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Photochemical control of the distribution of Venusian water



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ABSTRACT

We use the JPL/Caltech 1-D photochemical model to solve continuity diffusion equation for atmospheric constituent abundances and total number density as a function of radial distance from the planet Venus. Photochemistry of the Venus atmosphere from 58 to 112 km is modeled using an updated and expanded chemical scheme (Zhang et al., 2010, 2012), guided by the results of recent observations and we mainly follow these references in our choice of boundary conditions for 40 species. We model water between 10 and 35 ppm at our 58 km lower boundary using an SO₂ mixing ratio of 25 ppm as our nominal reference value. We then vary the SO₂ mixing ratio at the lower boundary between 5 and 75 ppm holding water mixing ratio of 18 ppm at the lower boundary and finding that it can control the water distribution at higher altitudes. SO₂ and H₂O can regulate each other via formation of H₂SO₄. In regions of high mixing ratios of SO₂ there exists a "runaway effect" such that SO₂ gets oxidized to SO₃, which quickly soaks up H₂O causing a major depletion of water between 70 and 100 km. Eddy diffusion sensitivity studies performed characterizing variability due to mixing that show less of an effect than varying the lower boundary mixing ratio value. However, calculations using our nominal eddy diffusion profile multiplied and divided by a factor of four can give an order of magnitude maximum difference in the SO₂ mixing ratio and a factor of a few difference in the H₂O mixing ratio when compared with the respective nominal mixing ratio for these two species. In addition to explaining some of the observed variability in SO₂ and H₂O on Venus, our work also sheds light on the observations of dark and bright contrasts at the Venus cloud tops observed in an ultraviolet spectrum. Our calculations produce results in agreement with the SOIR Venus Express results of 1 ppm at 70–90 km (Bertaux et al., 2007) by using an SO₂ mixing ratio of 25 ppm SO₂ and 18 ppm water as our nominal reference values. Timescales for a chemical bifurcation causing a collapse of water concentrations above the cloud tops (> 64 km) are relatively short and on the order of a less than a few months, decreasing with altitude to less than a few days.

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1. Introduction

Venus is the closest planet to the Earth, in terms of both distance and mass. However, the Venus has lost most of its atmospheric and surface water, most likely as an indirect consequence of its greater proximity to the Sun. Hence, much of the carbon dioxide on the Earth that has been processed by the oceans to produce carbonates is still free in the atmosphere of Venus. Subsequently, the Venus atmosphere is very massive by terrestrial standards with a surface pressure of about 92 bar and a relatively high surface temperature at around 725 K. In the modern atmosphere of Venus, chemical

reactions coupled with transport and radiative processes regulate the abundances of the most significant minor constituents. Of the utmost importance are the cycles involving water vapor, sulfuric acid, and their products, which maintain the cloud layers and involve reactions between the atmosphere and the surface.

The atmosphere of Venus can be organized into regions determined by composition, chemistry, and clouds. The upper atmosphere, above ~110 km, has low densities and overlaps with the ionosphere so that photodissociation, ion–neutral, and ion–ion reactions are increasingly dominant with increasing altitude. The middle atmosphere, ~60–110 km, receives sufficiently intense ultraviolet (UV) radiation from the sun so that it is dominated by photochemistry. The lower atmosphere, below ~60 km, receives little UV radiation from the sun, and thermochemistry dominates increasingly with decreasing altitude owing to the high atmospheric temperatures. In the

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region near the boundary between the lower and middle atmospheres are the cloud and haze layers which extend from ~ 30 to 90 km with the main cloud deck lying at ~ 45 –70 km. Competing processes between the middle atmosphere, dominated by photochemistry, and the lower atmosphere, dominated by thermochemistry (Esposito et al., 1997; Mills, 2007) play a key role in this upper cloud deck region. Owing to massive cloud formation, lightning could occur and produce NO (Krasnopolsky, 2007) and heterogeneous chemistry on aerosol and cloud particle surfaces may be important (Mills, 2006; Parkinson et al., 2006; Yung et al., 2009). Finally, in the lowest scale height of the atmosphere a region exists where surface/atmosphere interactions most likely dominate.

Following Yung and DeMore (1982), Krasnopolsky and Pollack (1994), Mills (2006), Yung et al. (2009) and others, three dominant chemical cycles have been identified in the Venus atmosphere: the CO₂ cycle, the sulfur oxidation cycle, and the polysulfur cycle. The CO₂ cycle features photodissociation of CO₂ on the dayside with subsequent transport of a significant fraction of the products, CO and O, to the night side. Also important is the production of O₂, emission of highly variable oxygen airglow on both the day and night sides, and conversion of CO and O₂ into CO₂ via catalytic processes. CO is very abundant (with mixing ratios of the order of a few parts per thousand by volume) in the upper atmosphere of Venus, as would be expected from the action of solar ultraviolet radiation on carbon dioxide. On the other hand, it is strongly depleted in the cloud layers (< 1 ppmv) since it is involved in reactions with SO₂ and the other species that make up the sulfur cycle. However, below the clouds and near the surface, the carbon monoxide value recovers to some few tens of parts per million by volume and shows a marked equator-to-pole increasing gradient (Collard et al., 1993; Taylor, 1995). It seems likely that CO is transported downwards rapidly from the thermosphere in the polar vortices to the troposphere, where it is gradually removed by reactions in the hot lower atmosphere and at the surface.

The sulfur oxidation cycle involves conversion of OCS into SO₂ and its subsequent upward transport, whereupon a significant fraction of the SO₂ is oxidized to form H₂SO₄, which condenses with H₂O to form most of the cloud and haze layers. The sulfuric acid is then transported downwards in the form of cloud droplets, which evaporate back into H₂SO₄ and H₂O vapor below the clouds. The cycle is completed with the production of SO₂ from the thermal decomposition of H₂SO₄. There is solid observational evidence for both the CO₂ and the sulfur oxidation cycles.

The putative polysulfur cycle until recently has been seen as more speculative but plausible based on existing laboratory data and limited observations. Recently, Yung et al. (2009) described an innovative scheme involving the upward transport of sulfur as either SO₂ or OCS, photodissociation to produce S, formation of polysulfur (S_x) via a series of association reactions, downward transport of S_x, thermal decomposition of S_x, and reactions with oxygen and CO to produce SO₂ and OCS, respectively. Each of the cycles involves a number of trace species, such as ClO_x, HO_x, NO_x, and SO_x. The three cycles most likely interact through these trace species. The strength of these links between the cycles in existing models depends on parameters that have significant uncertainties and few constraints from direct observational evidence.

2. Model description

2.1. Photochemistry and chemical kinetics

The JPL/Caltech KINETICS model is a 1-D photochemical model that solves the continuity diffusion equations for the constituent abundances and total number density, n , as a function of radial distance from the planet (Allen et al., 1981). The number densities

of the chemical species are calculated by solving the continuity equation for each species, i ,

$$\frac{\partial n_i}{\partial t} + \frac{\partial \phi_i}{\partial z} = P_i - L_i \quad (1)$$

where the vertical flux ϕ_i is given by

$$\phi_i = \phi_i^k + \phi_i^D \quad (2)$$

The eddy flux ϕ_i^k

$$\phi_i^k = -K \left(\frac{\partial n_i}{\partial z} + \frac{n_i}{H_{av}} \right) \quad (3)$$

represents the vertical flux that parameterizes macroscopic motions, such as the large scale circulation and gravity waves, while ϕ_i^D

$$\phi_i^D = -D_i \left(\frac{\partial n_i}{\partial z} + \frac{(1 - \alpha_i) \partial T}{T} \right) + \frac{n_i}{H_i} \quad (4)$$

is the vertical flux as a result of molecular diffusion. H_i and H_{av} denote the species and atmospheric scale heights, respectively. The thermal diffusion factor, α_i , which is due to temperature gradients has been neglected in our calculations as its inclusion contributed less than 1% to a given species column in test runs (Parkinson, 2002). P_i and L_i are the chemical production and loss rates ($\text{cm}^{-3} \text{s}^{-1}$), respectively, at altitude z and time t (see, e.g., Chamberlain and Hunten (1987), Yung and DeMore (1999)). All the chemistry is contained in the P_i and L_i terms. $D_i(z)$ and $K(z)$ are respectively the molecular and eddy diffusion coefficients. The former is rigorously based on fundamental physics and laboratory measurements. The latter is usually derived empirically from observations of tracers in the atmosphere and is taken from Mason and Marrero (1970) and Atreya (1986) where applicable.

We use the JPL/Caltech KINETICS 1-D photochemical model to produce an atmosphere with number densities of key species as a function of temperature and altitude. Our nominal reference model atmosphere parameters are the species volume mixing ratio, f , at the lower boundary (cf. Table 1) and the eddy diffusion at the homopause, K_h . The standard reference atmosphere used for this paper uses the mixing ratios from the models of Yung and DeMore (1982), Krasnopolsky and Pollack (1994), Mills et al. (2007), Yung et al. (2009), and Zhang et al. (2010, 2012). Also included in Table 1 are the concentration gradient at lower boundary, g , and the fixed flux at top of the atmosphere, ϕ , for some key species.

The photochemistry of the Venus atmosphere from 58 to 112 km is modeled using an updated and expanded chemical scheme from Zhang et al. (2010, 2012) for trace species, such as ClO_x, HO_x, and SO_x combined with the results of recent observations. In this study, the reactions involving the NO_x cycle were found to contribute minimal differences and the main results of the paper are unaffected by not including it. The S_x polysulfur cycles (model B of Zhang et al., 2012) are also not included since it is a separate case and we were only considering Zhang et al. (2012) model A for this study, and so we leave this to future studies. The results from our study and those of Zhang et al. (2012) model A are similar, except differences owing to the lower boundary condition and fixed versus calculated water mixing ratio profiles. Sensitivity studies including an observationally constrained parameter space search of water and SO₂ lower boundary mixing ratios have been considered. Reactions using the peroxychloroformyl radical (ClC(O)OO) described by Per-nice et al. (2004) are included and O₂ column values are within a factor of 2 of what was expected. ClC(O)OO is the key species to convert CO and O₂ to CO₂ (Mills et al., 2007). We use an HCl lower

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