 6122$ km).

The obtained temperature and density profiles are shown in Fig. 2. Temperature profiles measured by radio occultations and thermal inversion of the CO₂ band at 15 μm extend typically up to 100 km. The profile is extrapolated to 110 km using some data from Bougher et al. (2010).

The H₂O mixing ratio in the SOIR observations is almost constant at ~ 1 ppm in the altitude range of 75–105 km (Fig. 2). Yung and DeMore (1982) adopted the same H₂O mixing ratio for 56–112 km in their photochemical models three decades ago.

Properties of haze in the mesosphere of Venus were studied from the Venera 9 and 10 (Krasnopolsky, 1980, 1983, 1986), Pioneer Venus (Lane and Opstbaum, 1983), and Venus Express (Wilquet et al., 2009; de Kok et al., 2011) orbiters. There is a reasonable mutual agreement between these publications. We choose a profile of the haze extinction coefficient at 220 nm observed by

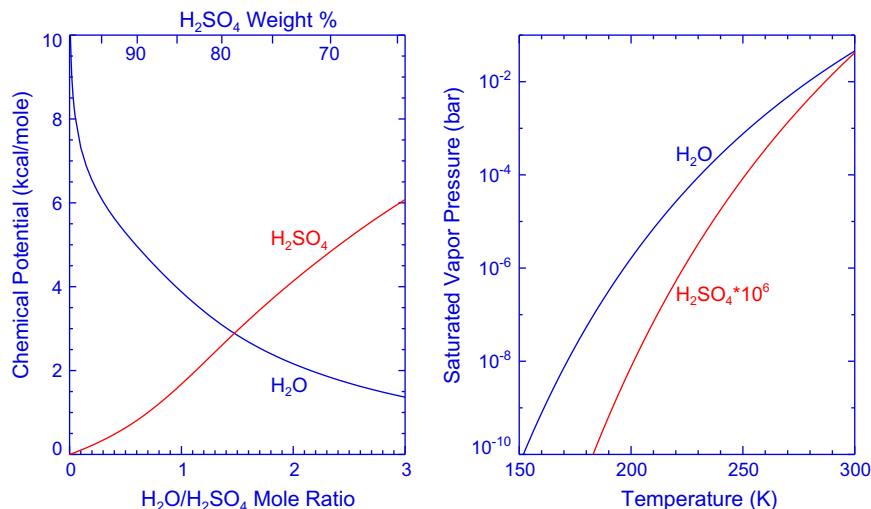


Fig. 1. Left panel: negative chemical potentials of H₂O and H₂SO₄ as functions of the H₂O/H₂SO₄ mole ratio in the sulfuric acid solution relative to the pure substances (Giauque et al., 1960). Right panel: saturated vapor pressures of H₂O and H₂SO₄ as functions of temperature.

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