

Photolysis of sulphuric acid as the source of sulphur oxides in the mesosphere of Venus

Xi Zhang^{1*}, Mao-Chang Liang^{2,3,4}, Franck Montmessin^{5,6}, Jean-Loup Bertaux^{5,6}, Christopher Parkinson⁷ and Yuk L. Yung¹

The sulphur cycle plays fundamental roles in the chemistry¹⁻³ and climate^{4,5} of Venus. Thermodynamic equilibrium chemistry at the surface of Venus favours the production of carbonyl sulphide⁶ and to a lesser extent sulphur dioxide. These gases are transported to the middle atmosphere by the Hadley circulation cell^{7,8}. Above the cloud top, a sulphur oxidation cycle involves conversion of carbonyl sulphide into sulphur dioxide, which is then transported further upwards. A significant fraction of this sulphur dioxide is subsequently oxidized to sulphur trioxide and eventually reacts with water to form sulphuric acid³. Because the vapour pressure of sulphuric acid is low, it readily condenses and forms an upper cloud layer at altitudes of 60–70 km, and an upper haze layer above 70 km (ref. 9), which effectively sequesters sulphur oxides from photochemical reactions. Here we present simulations of the fate of sulphuric acid in the Venusian mesosphere based on the Caltech/JPL kinetics model^{3,10}, but including the photolysis of sulphuric acid. Our model suggests that the mixing ratios of sulphur oxides are at least five times higher above 90 km when the photolysis of sulphuric acid is included. Our results are inconsistent with the previous model results but in agreement with the recent observations using ground-based microwave spectroscopy¹¹ and by Venus Express¹².

A model SO₂ profile computed by the Caltech/JPL kinetics model with standard chemistry^{3,10} without the H₂SO₄ photolysis (henceforth model A) is shown in Fig. 1a (black solid curve). The rapid decline of SO₂ mixing ratio with height in the upper cloud region (60–70 km) is in agreement with the recent observations by Venus Express (blue data point)¹³. However, the high SO₂ mixing ratios observed above 90 km from ground-based microwave measurements¹¹ (black dashed line) and from the Spectroscopy for Investigation of Characteristics of the Atmosphere of Venus (SPICAV) solar occultation on board Venus Express¹² (purple curve) clearly exceed the model prediction by orders of magnitude. More information on the SPICAV measurements is available in Supplementary Information.

Although the 90–100 km region is generally considered to be the transition zone between the retrograde super-rotating zonal flow and the global subsolar-to-antisolar circulation¹⁴, it is difficult for any dynamical process such as advection or eddy mixing to transport large amounts of SO₂ from below and maintain a vertical profile that is increasing with altitude. Such a profile is also not likely to be the result of an ephemeral injection event induced by

the atmospheric disturbance, because the high-SO₂-mixing-ratio features have been observed for an extended period^{11,12}. Volcanoes¹⁵ may provide a significant source of SO₂ to the bulk atmosphere, but a recent convective plume model shows that volcano eruption on Venus cannot reach higher than 69 km (ref. 16). Therefore volcanism may only be able to contribute to the long-term natural variability of SO₂ at the cloud top (~70 km; ref. 13), and our model simulations show that the SO₂ variation at the lower boundary of the model (58 km) has a negligible effect on the SO₂ abundance enhancement observed above 90 km.

A more plausible explanation is the existence of a missing source of SO₂ in the upper atmosphere. In this study, we propose that the missing source could be the photolysis of H₂SO₄ vapour derived from evaporation of H₂SO₄ aerosols. The photolysis product SO₃ can be further photolysed by ultraviolet light below 300 nm to yield SO₂. This mechanism is already known to be a significant process during SO₂ formation in the upper atmosphere of Earth¹⁷, but has not been considered in any previous photochemical model for Venus. The new sulphur cycle is summarized in Fig. 2 and the important reactions are listed in Supplementary Table S1.

The concentration of SO₂ depends on the abundance and photolysis cross-section of gaseous H₂SO₄. The H₂SO₄ saturation vapour pressure is determined by the temperature and the concentration of the acid (see the discussion in Supplementary Information) and is calculated using data from ref. 18 and from the rest of the literature. The other two vapour-pressure expressions are used for the sensitivity study (see the discussion in Supplementary Information). Sulphuric acid can be photolysed by Lyman- α and ultraviolet radiation¹⁹, but ultraviolet photolysis is much less efficient than that by visible light (mostly red light ~740 nm) owing to the solar pumping of the vibrational overtones²⁰. The H₂SO₄ hydrates, such as sulphuric acid monohydrate (SAM) (and probably other hydrates, such as sulphuric acid dihydrate, SAD), have larger cross-sections than pure H₂SO₄ vapour by two orders of magnitude²⁰.

Based on the cross-sections of vibrational OH stretching and SOH bending of H₂SO₄ vapour¹⁷, we applied scaling factors to the photolysis cross-sections in the visible region and the H₂SO₄ saturation vapour abundance based on one of the warmest night-time temperature profiles obtained by Venus Express²¹ (see the discussion in Supplementary Information) to carry out the sensitivity study. The SO₂ abundances from the microwave observations and the SPICAV occultation measurements are not fully compatible quantitatively¹¹. This might be the result of

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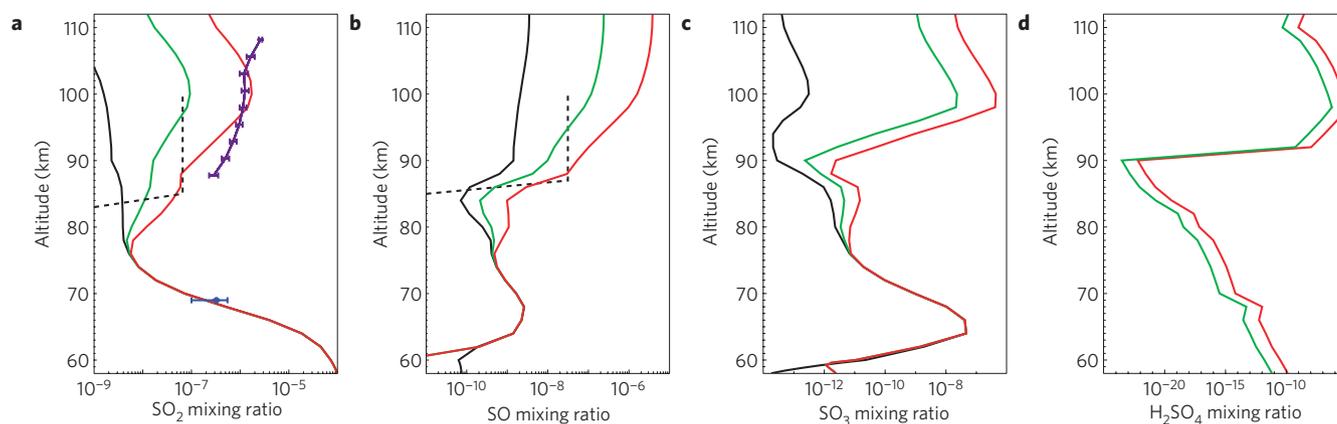


Figure 1 | Model results. **a–d**, SO₂ (**a**), SO (**b**), SO₃ (**c**) and H₂SO₄ (**d**) mixing ratio profiles for models A (black solid), B (green) and C (red). The purple curve with 1- σ error bars is one of the observed SO₂ profiles from Venus Express. The blue data point at ~69 km is taken from ref. 13. The black dashed lines refer to the maximum values of SO₂ (67 ppb) and SO (31 ppb) mixing ratios from the ground-based microwave measurements¹¹.

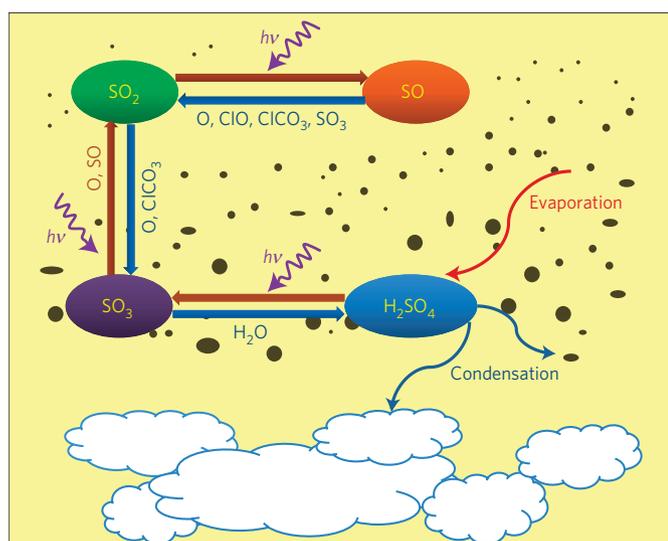


Figure 2 | Illustration of the important reaction pathways connecting SO, SO₂, SO₃ and H₂SO₄.

the spatial and temporal variations of SO₂ (the difference of the observation techniques may also matter; see Supplementary Information for details). Here, we present two models that could successfully produce amounts of SO₂ (green curve from model B and red curve from model C in Fig. 1a) in agreement with the ground-based measurements and Venus Express observations, respectively. Compared with model A, the new mechanism enhances the SO₂ mixing ratios 5–50-fold at 90 km and 50–1,000-fold above 100 km. Model B produces 10 ppb SO at 90 km and 100 ppb at 100 km (green line in Fig. 1b), which is also consistent with the microwave data, whereas that from model A is much lower than the observations. However, the photolysis cross-sections are scaled by 100 in both models, equivalent to adopting the cross-sections of SAM. Therefore the results imply that the hydrates might be the dominant phase of sulphuric acid in the mesosphere of Venus. In fact, according to the phase diagram²², concentrated sulphuric acid (weight per cent larger than 75%) is favoured to be in the forms of SAM and SAD in the Venus mesospheric region, although the estimated abundance of SAM is less than 5% of that of pure H₂SO₄ if we take the equilibrium constants from the previous calculation²⁰ for the terrestrial atmosphere and extrapolate to Venus. Models B and C require H₂SO₄ saturation ratios of 0.5 and 10, respectively. The higher H₂SO₄ saturation ratio (10 for

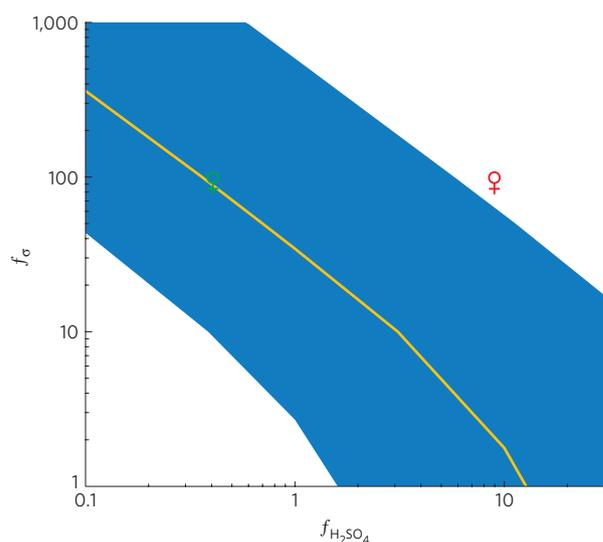


Figure 3 | Parameter space for possible solutions. The blue shaded area shows the parameter space within which the model predicts SO₂ mixing ratios between 0.01 ppm and 1 ppm at 100 km. The horizontal coordinate is the saturation ratio of the H₂SO₄ vapour, and the vertical coordinate is the scaling factor of H₂SO₄ photolysis cross-section. The yellow line refers to the maximum values of SO₂ (67 ppb) from the microwave measurements in ref. 11. Models B and C are labelled with the green and red Venus symbols, respectively.

model C) can be achieved if the aerosol nucleation time is long, because the actual H₂SO₄ vapour abundance is determined by the chemical production rate and the loss rate to the condensed aerosols²³. Evidence of such supersaturation has been found in the lower stratospheric aerosol layer (below 25 km) on Earth, where the sulphuric acid abundances are larger than its saturation vapour pressures by two orders of magnitude²⁴. At the tropopause, where the temperature is the lowest, the saturation ratio of gaseous H₂SO₄ can be as large as a thousand.

A sensitivity study is summarized in Fig. 3. In this parameter space, each point refers to a photochemical model with a specific H₂SO₄ vapour saturation ratio and a photolysis cross-section scaling factor. The blue shaded area highlights the parameter space where the model produces an SO₂ mixing ratio between 0.01 ppm and 1 ppm at 100 km. The shape of the contour lines suggests that, for a given SO₂ mixing ratio, the required H₂SO₄ vapour saturation ratio and photolysis cross-section scaling factor are approximately

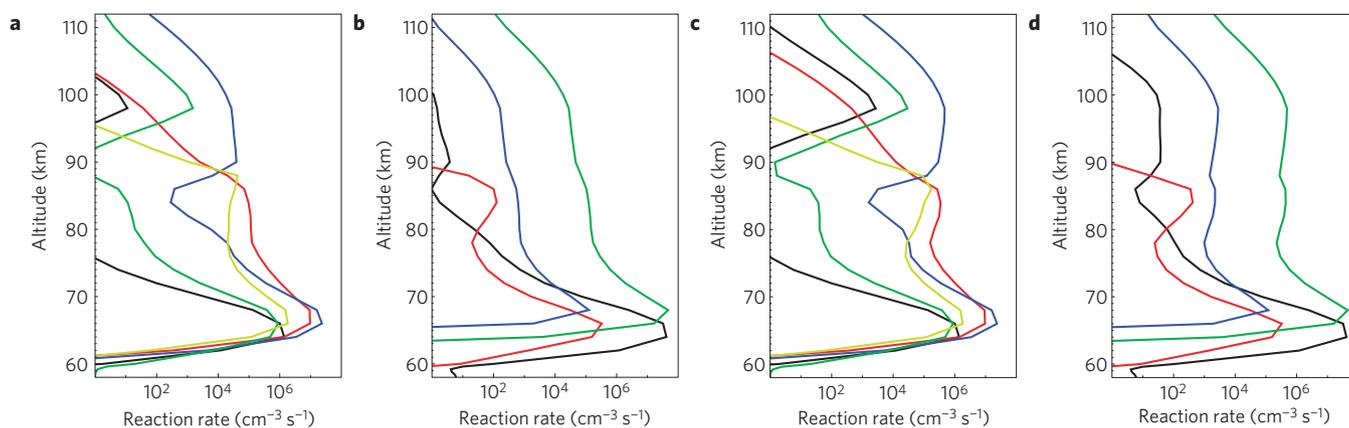


Figure 4 | Production/loss-rate profiles of SO₂. **a–d**, Rates of important reactions involved in producing (**a** and **c**) and destroying (**b** and **d**) SO₂ for models B (**a** and **b**) and C (**c** and **d**). Different colours refer to different reactions listed in Supplementary Table S1. **a,c**, R4:SO₃ + hv (green), R6:ClO + SO (red), R9:O + SO (blue), R10:ClCO₃ + SO (light green), R15:SO + SO₃ (black). **b,d**, R2:SO₂ + hv → S + O₂ (blue), R3:SO₂ + hv → SO + O (green), R12:O + SO₂ (black), R13:ClCO₃ + SO₂ (red).

inversely proportional to each other. In other words, the amount of SO₂ produced in the mesosphere of Venus is proportional to the total number of photons absorbed by the sulphuric acid vapour. Because the H₂SO₄ saturation vapour pressure is highly dependent on the temperature profile and the concentration of the acid, the observed temporal and spatial variations of SO₂ abundance^{11,12} could result from the temperature variations²¹ and also relate to the change of the water-vapour abundance²¹ in the Venus mesosphere.

The main production/loss-rate profiles of SO₂ as functions of altitude are shown in Fig. 4. The upper panels (a and b) and lower panels (c and d) refer to models B and C, respectively. The profiles from the two models have similar patterns but differ in magnitude. The main sources of SO₂ are the photolysis of SO₃, as well as the oxidation of SO by peroxychloroformyl radical (ClCO₃) and monochlorine monoxide (ClO) below 90 km and by the three-body reaction with an oxygen atom in the upper atmosphere, but SO₂ can be quickly destroyed through photolysis and produce SO and sulphur atoms. Therefore, the net production of SO₂ is through the photolysis of SO₃. The fast recycling between SO and SO₂ results in a steady state between these species. This implies that there are comparable amounts of SO (Fig. 1b) and SO₃ (Fig. 1c). Models B and C predict about 0.1–1 ppm SO and 0.01–0.5 ppm SO₃ at 100 km, values that should be compared with 2 ppb and 0.3 ppt, respectively, predicted by model A. The ground-based microwave measurements have already shown the agreement with the SO abundances from model B. More future measurements are needed to verify the profiles of SO and SO₃. The H₂SO₄ mixing-ratio profiles (Fig. 1d) used in the new models have peak values of 0.25–5 ppm at 100 km, which should also be observable.

In summary, H₂SO₄ photolysis could play a dominant role in producing an enhanced amount of SO₂ and SO in the mesosphere of Venus. The sensitivity study suggests that the model successfully approximates the observations only when we posit a very large abundance and large photochemical cross-section of H₂SO₄, which might imply that the SAM and SAD would be the dominant phase of H₂SO₄ in the mesosphere of Venus. The concentration and photodissociation cross-sections of H₂SO₄ are the two main uncertain parameters in our model. The uncertainty arises from the difficulties in determining the H₂SO₄ saturation vapour pressure and the phase of H₂SO₄ hydrates, and from the lack of photolysis data. In the literature, the H₂SO₄ saturation abundance is calculated based on the expression in ref. 18, which is larger than the other two experiments and one of the warmest night-time temperature profiles ever measured in the Venus mesosphere²¹. Therefore the saturation ratios of H₂SO₄ should be regarded as a lower estimate. The H₂SO₄

profile should be verified by future laboratory measurements in the temperature range 150–300 K and a more detailed microphysical aerosol coupled photochemical model such as that in ref. 25. On the other hand, more experimental work is needed to investigate the molecular dynamics of the photolysis of SAM to determine the relative yield of the branch that produces SO₃ and 2H₂O versus that of an alternative branch²⁶ that results in the products H₂SO₄ and H₂O. In the event that the photolysis of H₂SO₄ is insufficient to provide a source of sulphur oxides in the upper atmosphere, another possibility is the oxidation of polysulphur (S_x) to SO₂. S_x is a leading candidate for the unknown ultraviolet absorber^{27,28} and can be formed from photolysis of OCS near the cloud tops, followed by transport to the upper atmosphere. The transport of the chemical tracers (for example, aerosols, polysulphur) will provide a test of the complicated dynamics of the transition zone in the mesosphere of Venus. As there is a high degree of similarity between the upper haze layer on Venus and the terrestrial stratospheric sulphate layer (Junge layer), which is an important regulator of the Earth's climate and the abundance of ozone, these experimental and modelling results may be relevant to stratospheric aerosol chemistry and the applications of this chemistry for geoengineering of the Earth's climate, as recently suggested in refs 29 and 30.

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Author contributions

X.Z., Y.L.Y., C.P. and F.M. contributed to the paper writing. X.Z. carried out the modelling work; M-C.L. helped with the modelling; F.M. and J-L.B. provided the data from the SPICAV instrument on board Venus Express; C.P. provided critical evaluation of the H₂SO₄ photolysis data; Y.L.Y. conceived and supervised the research.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://npg.nature.com/reprintsandpermissions>. Correspondence and requests for materials should be addressed to X.Z.

Supplementary Material for ‘Photolysis of sulphuric acid as the source of sulphur oxides in the mesosphere of Venus’

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In this supplementary material, we will first provide the details of the SPICAV solar occultation measurements of sulphur dioxide at the terminator in section 1. In section 2 we will show how we obtain the H₂SO₄ saturation vapor pressure (SVP) for this study, and discuss the uncertainties of our calculation and the other possible factors that might influence the H₂SO₄ SVP in the Venus mesosphere. The Caltech/JPL kinetics photochemical model is described in section 3. The model parameters and the chemical reaction rates of other sulphur oxides (SO and SO₃) are also presented.

1. SPICAV measurements

Solar occultation is known to be one of the most reliable and accurate techniques to probe planetary atmospheres. It requires no instrument calibration and is only based on the simplest laws of radiative transfer. Spectroscopy for Investigation of Characteristics of the Atmosphere of Venus (SPICAV) onboard Venus Express (see previous publications¹⁻² for more description) has provided a wealth of high-quality data through this technique during several orbits since 2006. The solar occultation performed by SPICAV probes the state of the atmosphere at the terminator, which is known to possess a very peculiar dynamical regime with downwelling and upwelling motions streamlining close together, potentially creating strong spatial contrasts at small scales that are unattainable by the sub-mm JCMT beam from the ground-based measurement. This could be one of the possible reasons that cause the incompatible SO₂ abundances from the two observation techniques³. However, both of the ground-based sub-mm spectroscopy³ and the Venus Express occultation measurements⁴ suggest the presence of an unexpected separate SO₂ layer above 90 km in the Venus mesosphere.

The observed SO₂ profile used in Fig. 1a is taken in orbit 334, at longitude 315.7°, latitude -10.2° and the local time 18h. Errors on SO₂ concentrations are established during spectral inversion as a by-product of the Levenberg-Marquardt routine used for the chi-square minimization (square root of the diagonal terms in the covariance matrix). They are then propagated after vertical inversion following. Error bar determination employs the same procedure as the one used to derive O₃, CO₂ and aerosol profiles on Mars with SPICAM⁵⁻⁷.

2. H₂SO₄ saturation vapor pressure (SVP)

The SVP of sulphuric acid is determined by the relative humidity of H₂SO₄-H₂O solution and the atmospheric temperature. The weight percent of sulphuric acid is assumed to be 85% for the upper clouds⁸ and 75% for the upper haze layer⁹ at about 70-90 km. Recent solar occultation measurements by SPICAV/SOIR onboard Venus Express¹⁰ suggest a bimodal distribution of particle sizes if one assumes that the haze droplets are composed of 75% H₂SO₄, and the same measurements suggest that only very small size particles (less than 0.2 micron) exist above 90 km. Since there are more collisions of aerosol particles with H₂O molecules than with H₂SO₄ molecules, the sulfate aerosol will quickly establish equilibrium with respect to water. The relative humidity of H₂O in the mesosphere decreases with height above the cloud top because the temperature is increasing and the mixing ratio of water vapor is decreasing with altitude¹¹. Therefore, the weight percent of the droplets could be larger than 75%, which results in higher H₂SO₄ vapor pressure. The more highly concentrated H₂SO₄ has a higher extinction coefficient due to the Lorentz relation¹², leading to even smaller retrieved particle size. Therefore, the Kelvin effect¹³, by which vapor pressure increases over a curved interface,

would become more important and enhance the gaseous H₂SO₄ abundance in the mesosphere.

Stull's measurements¹⁴ of the SVP of H₂SO₄ can be fitted by the expression $\log_{10}P(\text{H}_2\text{SO}_4) = -3954.90/T + 9.4570$, for a temperature range approximately between 420 K and 580 K, where $P(\text{H}_2\text{SO}_4)$ is the SVP of H₂SO₄ in mmHg and T is temperature. Fig. S1 shows this in comparisons with the expression from Richardson et al.¹⁵ given by $\log P(\text{H}_2\text{SO}_4) = (20.70 \pm 1.74) - (9360 + 499)/T$ and the expression from Ayers et al.¹⁶ corrected by Kulmala and Laaksonen¹⁷. We see from this difference in the three SVP expressions that we can obtain significantly difference SVP values for temperature values of interest to the mesosphere of Venus (grey area in Fig. S2). Over the temperature range of our model atmosphere, our calculation shows that the SVP from Stull is larger than that from Ayers et al. by a factor of ~1000 and ~20, and larger than that from Richardson et al. by a factor of ~12 and ~7, corresponding to 179 K (0.0036 K⁻¹) at the bottom of our model atmosphere and 274 K (0.0056 K⁻¹) at the top. Thus, the expression from Stull allows for the SVP of H₂SO₄ to be large enough to produce higher concentrations of SO₂ at ~100 km. If even higher values for the SVP were used as in our sensitivity study, higher abundances of H₂SO₄ at 100km would be obtained, resulting in even higher concentrations of SO₂ as observed by Belyaev et al.⁴. The expression from Stull has been used by Wong et al.¹⁸ and Parkinson et al.¹⁹. The actual H₂SO₄ vapor mixing ratio is dependent on a number of factors, including water abundance, sulphuric acid concentration, degree of supersaturation, and the range of validity of the SVP extrapolation¹⁸.

3. Photochemical model

The Caltech/JPL kinetics photochemical model solves the continuity equation for all important species in the Venus atmosphere above the cloud top and includes the oxygen, chlorine and sulphur chemistry recommended by Yung et al.²⁰ and Mills²¹ with updated reaction coefficients. The model covers the Venus atmosphere from 58 km (cloud top) to 112 km. Table S1 lists the important reactions involving SO, SO₂ and SO₃.

Venus is a slowly rotating planet with very high temperature contrast between its day side and night side. The unexpected warm layer on the night side at about 90 km was detected by SPICAV and is believed to be the result of adiabatic heating by downwelling motion on the night side¹¹. The aerosol particles would evaporate when transported by winds to the night side. In this study, we adopt the temperature profile measured in orbit 104 at latitude 4° S and local time 23:20 h (black curve in the Fig. 1 of Bertaux et al.¹¹). This temperature profile has a peak value about 234K around 97km which is larger than the other measurements²²⁻²⁵ by 40-50 K. Fig. S2a shows the daytime and nighttime temperature profiles.

Fig. S2b shows the H₂SO₄ saturated vapor mixing ratio profiles given by Stull¹⁴. In this study, the H₂SO₄ vapor pressure is calculated based on H₂SO₄ weight percent as 85% below 70 km, 75% from 70 to 90 km and 100% (i.e., pure sulphuric acid) above 90 km. We applied a scaling factor to the saturation ratio on the night time H₂SO₄ SVP profile above 90 km for the sensitivity study. The observed SO₂ mixing ratio at ~69 km by Solar Occultation in the Infrared (SOIR) instrument onboard Venus Express is larger than 0.1 ppm and agrees with the natural variability of SO₂ with time above the cloud top, which is a well-known problem²⁶. It may indicate either there is more SO₂ within the clouds or the eddy mixing processes above the cloud top transport the SO₂ more efficiently. In this study, SO₂ mixing ratio at the lower boundary is set at 100 ppm to reproduce the data.

However, this adjustment has no effect on the SO₂ abundances above 90 km. The eddy mixing coefficient profile from Mills²¹ is shown in Fig. S2c.

Figures S3 and S4 show the main production/loss rate profiles of SO and SO₃ as function of altitude, respectively. The upper panels (a and b) and lower panels (c and d) in each figure refer to models B and C, respectively. Each curve corresponds to a reaction in Table S1. The main sources of SO are the SO₃ photolysis and the oxidization of sulphur atoms, and the main loss is through photolysis to yield sulphur atoms in the upper atmosphere. SO is also oxidized back to SO₂ by the reactions with O, ClCO and ClCO₃. Without H₂SO₄ photolysis, SO₃ is only produced by SO₂ reacting with O and ClCO₃, the reaction rates of which decrease rapidly with altitude. Therefore, only photodissociation of sulphuric acid is able to provide the SO₃ source in the mesosphere of Venus. SO₃ is mostly destroyed by the photolysis and reacting with water to form H₂SO₄ and also can be reduced to SO₂ by reacting with SO and O atoms. The important reaction pathways of sulphur chemistry are summarized in Fig. 2 of the main text.

Figure Legends

Figure S1 | H₂SO₄ saturation vapor pressure as function of temperature. Three SVPs are calculated by Stull¹⁴ (red), by Richardson et al.¹⁵ (green), and by Ayers et al.¹⁶ corrected by Kulmala and Laaksonen¹⁷ (blue). The filled diamonds indicate the ranges of the experimental data. The gray area shows the temperature range of the Venus mesosphere.

Figure S2 | Model parameters. **a**, daytime (black) and nighttime (red) temperature profiles as function of altitude. **b**, H₂SO₄ saturated vapor pressure profiles corresponding to the temperature profiles on the left. **c**, eddy diffusion coefficient profile from Mills²¹.

Figure S3 | Rates of important reactions involved in producing (a and c) and destroying (b and d) SO for models B (a and b) and C (c and d). Different colors refer to different reactions listed in Supplementary Table S1. For panels **a** and **c**, R3 (blue), R7 (red). For **b** and **d**, R1 (purple), R6 (blue), R9 (green), R10 (light green), R11 (black), R15 (red).

Figure S4 | Rates of important reactions involved in producing (a and c) and destroying (b and d) SO₃ for models B (a and b) and C (c and d). Different colors refer to different reactions listed in Supplementary Table S1. For **a** and **c**, R5 (black), R12 (red), R13 (blue). For **b** and **d**, R4 (black), R8 (red), R14 (blue), R15 (green).

Table S1

^a Important Reactions Involving SO, SO₂ and SO₃

Reaction	Rate Constant ^b	Reference
(R1) SO → S + O	3.61×10^{-4}	c
(R2) SO ₂ → S + O ₂	1.38×10^{-6}	c
(R3) SO ₂ → SO + O	1.92×10^{-4}	c
(R4) SO ₃ → SO ₂ + O	3.94×10^{-5}	27
(R5) H ₂ SO ₄ → SO ₃ + H ₂ O	2.72×10^{-7}	28
(R6) ClO + SO → Cl + SO ₂	2.80×10^{-11}	29
(R7) S + O ₂ → SO + O	2.30×10^{-12}	29
(R8) SO ₃ + H ₂ O → H ₂ SO ₄	$2.26 \times 10^{-43} T e^{-(6544/T)} [\text{H}_2\text{O}]$	30
(R9) O + SO + M → SO ₂ + M	$k_0 = 4.50 \times 10^{-27} T^{1.6}$	31-32
(R10) ClCO ₃ + SO → Cl + SO ₂ + CO ₂	1.00×10^{-11}	c
(R11) SO + SO + M → (SO) ₂ + M	$k_0 = 4.40 \times 10^{-31}$ $k_\infty = 1.00 \times 10^{-11}$	c
(R12) O + SO ₂ + M → SO ₃ + M	$k_0 = 4.00 \times 10^{-32} e^{-(1000/T)}$	33
(R13) ClCO ₃ + SO ₂ → Cl + SO ₃ + CO ₂	1.00×10^{-15}	c
(R14) O + SO ₃ → SO ₂ + O ₂	$2.32 \times 10^{-16} e^{-(487/T)}$	34
(R15) SO + SO ₃ → 2SO ₂	2.00×10^{-15}	35

^a The model includes all reactions from Mills (1998)²¹.

^b M represents the third body such as CO₂ for three-body reactions. Two-body rate constants and high-pressure limiting rate constants for three-body reactions (k_∞) are in units of cm³s⁻¹. Low-pressure limiting rate constants for three-body reactions (k_0) are in units of cm⁶s⁻¹. Photolysis coefficients (J values) refer to the top of mesosphere (112 km in the model).

^c See discussion in Mills (1998)²¹ and references therein.

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Figure S1

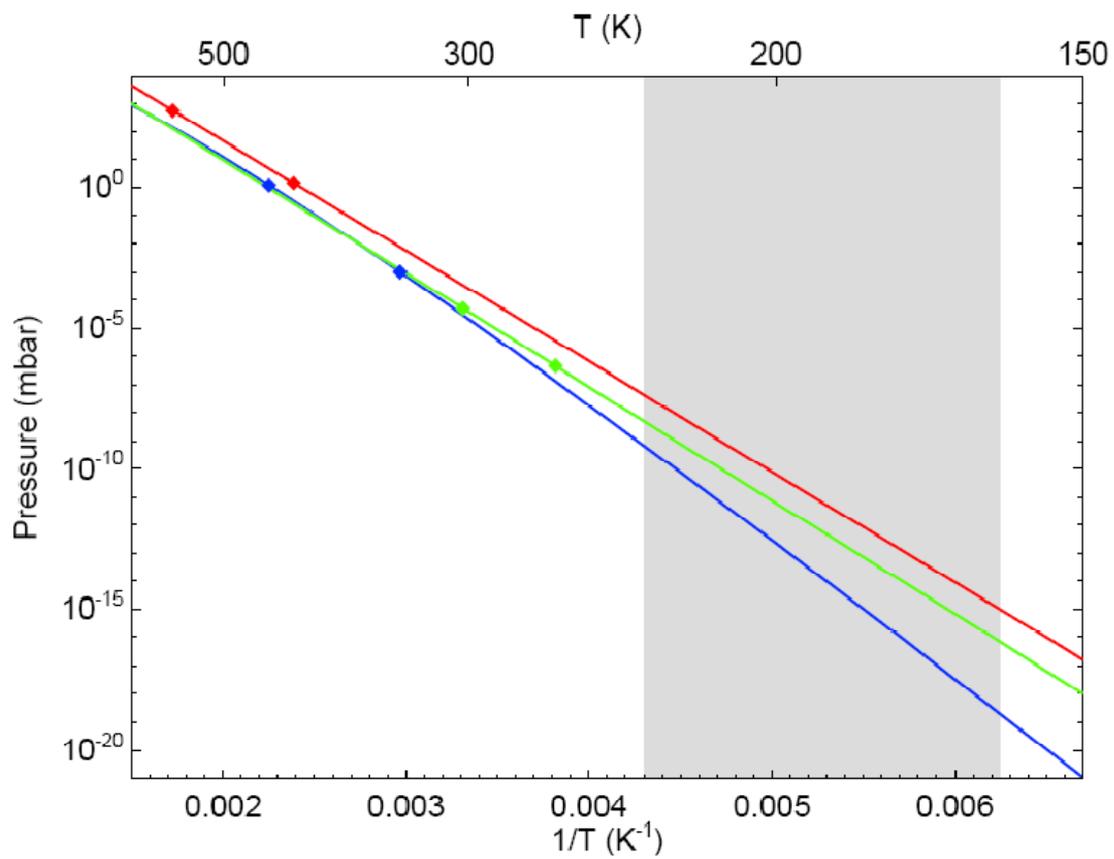


Figure S2

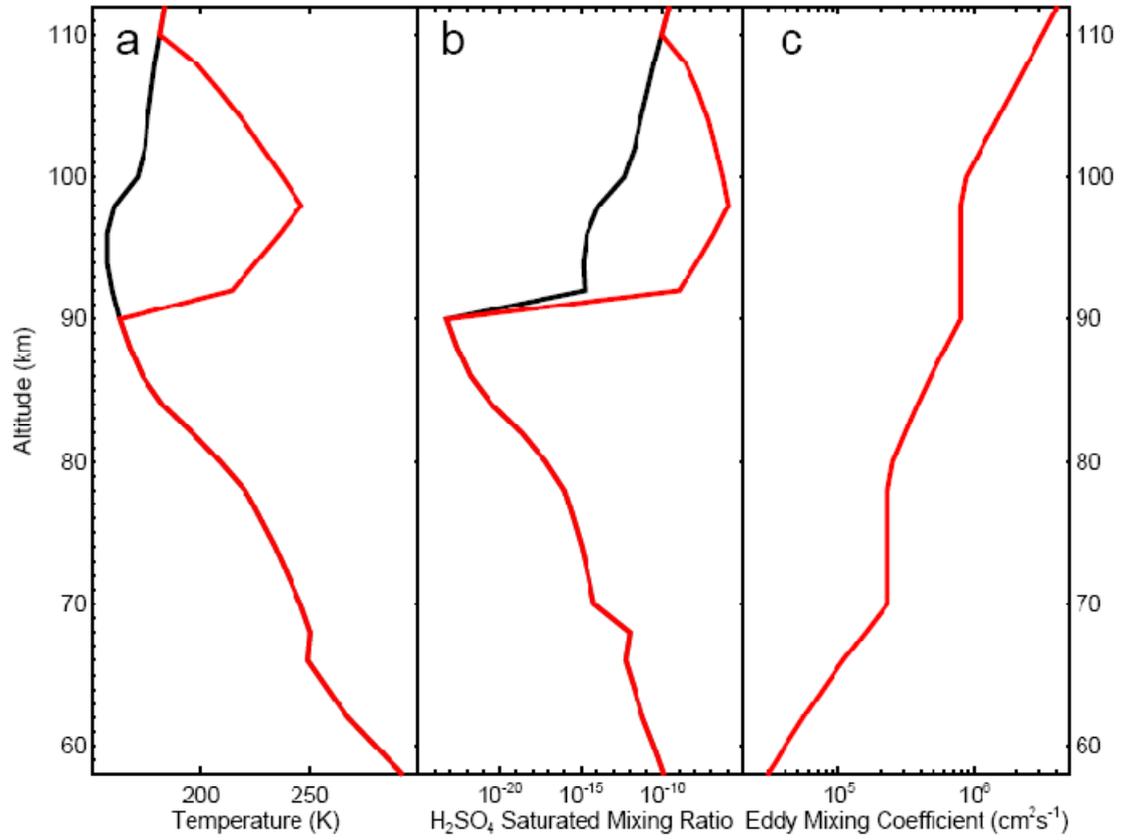


Figure S3

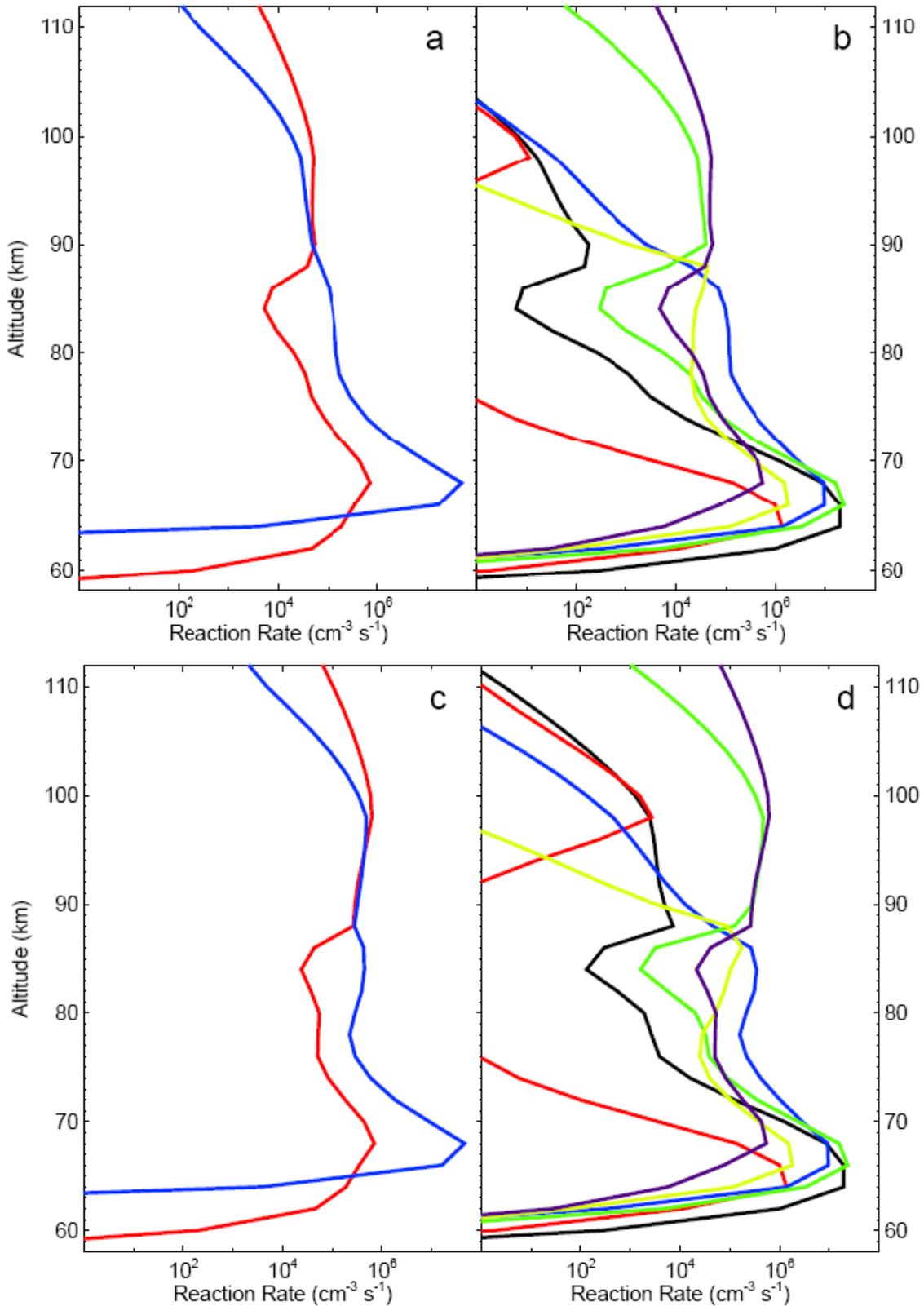


Figure S4

