

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

¹Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, 91125, USA, ²Research Center for Environmental Changes, Academia Sinica, Taipei 11529, Taiwan, ³Graduate Institute of Astronomy, National Central University, Zhongli 32001, Taiwan, ⁴Institute of Astronomy and Astrophysics, Academia Sinica, Taipei 10617, Taiwan, ⁵LATMOS, CNRS/INSU/IPSL, Université de Versailles-Saint-Quentin, Quartier des Garennes, 78280 Guyancourt, France, ⁶Université Pierre et Marie Curie, 75252, Paris, France, ⁷Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, 2455 Hayward Street, Ann Arbor, Michigan 48109, USA. *e-mail: xiz@gps.caltech.edu.

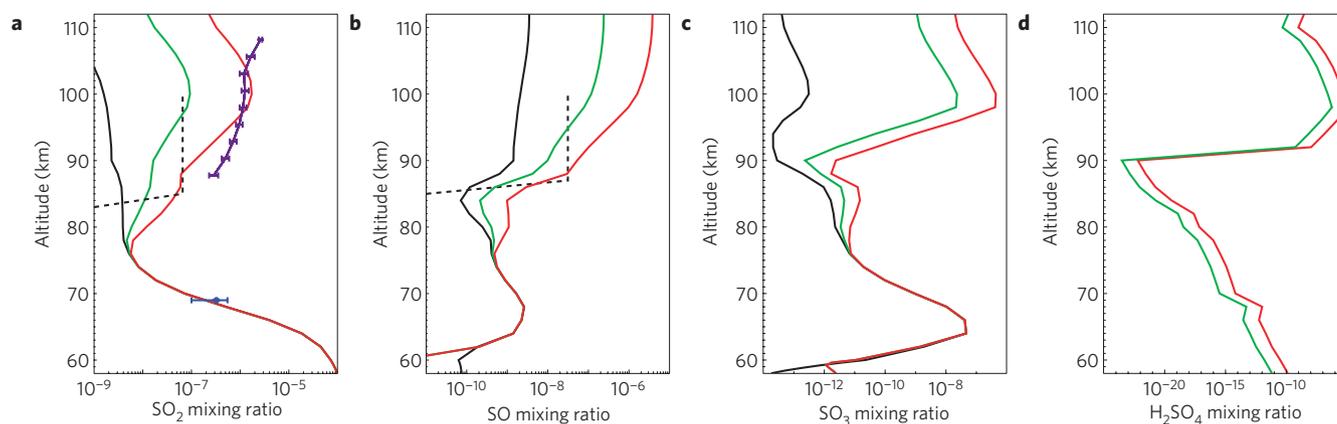


Figure 1 | Model results. **a–d**, SO_2 (**a**), SO (**b**), SO_3 (**c**) and H_2SO_4 (**d**) mixing ratio profiles for models A (black solid), B (green) and C (red). The purple curve with $1\text{-}\sigma$ error bars is one of the observed SO_2 profiles from Venus Express. The blue data point at ~ 69 km is taken from ref. 13. The black dashed lines refer to the maximum values of SO_2 (67 ppb) and SO (31 ppb) mixing ratios from the ground-based microwave measurements¹¹.

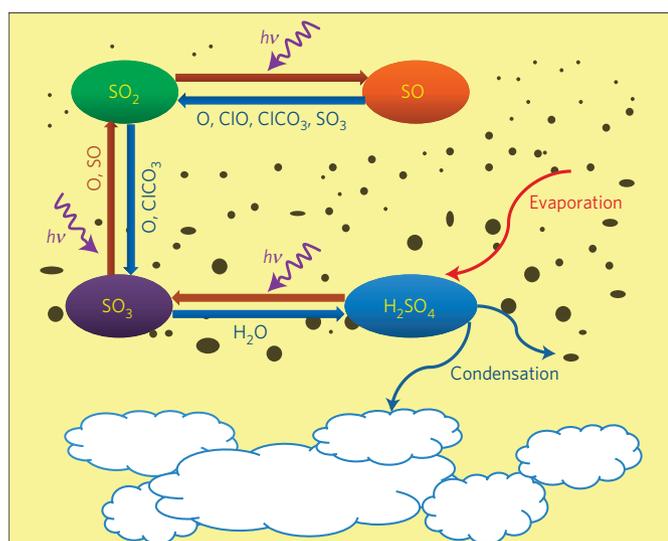


Figure 2 | Illustration of the important reaction pathways connecting SO , SO_2 , SO_3 and H_2SO_4 .

the spatial and temporal variations of SO_2 (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 SO_2 (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 SO_2 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 H_2SO_4 if we take the equilibrium constants from the previous calculation²⁰ for the terrestrial atmosphere and extrapolate to Venus. Models B and C require H_2SO_4 saturation ratios of 0.5 and 10, respectively. The higher H_2SO_4 saturation ratio (10 for

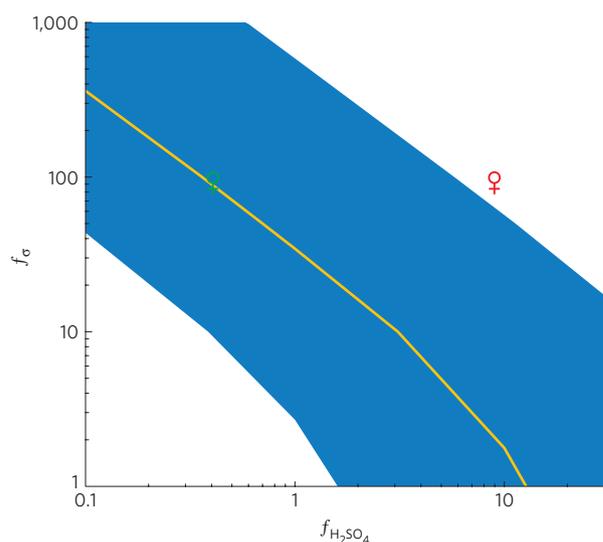


Figure 3 | Parameter space for possible solutions. The blue shaded area shows the parameter space within which the model predicts SO_2 mixing ratios between 0.01 ppm and 1 ppm at 100 km. The horizontal coordinate is the saturation ratio of the H_2SO_4 vapour, and the vertical coordinate is the scaling factor of H_2SO_4 photolysis cross-section. The yellow line refers to the maximum values of SO_2 (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 H_2SO_4 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 H_2SO_4 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 H_2SO_4 vapour saturation ratio and a photolysis cross-section scaling factor. The blue shaded area highlights the parameter space where the model produces an SO_2 mixing ratio between 0.01 ppm and 1 ppm at 100 km. The shape of the contour lines suggests that, for a given SO_2 mixing ratio, the required H_2SO_4 vapour saturation ratio and photolysis cross-section scaling factor are approximately

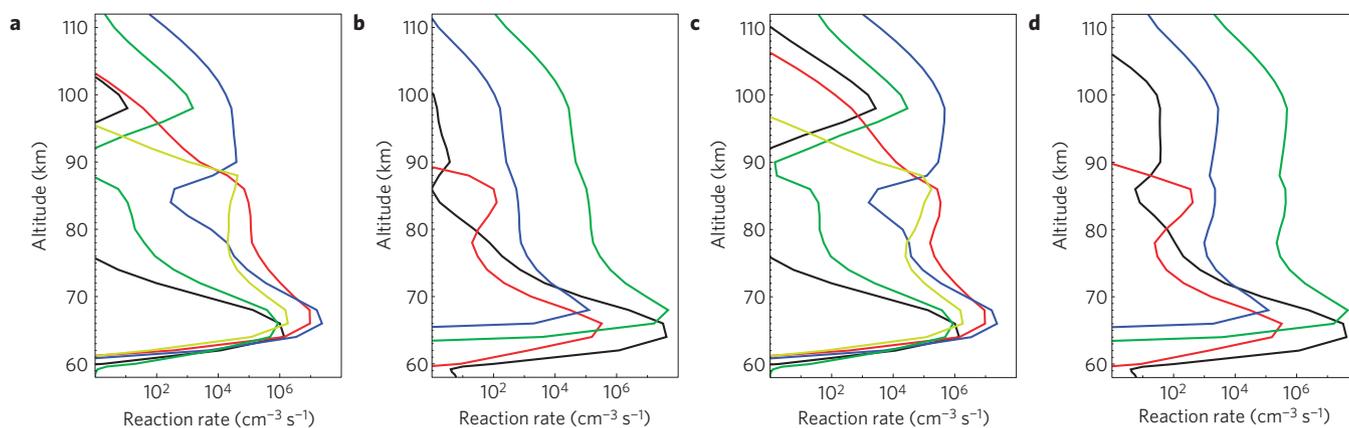


Figure 4 | Production/loss-rate profiles of SO₂. **a–d**, Rates of important reactions involved in producing (**a** and **c**) and destroying (**b** and **d**) SO₂ for models B (**a** and **b**) and C (**c** and **d**). Different colours refer to different reactions listed in Supplementary Table S1. **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.