Photochemical and thermochemical pathways to S₂ and polysulfur formation in the atmosphere of Venus

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Polysulfur species have been proposed to be the unknown near-UV absorber in the atmosphere of Venus. Recent work argues that photolysis of one of the (SO)₂ isomers, cis-OSSO, directly yields S₂ with a branching ratio of about 10%. If correct, this pathway dominates polysulfur formation by several orders of magnitude, and by addition reactions yields significant quantities of S₃, S₄, and S₈. We report here the results of high-level ab-initio quantum-chemistry computations that demonstrate that S₂ is not a product in cis-OSSO photolysis. Instead, we establish a novel mechanism in which S₂ is formed in a two-step process. Firstly, the intermediate S₂O is produced by the coupling between the S and Cl atmospheric chemistries (in particular, SO reaction with ClS) and in a lesser extension by O-abstraction reactions from cis-OSSO. Secondly, S₂O reacts with SO. This modified chemistry yields S₂ and subsequent polysulfur abundances comparable to the photolytic cis-OSSO mechanism through a more plausible pathway. Ab initio quantification of the photodissociations at play fills a critical data void in current atmospheric models of Venus.

Spacecraft missions and Earth-based observations have reported images of the Venusian atmosphere at different wavelengths with the aim of characterizing the cloud morphology and the exotic chemical processes that take place in this planet. At visible wavelengths, the planet is bland and smooth, whereas recordings at near-ultraviolet light (around 365 nm) reveal intriguing “dark” and “light” areas indicating highly active UV absorption in the top clouds.

The identity of the “unknown UV absorber(s)” in Venus represents an important enigma in the current field of research on planetary atmospheres. Even though several particulate and gaseous candidates have been proposed, the nature of the unidentified absorber remains an unsolved problem as no satisfactory match has been found yet in terms of atmospheric abundance and spectral properties. Since sulfur is abundant in the Venusian atmosphere, it is not surprising that many candidates are sulfur-based compounds. It has been proposed that (SO)₂ isomers (mostly cis- and trans-OSSO) generated from the association reaction of 3SO (Eq. 1),

\[ \text{SO} + \text{SO} \rightarrow (\text{SO})₂ \]  

could be the UV absorber since the calculated absorption spectra match previous estimates of the spectral properties of the unknown UV absorber. The short photochemical lifetimes of their (SO)₂ (between 2 and 5 s) derived from photolysis rates imply a short existence of these species during daytime, nevertheless, the chemical equilibrium with SO will be continuously replenishing (SO)₂. Since both SO association (Eq. 1) and photochemical dissociation to SO + SO are swift processes, the global (SO)₂ lifetime is controlled by SO

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concentrations\(^{13-19}\). These can vary greatly, in agreement with observations\(^{20,21}\). Since the lifetimes of the UV dark features range from minutes to hours, to an excess of 12 h\(^2\), a long-lived absorber is unlikely since short lived features would then not be possible. Therefore, the UV absorber concentration is likely tied to something other than direct sunlight, which matches the \(^1\text{SO}_2\) behavior dependent on the \(^3\text{SO}\) levels. Recent literature has brought into question the level of contribution of the two \(^3\text{OSO}\) isomers to the UV absorption\(^{37-19,21}\) pointing to a too low \(^3\text{SO}\) concentration at lower altitudes of the Venus middle atmosphere (ca. 60 km). However, there is still significant uncertainty in these \(^3\text{SO}\) data, and \(^3\text{OSO}\) role as the UV absorber has not been fully refuted yet.

Using data from the Venus Express mission and a photochemical model, Pinto et al.\(^{19}\) have recently assessed in detail the role of \(^3\text{SO}\) dimers as key intermediates in the production of polysulfur (\(^{3}\text{S}\)) oxides (\(^{3}\text{SO}\)). Yellow light irradiation (358 nm) depleted the 375 nm band with a vibrational structure shown by the absorption band, motivating in this way the proposal of photoreaction (Eq. 2) by Pinto et al.\(^{19}\). Nevertheless, Wu et al. also pointed to other decomposition products (\(^1\text{OSSO}\), \(^1\text{OS(=O)S}\), \(^1\text{SO}_2\), \(^1\text{C}_2\text{H}_4\), \(^1\text{SO}\)) as contributors to the 287 nm strong band, while subsequent self-propagation polymerizations of \(^1\text{S}_2\) give access to \(^1\text{S}_2\) through deoxygenation reactions of \(^1\text{SO}_2\) mediated by \(^1\text{SO}\) (Eqs. 3 and 4):

\[
\begin{align*}
^1\text{cis} - \text{OSSO} + h\nu & \rightarrow ^1\text{S}_2 + ^1\text{O}_2 \\
^1\text{S}_2 + ^3\text{SO} & \rightarrow ^3\text{S}_2 + ^3\text{SO}_2
\end{align*}
\]  

and other species X=NO, O, S. H present in Venus' atmosphere\(^{21-23}\). We also add high-level quantum chemistry information for the reaction involving Cl (Eq. 5), which is an important source of \(^3\text{SO}\) (see Pinto et al.\(^{19}\)):

\[
^2\text{CIS} + ^3\text{SO} \rightarrow ^1\text{S}_2\text{O} + ^2\text{Cl}
\]  

**Results**

**(SO\(_2\))\(_2\)** excited-state dynamics

The distribution of the \(^1\text{cis}\)- and \(^1\text{trans}\)-\(^3\text{OSSO}\) photoproducts simulated for the atmosphere of Venus, and that of other relevant isomers, is shown in Fig. 1a, b, including quantum yields and illustrative snapshots of the geometries along the dynamics (see also Supplementary Tables 1 and 4). Note that the yields can be directly implemented as quantum yields for the photoinduced dissociations in the present and future Venus atmospheric modelings. Excitation of \(^1\text{cis}-\text{OSSO}\) and \(^1\text{trans}-\text{OSSO}\) in the atmospherically relevant window (310–496 nm), which mainly populates their second excited electronic state (\(^3\text{S}_2\)), triggers exclusively photodissociations into \(^1\text{SO} + ^1\text{SO}\) in less than 140 fs, with quantum yields of ca. 95% and 90%, respectively. These results clearly establish previous proposals by Frandsen et al.\(^9\). The decay of the \(^1\text{S}_2\) state into the energetically lower \(^1\text{S}_2\) state is faster in the \(^1\text{cis}\) isomer as compared to the \(^1\text{trans}\) species (Supplementary Figs. 8 and 10, respectively), whereas the triplet population is negligible for both isomers. Within our simulation time, 5% of \(^1\text{cis-}\text{OSSO}\) and 10% of \(^1\text{trans-}\text{OSSO}\) did not show any photolysis. Instead, the systems showed motions that could lead either to photoisomerizations (e.g., \(^1\text{cis} \leftrightarrow ^1\text{trans}\) or \(^1\text{cyclic-OS(O)-OS}\)) or to non-reactive decays. \(^1\text{O}-\text{bond}\) breakings in the populated low-lying states are hindered by high-energy requirements (Supplementary Fig. 12).

Excitation at 225–496 nm of the \(^1\text{cyclic-OS(O)-OS}\) species (which has been recently detected\(^1\) in the laboratory using matrix isolation spectroscopy) populates mostly the \(^1\text{S}_2\) and \(^1\text{S}_1\) states (Supplementary Fig. 24), producing a mixture of photoproducts (Fig. 1c). The dominant (67%) photodissociation gives rise to \(^1\text{S} + ^1\text{SO}\), whereas 33% leads to \(^1\text{S} + ^1\text{SO}\) via either \(^1\text{cis}-\text{trans-OSOS}\) or the trigonal isomer \(^1\text{S}_2\). Surprisingly, 1% of molecules produced \(^1\text{S}_2\text{O} + ^1\text{O}\), a reaction that has not been documented until now.

As expected, the trigonal \(^1\text{S}_2\) isomer is the most stable \(^1\text{SO}_2\) isomer in the ground-state\(^3\). \(^1\text{cis, trans}\) photodissociates exclusively into \(^1\text{S} + ^1\text{SO}\) when irradiated at 225–496 nm (Fig. 1d), confirming the proposal of \(^1\text{SO}\) photolysis from Krasnopolsky et al. based on theoretical estimations of energy profiles\(^32\). On the other hand, excitation (310–496 nm) of \(^1\text{cis-OSOS}\) (Fig. 1e) activates the dominant fragmentation into \(^1\text{SO} + ^1\text{SO}\) (67%), whereas the photolysis into \(^1\text{S} + ^1\text{SO}\) is less competitive (27%) although significant. A similar scenario is found for \(^1\text{trans-OSOS}\) (Fig. 1f).

Overall, the photodynamics of \(^1\text{SO}_2\) dimers give rise mainly to \(^1\text{SO}\), while \(^3\text{S}\) atoms are produced from \(^3\text{SO}\) photodissociation (Supplementary Table 13) and are also generated indirectly from the minor isomeric photoproducts of \(^1\text{cis}-\text{trans-OSOS}\) (cyclic-\(^1\text{OS(O)-OS}\), \(^3\text{SO}_2\), \(^1\text{cis-OSOS}\), and \(^1\text{trans-OSOS}\)) as found herein from the simulations. Considering the photolysis rate of \(^1\text{cis-OSOS}\) and \(^1\text{trans-OSOS}\) of 0.20 and 0.62 s\(^{-1}\) (ref. 16), respectively, and the yields computed in this work for the non-photoreactive species (Fig. 1), an upper limit of 0.01–0.03 s\(^{-1}\).
can be established for the rate of photoproduction of $^3S$ from $^1$(SO)$_2$. Such $^3S$ atoms could recombine giving rise to $^3S_2$ via reaction (Eq. 6) or oxidized by $^3O_2$ (Eq. 7). Measured 3-body rate constants for reaction (Eq. 6) differ by nearly a factor of 10⁴ (see Supplementary Table 13). Nevertheless, as shown in Supplementary Table 6, when considering high-pressure conditions for (Eq. 6) and the concentrations of $^3S$ and $^3O_2$ at the relevant altitude of ~64 km from Zhang et al.¹², the pseudo-first order rate $(k)$ appears lower for $^3S$ recombination (Eq. 6) than that for oxidation (Eq. 7).

\[
^3S + ^3S + M \rightarrow ^3S_2 + M \tag{6}
\]

\[
^3S + ^3O_2 \rightarrow ^3S_2 + ^3O \tag{7}
\]

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$^3S_2$ deoxygenation reactions

Taking into account the significant photoproduction of $^3SO$ from cis-/trans-OSO, cyclic-OS(=O), and cis-/trans-OSOS (Fig. 1), formed in situ, we characterized the thermal (i.e., ground-state) deoxygenation reactions (Eqs. 3 and 4) that yield $^1$S$_2$O, $^1$SO, and $^1$S$_2$O (Fig. 2, Supplementary Figs. 25 and 27, and Supplementary Table 6), which open the path toward aerosols ($^1$S$_2$O and $^1$SO). Since other species (NO, $^1$O, $^1$S, and $^1$H) could also produce analogous reactions, we accurately determined their reactivity with cis-OSO (Supplementary Table 6 and Supplementary Figs. 28–35) to update previous estimations for the rate of these reactions.
Furthermore, reaction between the abundant \(^3\)SO species and \(^3\)CIS (Eq. 5), which gives \(^1\)S\(_2\)O, and subsequently \(^3\)S\(_2\) via (Eq. 4), was also characterized (Supplementary Figs. 39–41). The strong electron correlation character of the involved species forbids the general use of the single-reference DFT- or CC-based methodologies, which are popular in this field, requiring high-level multiconfigurational quantum chemistry (see analyses in the Supplementary Note 7). The obtained results indicate that reaction (Eq. 3) generates \(^3\)S\(_2\)O with an energy barrier of \(-9\) kcal mol\(^{-1}\), in reasonable agreement with the estimates from reported rate constants (\(-7.5\) kcal mol\(^{-1}\))\(^{36}\). Production of \(^1\)S\(_2\)O by the reaction between cis-OSSO and \(^3\)NO, \(^0\)O, \(^0\)S, \(^0\)H, and \(^0\)CIS reported by Zhang et al.\(^{38}\) were also used. We treated \(^3\)S\(_2\) as a proxy for sulfur aerosols, but we did not include sulfur allotrope condensation reactions.

According to the calculated pseudo-first order rates (\(k\)) (Supplementary Table 6), thermal reactivity of cis-OSSO (\(k < 10^{-4}\) s\(^{-1}\)) is clearly much slower than its photochemistry (0.19 s\(^{-1}\)). This confirms previous assessments made by Frandsen et al.\(^{39}\) based on their calculated photochemical lifetime (0.20 s\(^{-1}\))\(^{40}\) and the thermal reactivity of OSSO reported by Yung and DeMore\(^{41}\). In the present work, we expand the amount of thermal reactions and the level of accuracy, which clearly strengthen the argument that OSSO photochemistry dominates over thermochemistry. Regarding the comparison for the thermal reactivity between cis-OSSO and \(^3\)NO/\(^0\)O/\(^0\)S/\(^0\)H (see reaction rates in Supplementary Figs. 54 and 55), \(^0\)O has a rate constant of \(1 \times 10^{-14}\) cm\(^3\) s\(^{-1}\) (solid lines) and for a rate constant of \(1 \times 10^{-14}\) cm\(^3\) s\(^{-1}\) (dashed lines). The higher rate constant is consistent with ab initio calculations presented here and yields substantial \(^3\)S\(_2\).

**Photochemical steady-state model for Venus middle atmosphere**

With our \(^3\)SO\(_2\) photoreaction rates and branching ratios and the thermal reactivity properties, an approximate photochemical steady-state model was built to determine the reaction rate profiles and number densities for the key sulfur species for Venus middle atmosphere. Apart from \(^3\)SO\(_2\), most middle and upper atmosphere sulfur species have photochemical lifetimes shorter than their vertical transport timescales, making a steady-state approximation viable. Using \(^3\)SO\(_2\) number density and photodissociation rate profiles from Zhang et al.\(^{38}\) we computed steady abundances of \(^3\)SO, cis-OSSO, \(^3\)S\(_2\)O, and \(^3\)S\(_2\) (see Supplementary Note 8). Number densities of \(^3\)NO, \(^0\)O, \(^0\)S, \(^0\)H, and \(^0\)CIS reported by Zhang et al.\(^{38}\) were also used. We treated \(^3\)S\(_2\) as a proxy for sulfur aerosols, but we did not include sulfur allotrope condensation reactions.

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Discussion

The photochemistry study of (SO)₂ isomers, herein performed with state-of-the-art photodynamics simulations reproducing Venus' atmosphere conditions, points to an overwhelming prevalence of the S–S photodissociations over the S–O ruptures, which must be attributed to the larger S–O bond strength in comparison to that of S–S. Clearly, the S–S cleavage drives the photochemistry of (SO)₂. The findings (displayed in Fig. 1) show that the major photoproducts are 3SO, 3S₂, and SO₂. This seriously questions a significant occurrence of (Eq. 2), as assumed by Pinto et al.¹⁰ on the basis of experiments by Wu et al.¹¹ in cold conditions and solid matrices, since no S₃ + O₂ production has been observed in our thorough simulations. As a matter of fact, the release of a single oxygen atom rarely takes place. Therefore, it is reasonable to conclude that the reaction shown in Eq. 2 is not able to explain a significant generation of polysulfur reactions in Venus through irradiation of (SO)₂ species. The more usual mechanism for S₂ formation is S atom recombination (Eq. 6). S atoms are produced from SO photodissociation and are also generated indirectly from the minor isomeric photoproducts of cis/trans-OSSSO (cyclic-OS(O)S), S–S₂O, cis-OSOS, and trans-OSOS) as obtained in the present study (Fig. 1). However, polysulfur production by Eq. 6 is limited when formation of allotropes of size S₃ and larger must proceed through this pathway as S⁻⁻⁻ atoms are lost rapidly through oxidation by O₂ (Eq. 7). This S⁻⁻⁻ atom bottleneck greatly prevents significant production of polysulfur species in the Venusian atmosphere from this source.

Contrary to the situation in Venus' atmosphere, the production of S₂ in matrix monitored by Wu et al.¹¹ through the absorption increase at 287 nm seems to be the result of the recombination (Eq. 6), fed by the sulfur atoms largely released by four out of six (SO)₂ isomers (Fig. 1c–f), whereas the depletion of the 375 nm absorption band is likely the result of the fragmentations exposed in Fig. 1. It must be emphasized that the experimental conditions (cold molecules adsorbed on a solid matrix) are not strictly comparable to our simulations in the gas-phase at standard temperature neither to those of the Venus atmosphere, even more considering the extremely long irradiation times (tens of minutes) used by Wu et al.¹¹ as compared to the ultrafast photodissociations studied in our work.

Instead of an S⁻⁻⁻ atom pathway, we propose that S₂ formation in the atmosphere occurs primarily from the precursor S₂O by Eq. 4, which is generated by Eqs. 3 and 5, and other sources reported in the literature (see Supplementary Figs. S4 and S5). This is motivated by the fact that when switching on our highly accurate energetics and rate for Eq. 4 computed herein and S₂O generation rates available in the literature (supported in this work for the relevant Eqs. 3 and 5 by quantum chemistry profiles) in our photochemical steady-state model of the Venus middle atmosphere, S₂ abundance increases 4 orders of magnitude approaching the number density reported by Pinto et al.¹⁰, but without the photochemical pathway shown in Eq. 2. A similar peak of S₂ abundance is found although the vertical distribution is narrower in our case. We can clearly state that the sulfur cycle in the Venus middle atmosphere can maintain a high fraction of elemental sulfur aerosols by converting SO or (SO)₂ to S₂ via the S₂O intermediate and the coupling between S and Cl chemistry in Venus. Assessment of deoxygenation pathways analogous to Eqs. 3 and 4 but mediated by NO, O, S, and H shows that they are not competitive with SO. Therefore, SO is a more efficient agent in comparison to NO, O, S, and H to convert thermally cis-OSSSO (predominant (SO)₂ isomer in Venus' atmosphere) first into S₂O by Eq. 3 and subsequently to S₂ by Eq. 4. Nevertheless, the most efficient process leading to the intermediate S₂O involves the reaction between SO and cis CIS (Eq. 5). Reactivity of two cis-OSSSO molecules can produce SₓO, Sₓ, and SO₂ via a complex mechanism as shown herein. However, it does not compete with reactions shown in Eqs. 3–5, also since this reaction is limited by the lower concentration of cis-OSSSO in the Venusian atmosphere predicted by the present modeling. This reactivity can be expected during the night or in conditions of weak radiation, and it should contribute to the reported day/night variation of the SO₂/3SO concentration ratio.¹⁶

The findings obtained in this study allow for a more complete understanding of the current Venusian atmosphere. Because of the complexity of the sulfur chemistry in the middle atmosphere, which includes many species of the form SₓOₓClᵧ, and because of the paucity of laboratory rate coefficient data for most of the reactions among these species, high-level ab initio calculations are essential for understanding the chemistry of the Venus atmosphere. Those improvements are needed also to guide the next terrestrial measurements, spacecraft missions (recently announced by the National Aeronautics and Space Administration motivated in part by the studies on the phosphine detection in Venus atmosphere¹⁹⁾, and to assist with geoengineering of Earth’s climate and monitor stratospheric volcanic eruptions' cloud. Furthermore, they are beneficial to better understand the atmosphere of early Earth (pre-oxygenation of Earth’s atmosphere) and shall be used in describing Earth-like exoplanet atmospheres in conjunction with future high-resolution spectroscopy measurements of said exoplanets.

Methods

Thermal and photochemical reaction channels and associated rates

Herein, photolysis of (SO)₂ has been studied in detail by means of NAMD propagated with the multi-state complete-active-space second-order perturbation theory (MS-CASPT2) method²¹,²²,²³ with the OpenMolcas and SHARC programs³,⁴, including the mixing of singlet and triplet states (see active space orbitals in Supplementary Fig. 1). Multireference configuration interaction (MRCI)⁷⁰⁻⁷¹ profiles validate this level of theory (Supplementary Figs. 2–5). These high-level results have been used to validate NAMD simulations propagated at the faster time-dependent density functional theory (TD-DFT) method²⁴–²⁶ with the Gaussian and SHARC programs²⁵,²⁶ (Supplementary Figs. 11–17 and Supplementary Table 3). Simulation settings and method validations are fully detailed in the Supplementary Information (SI), Supplementary Notes 1–3 and Supplementary Tables 2 and 3,⁷³⁻⁷⁵

Minima and transition states that describe the thermal reaction profiles have been optimized for the lowest-lying electronic state, with the single-state (SS)-CASPT2 method using state-specific complete-active-space self-consistent field (SS)-CASSCF wave functions as reference. The nature of the stationary points has been verified through the corresponding frequency analyses whereas the transition states have been unambiguously connected with their corresponding reactants and products through intrinsic reaction coordinates determinations. To allow the coupling between nearby electronic states, state-average (SA)-CASSCF wave functions have been computed on top of the mentioned optimized structures and the final energy profiles were corrected with the MS-CASPT2 method using the same protocol as for the SS-CASSCF determinations. The strong electron character and the multiconfigurational nature of some of these ground-state reactions have been evidenced by comparisons with the DFT and coupled-cluster methods used in Gaussian’ and ORCA. Static excited-state pathways and ground-state reaction channels with problematic transition-state optimizations have been explored through relaxed scans of the reaction coordinate or by means of linear interpolations of internal coordinates between relevant structures. Further information on the specific computational parameters (active spaces, basis sets, number of computed states), the employed optimization algorithms, and data used for computing rates can be found in the SI, Supplementary Notes 4–7, Supplementary Figs. 25–50 and Supplementary Tables 5–12.
Photochemical steady-state calculations: abundances of sulfur species

We use photochemical steady-state calculations to estimate the abundance profiles for several sulfur species of particular importance in the Venus atmosphere. As the photochemical lifetimes of many of the trace sulfur species are shorter than the eddy transport timescale, this approximation is valid to first order, and allows us a rapid assessment of the implications of the new chemical schemes proposed here based on our ab initio results. For non-sulfur species, long-lived sulfur species, and photodissociation rate constants, we use profiles from Pinto et al.\textsuperscript{19} and Zhang et al.\textsuperscript{21}. Mixing ratio profiles for \([\text{O}_2],[\text{O}_3],[\text{NO}], [\text{H}], [\text{SO}_2],[\text{S}],\) and \([\text{ClS}]\) are digitally read-in from Zhang et al.\textsuperscript{22} or Pinto et al.\textsuperscript{19}. The vertical profiles for the photodissociation rate coefficients for \(\text{SO}\) and \(\text{SO}_2\) were taken from the bibliography as described in Supplementary Note 8. Condensation reactions for sulfur allotropes have not been included here, as appears to be the case for Pinto et al.\textsuperscript{19}. Photochemical steady-state calculations are carried out from \(58\) to \(112\) km, following the temperature and total number density profiles given by Zhang et al.\textsuperscript{12}. Steady-state number densities are computed for \(\text{SO}, \text{SO}_2\), which we assume in these calculations to be primarily \((\text{SO})_2, \text{SO}_2,\) and \(\text{S}_2\). A reduced set of \(19\) reactions involving these species is given in Supplementary Table 13. Setting production rate equal to loss rate for each of the \(4\) species of interest, and using the reactions in Supplementary Table 13, we arrive at the Equations for steady-state number density \(S_1\)–\(S_4\). These Equations are solved in the order presented in the SI, Supplementary Note 8, and the steady-state values are used as applicable. Loss of \(\text{S}_2\) to \(\text{S}_1\) formation is accounted for, but we are not attempting to accurately account for sulfur allotrope abundances. For this reason, \(\text{S}_2\) may be taken as a proxy for total sulfur aerosol production. Further details on the photochemical steady-state model and benchmarking analyses can be found in the SI, Supplementary Note 8 and Supplementary Figs. 51–53.

Data availability

All data to evaluate the conclusions in the paper are available in the main text and/or the Supplementary Materials.

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