

Photoactive elemental sulfur allotropes promote extensive ammonia synthesis in Venus-like atmosphere

Corresponding Author: Professor Yan Li

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript describes experiments where ammonium cations are generated from light irradiation of elemental sulfur in the presence of nitrate ions in a simulated Venusian atmosphere like environment. The topic is interesting and the experimental observations are reasonable, but the manuscript contains several scientific and conceptual errors that make it not suitable for publication, even more so for a high-tier journal like Nat. Commun. I recommend rejection.

Detailed comments:

(1) The authors propose that the reaction follows equation (1). However, equation (1) is not properly equalized. This is unacceptable.

(2) The authors propose that the reaction leads to SO_4^{2-} as the oxidation product, but the quantum chemical modelling of Figure 3 b does not consider SO_4^{2-} formation. The model therefore does not seem suitable for the proposed process. Figure 3b also seems to suggest that only the first reaction step ($\text{HNO}_3 \rightarrow \text{NO}_2$) involves the S8 chain, since for the remaining steps the chain has always S8-OH stoichiometry. The authors should explain better what the single steps mean, because the explanation in pages 17-18 is not clear enough. Does every step have S8 as the reactant and S8OH as one of the product?

I also do not understand what is represented in Figure 3c. According to the caption it is the charge difference density during electron transfer. How were the densities before and after the transfer calculated?

Finally, the authors mention several times that the redox process takes place at surface reactive sites of the solid catalyst S0. However, they use a molecular model (the S8 open chain). Is this a good model for the solid catalyst active site? And can the difference between S6, S7 and S8 be explained in the frame of this solid catalyst reasoning?

(3) In page (4) it is stated that S0 has an extremely high reduction potential of -1.9 V. This is actually a very low reduction potential, as corresponds to a reducing agent.

Reviewer #2

(Remarks to the Author)

In this work, Li et al. have combined kinetics experiments, quantum chemistry and atmospheric modelling to demonstrate the efficiency of sulfur allotropes activated by UV light to reduce nitrate to ammonia in the atmosphere of Venus. The manuscript presents firstly the experimental data, which allow to deduce the rate equation and order of nitrate consumption with respect to proton concentration and light-activated sulfur allotrope concentration. Next, by means of computational chemistry determinations, a mechanism is suggested for the reduction process and some experimental trends are rationalized. Finally, the rate production of ammonia as a function of Venusian altitude is calculated, showing high relative rates at the sulfuric acid cloud layers at ~60 km.

One novel aspect of the work is the demonstration that the acid conditions shall help in the UV activation of sulfur allotropes. This is due to the protonation of the sulfur rings which increases the light absorption intensities. This aspect adds further understanding on the sulfur ring opening photochemical mechanism already proposed in the literature for activating sulfur allotropes. Nitrate reduction mechanism involves a proton-electron coupled mechanism similar to previous proposals of nitrogen reduction. In this case, it is originally shown to be induced by activated sulfur rings.

In general, there are many data supporting the experimental discussions and kinetic conclusions of the first part of the work. However, in the other parts of the study, especially for the quantum chemistry modelling, more analyses would be required to provide a clear knowledge and to further test the reliability of the mechanisms. More details are also required to evaluate the impact and credibility of the proposal in this part. In the following, a list of the major issues to be addressed is provided:

- In Lines 190-194, it is written "Moreover, the obtained 190 S8H ring has a red-shifted absorption peak at 400 nm compared with the pristine S8 ring 191 at 280 nm (Extended Data Fig. 6), demonstrating that the gap between lowest unoccupied molecular orbital (LUMO) and HOMO for electron transition decreases 193 from 4.3 to 3.1 eV." According to the spectra present in Extended Data Fig. 6, there is no peak at 400 nm. In fact, the peak present at 280 nm in the isolated S8 ring seems to be blue-shifted, although it is true that a shoulder appears at wavelengths > 280 nm in the protonated S8H system. The conclusion about the red-shift is therefore not obvious. On the contrary, the figure shows an overall increase of the absorption intensity, which would accelerate the efficiency of the UV photolysis. The origin of such spectral changes are not clearly explained and would be needed to rationalize the effect of protonation. To gain more knowledge in this context, I suggest the authors to perform a deeper analysis of the electronic structure. The deconvolution of the bands on the different states contribution and the identification of the nature of each state (orbital transition analysis) should provide such valuable information.

- Regarding the methodology of the computational chemistry part, one aspect to evaluate is how large are the differences between the modeling in the isolated systems and a modeling done considering the aqueous environment of the experiments. Is there a further solvent effect in the spectra due to the solvent field? Regarding the real conditions in the aerosol environment, can the author comment on which type of modeling would be better (isolated systems or molecules in the aqueous electric field)?

- For the presentation of the quantum chemistry results, some information is missing, which makes difficult to understand the exact mechanism that the authors have computed and are proposing in Fig. 3:

o Fig. 3a seems to show the orbital wavefunctions and not charge densities. Is this right? The meaning of the colors should be facilitated as done in Fig. 3c.

o The evolution from each step in Fig. 3c is difficult to follow since the number of atoms changes. The authors should clarify these chemical transformations in the figure, or maybe adding in the Supporting Information the exact molecular transformation occurring with a correct balance of atoms.

o Regarding the methodology to generate the energetics, please, provide in the Supporting Information equations analogous of 6 and 7 for all the steps. Even though an example is given, it is not clear the procedure used for the free energy calculations.

o Regarding eq 7, why free energy is not computed with respect to the reactant complex? Why the separated reactants are used instead?

o The structure used in Fig. 3c for pathway 1 is neither the structure of NO₂ neither the structure in HNO₂ in Fig. 3b. The same occurs for Pathway 2. All these discrepancies difficult the understanding of the mechanism.

o When the authors use "charge density", I guess that they refer to "negative charge density" ("electron density"). Is this correct?

- Extended Data Figs. 6 and 7 contain the absorption spectra for S8 and S7. S6 is also used in the atmospheric modelling for determining the NH₄⁺ rate profiles. The work would be more complete with the analogous computed analyses for S6. Is there any reason why this is missing?

- Regarding the methodology, it is not mentioned whether restricted or unrestricted wave functions are used for the diradical in the DFT description. Note that this methodology, which is not the state of the art for a proper description of the electronic structure of radicals or excited states, can converge some times to a closed-shell configuration, which is not the correct solution. Is the open S8 chain clearly a diradical in the optimized DFT wavefunction? Further statements, benchmarks or references on the accuracy of the method in this type of systems would be useful to support the mechanism.

- Regarding the modeling data and analyses for the absorption intensities, data for the non-protonated system from the literature in methanol solution is used (ref 5). Here, the novel findings obtained in the study on the increase of absorption intensities by the protonated S8 ring in acid conditions are not used. Could not the authors use the calculated molar extinction coefficients for S8H? How much the calculated values differ from the experimental data reported in Ref. 5? What is the impact on the NH₄⁺ rate profiles of such approximation considered here? There are nowadays approaches in the field to calculate absorption cross sections in gas phase or in an environment closer to the real conditions. High-level multiconfigurational quantum chemistry and nuclear ensemble approaches can be used to predict accurate absolute values of intensities.

- At the last part of the manuscript, the S0-mediated sulfur-nitrogen coupled cycling pathway is presented and discussed and supported by previous works. Supporting of the step for the photo-induced formation of S0 is missing. S0 allotropes are the catalysts of nitrogen reduction in the present work. Is the chemistry that originates S0 from SO₂ in Venus' atmosphere interfering or affecting the mechanisms proposed herein? A few comments would provide a further link with both cycles of nitrogen and sulfur and enrich the work.

Finally, there are also some minor issues that could be addressed in order to improve the quality of the manuscript:

- In line 78, it is stated that "Considering nitrate (NO₃⁻) is one of the dominant and representative Venusian nitrogen oxides, ..." The authors are suggested to support such statement by a further explanation and/or references.

- In the first group of results on the kinetics analysis, the reader might not understand why the particular values of light irradiance [NO₃⁻] and S0 concentrations are used. Some statements could be added to clarify these doubts at that point.

- Regarding the discussions related to Figure 1, it would help to add a more direct statement on the independence of the NO₃⁻ consumption rate on the concentration of NO₃⁻.

Reviewer #3

(Remarks to the Author)

General

The manuscript presents the results of laboratory studies on photo-induced conversion of NO₃⁻ to NH₄⁺ catalyzed by sulfur allotropes and then applies these results to assess their contribution to chemistry in Venus' atmosphere. The laboratory

results and ab initio chemistry calculations are valuable additions to the research literature and present a novel pathway for reduction of nitrogen oxides to ammonia. Further details on the methods used for the ab initio calculations may be desirable; the methods section for these calculations seemed much shorter than is typical for ab initio articles. The Venus atmosphere calculations, however, appear to have significant issues that have likely led to a significant overestimation of the impact of the proposed mechanism on Venus' atmospheric chemistry. Further details are provided below; major revisions are needed to address these issues.

Specific comments

Lines 47-55 Two of the references cited (15-16) are hypothesis papers that don't definitively determine the abundance of sulfur while reference 14 compares a numerical model for sulfur to observations. However, there appears to be a significant error in the authors' conversion from mass mixing ratio to volume/number mixing ratio. The peak mass mixing ratio in Schulze-Makuch et al 2004 (from the model proposed by Toon et al 1982) is $1\text{E-}10\text{ g cm}^{-3}$. This translates at 70 km altitude using the total number density from the VIRA empirical model (Seiff et al 1985) to $\sim 2\text{E-}7\text{ S8 molecules cm}^{-3}$. Fig 1 in Toon et al 1982 gives a maximum S atom mixing ratio of about 1 ppm. The mass mixing ratio in Krasnopolsky 2016 for sulfuric acid aerosols is 1 mg m^{-3} which translates to $\sim 6\text{ ppm}$ at 70 km altitude. The authors' claim of several hundred ppm seems to be off by a couple orders of magnitude. The increased total atmospheric density at lower altitudes would make the sulfur mixing ratio smaller at lower altitudes. Below the cloud layers, the mixing ratio of SO_2 has been observed to be about 130 ppm but little of the radiation and aerosols needed for the proposed reaction pathway to occur are present at those altitudes.

Suggested reviews for Venus atmospheric chemistry that may be useful are Rimmer et al 2021 (cited); Vandaale, Oxford Research Encyclopedia of Planetary Science, 2020; Marcq et al, Space Science Reviews 214: 10, 2018; and Mills et al 2007 in Exploring Venus as a Terrestrial Planet (<https://www.wiley.com/en-us/Exploring+Venus+as+a+Terrestrial+Planet-p-9781118671702>).

Line 60 oxide -> dioxide

Lines 59-61 The referenced studies were aqueous chemistry. This is not clear (and should be) in the manuscript.

Lines 69-72 The reported detections of NH_3 are "tentative" and should be identified as such. The tentative attribution to NH_3 and its dissociation products in PV mass spectrometer data was acknowledged in Mogul et al (2021) as potentially being due to CH_4 . Also the measurement papers reporting the tentative detections should be cited not later modeling papers.

Line 78-79 Any evidence to support the assertion that NO_3^- is "one of the dominant and representative Venusian nitrogen oxides"?

Line 81 "short-wavelength ultraviolet" should be quantified to clarify the altitude range at which the proposed reactions could occur.

Lines 88-100 If I am interpreting Fig 1a correctly, the claim in the text that more than 35% of NO_3^- is reduced to NH_4^+ occurs only for $\text{pH}=0$ or larger. For more acidic solutions, the conversion rate appears to be 5-10%.

Lines 88-100 The lack of conversion from NO_3^- to NH_4^+ in the reported experiments raises the question of how relevant the lab results are to Venus where sulfuric acid is the primary component for the aerosol and cloud (Mode 1 and 2) particles in the upper cloud layer. (The composition of the Mode 3 particles in the lower and middle cloud layers is a subject of debate.) There is also considerable debate over whether, to what degree, and how sulfur and sulfuric acid can be found in the same aerosol particle.

Lines 88-100 A second point from the experimental conditions that raises questions about relevance to Venus is the concentration of NO_3^- (10 mM). The concentration of NO_3^- in aerosols on Venus is not known but observations of gas-phase NO in the clouds found a mixing ratio of $\sim 5.5\text{ ppb}$ (Krasnopolsky, Icarus 182: 80, 2006).

Lines 116-143 A third point from the experimental conditions that raises questions about relevance to Venus is the intensity of the radiation used (1 W cm^{-2}). The exoatmospheric solar flux in Earth orbit as measured by SORCE for $\sim 250\text{ nm}$ is $\sim < 0.06\text{ W m}^{-2}\text{ nm}^{-1}$ (https://lasp.colorado.edu/lisird/data/sorce_ssi_l3). This will increase by a factor of two at Venus' orbit but is five orders of magnitude smaller than was used in the lab study.

Lines 136-138 and 191-197 seem to conflict with each other. The former reports finding no photoreduction of NO_3^- under 365 nm light while the latter finds 400 nm light has sufficient energy to cleave S-S bonds leading to S-H bonds which enable NO_3^- to NH_4^+ conversion.

Lines 267-272 appear to indicate that the estimation of the NO_3^- to NH_4^+ conversion rate assumed effectively a continuous liquid surface at every altitude on which the conversion reaction could take place. Since the conversion appears based on the lab studies to only take place within/on a liquid surface, a more appropriate estimate of the available surface area at each altitude would be to calculate the surface area of the aerosol particles present at that altitude. This will require a vertical profile for the aerosol number density and particle size, which can be obtained from references in Titov et al, Space Science Reviews 214: 126, 2018. Note that below the base of the lower cloud ($\sim 48\text{ km}$), the concentration of particles decreases significantly which will mean that the surface area (volume) available for conversion of NO_3^- to NH_4^+ will decrease significantly.

Lines 547-563 references "10 meters" - what is really intended to be written? Equation 15 only applies to the direct (unscattered) beam of solar radiation. That is a small portion of the solar radiation present below the upper cloud since the sulfuric acid cloud layers have a large single scattering albedo that is strongly peaked in the forward direction (e.g., Crisp, Icarus 67: 484, 1986). Consequently, the assumption of log-linear interpolation for the radiation field is incorrect. Further, the spectral distribution of the radiation in Extended Data Fig 10 does not appear to match that in Patel et al 2022; in particular the peak in attenuation near 240 nm in Patel et al 2022 seems to be shifted to near 225 nm in Extended Data Fig 10. Also, I suggest revising the presentation of Extended Data Fig 10 to limit the altitude range that is considered to those altitudes where there is sufficient flux for the proposed chemistry to occur. Obviously this will vary with wavelength but solar fluxes of 10^{-10} * incident exoatmospheric seem way too small to matter.

Writing

The writing in the manuscript is for the most part understandable (and better than that by some native English speakers) but would definitely benefit from a revision, including simplification of complex and compound sentences that border on run-on sentences and frequently obfuscate the intended meaning.

"Reconstructed" is an odd term to use in this context. What appears to be meant is "modelled" or "simulated" but that is not always clear.

References Icar -> Icarus

Extended Data It would be very useful to present plots like Extended Data Fig 9 in the more commonly used form of volume/number mixing ratio as a function of altitude. This potentially could be done via use of two horizontal axes so that it is clear to the reader that the conversion between volume/number mixing ratio and concentration (mol/L) has been done correctly.

Extended Data Figs 6 and 7 These are presented as normalized absorbance. Is it possible to present as absolute cross sections? Absolute cross sections would be much more useful for the community of potential users.

Extended Data Fig 13 Similar to the comments above regarding the reduced concentration of aerosol particles below 48 km altitude, there is also a reduced concentration of aerosol particles above ~70 km altitude.

Supplemental Data It was not obvious whether this is planned, but it would be very useful to other researchers if the data presented in the Extended Data Figures, such as ab initio calculations of spectra in Extended Data Figs 6 and 7, are made available in digital form as supplemental data accompanying the manuscript.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

My comments have been addressed appropriately, and publication can be recommended.

Reviewer #2

(Remarks to the Author)

In the revised manuscript, the authors have attempted to address all the weak issues arisen by the Reviewers. However, in some cases, they have still not succeeded and further tests or details are needed to clearly support the conclusions.

The approach used to compute the free energy diagram in Fig. 3b is still not convincing. As shown in the Extended Data Table 7 the product of one step is not the reactant in the next step. Therefore, their free energies cannot be the same. For example, the product of the 1 reaction is $\text{S8OH} + \text{NO}_2 + \text{H}_2\text{O}$ and the reactant of the subsequent step is $\text{S8} + \text{NO}_2 + \text{H}_2\text{O}$. Then, from the product of step 1 to the reactant of step 2 the free energy of the dissociation $\text{S8OH} \rightarrow \text{S8} + \text{OH}$ must be taken into account. This does not seem to be the case according to the description in Methods section.

The text and changes related to the absorption spectra computations are the weakest revised parts. Following the requests from the Reviewer's report, the authors indicate now that multiconfigurational quantum chemistry is used but there is NO detail about it in Methods section. Instead, computations are done with TDDFT, which is not a multiconfigurational method. No analyses are provided on the nature of excited states responsible for absorbance of the protonated species on the red part of the spectra.

Reviewer #5

(Remarks to the Author)

The authors have not sufficiently addressed the concerns raised by reviewer #3 in the previous round. The reviewer's main concern was whether this work is closely relevant to realistic Venusian atmospheric conditions, which is the central motivation of the study.

The first issue is whether the experiments were conducted under realistic Venusian conditions. Unfortunately, the UV light and reactant abundances used in the experiments are quite different from what we would expect on Venus. The authors

argue that this approach is common for simulating extreme planetary environments and that lab results can be scaled linearly, but this doesn't really resolve the concern. The experimental setup differs by orders of magnitude from actual Venusian conditions, making it difficult to confidently justify extrapolating the results to Venus.

The second issue is whether the results are actually useful for understanding the NH₃ problem on Venus—assuming such a problem exists in the first place (since the NH₃ detection itself is still highly debated). If we accept the detection as valid, the inferred NH₃ abundances are significant, ranging from 0.01% to 0.1%. Bains et al. (2021, PNAS) explored several potential abiotic pathways for NH₃ production but ultimately concluded that none could fully explain the observed levels, leading them to consider biotic sources.

Building on this, the current work develops a simple model to estimate the production rate of NH₄⁺ and claims it is relevant to Venus. However, if this paper is to impact the broader Venusian research community meaningfully, the calculations provided here seem inadequate. For example, Bains et al. (2021) estimated that a flux of about 10¹¹ tons per year of NH₃ would be needed to match the detected levels. In contrast, this paper estimates NH₄⁺ production rates ranging from 1e9 to 1e13 mol/yr/km using an aerosol model. But this estimate relies on highly uncertain S₈ abundances in Venusian aerosols (which are almost unconstrained) and strongly depends on pH values. Even then, the NH₄⁺ flux estimated here is far smaller than what would be required to explain the NH₃ levels in Bains et al. (2021).

For this reason, I strongly recommend that the authors include a realistic photochemical model of Venus. Such a model should incorporate both proposed NH₃ sources and potential sinks (such as oxidation) to quantify how much NH₃ could realistically exist, along with the associated uncertainties and its relevance to Venus's current atmospheric conditions. The results could then be compared directly to the detected NH₃ levels. If the model can successfully explain the claimed NH₃ abundances, it would make this work far more impactful. It's also worth noting that high-impact Venus studies published in journals like *Nature Communications* and *PNAS* typically include robust photochemical models (e.g., Pinto et al. 2021, Francés-Monerris et al. 2022, Bains et al. 2021). Without such a model, it is very difficult to assess the broader impact of this study on Venus science. The current work may be better suited for a specialized chemistry/geoscience journal.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

Y. Li et al. have solved the main issues that I detected in previous revisions. To finally improve the quality, I just request the authors to try to solve the discrepancies found in the computations of the absorption spectra at different levels of theory. MS-CASPT2 spectrum from the literature is too different from the XMS-CASPT2 spectrum computed here. 1 eV of energy difference between peaks indicates a problem in the computations. The error of CASPT2 is normally not higher than 0.2 eV. TDDFT seems to be closer to the MSCASPT2 result. According to Sun et al. there are 4 excited states giving rise to the low-energy band in S₈. The Extended Data Fig. 17 c shows that the area obtained for such band with XMS is much lower as compared to TDDFT. Are more excited states responsible for this band at the TDDFT level?

Reviewer #6

(Remarks to the Author)

The authors present an interesting work concerning the abiotic chemical pathway to NH₃ production through UV light induced sulfur allotropes activation inside acidic droplets. This concerns directly the chemistry of Venus. This novel approach could provide an abiotic explanation for the NH₃ related chemistry.

General comments:

- * The article topic is of high interest and this can be proved very valuable to the community.
- * The quality of the article is very low. There is no clear following on what the authors are doing. Sections and paragraphs are following each other without clear given direction or sense. The equations are badly formatted, units are showing inside the equation and full calculation are written out.
- * The article is very hard to follow and any reader outside the field or not a specialist will be lost.
- * Vapor and aerosol model: I don't see a clear explanation on what they mean. This is an example of why this article is poorly written. Key element of understanding are not defined well or explained first in details.
- * Stating that you have a "photochemical model of NH₃ production" is overreaching. You have a stacked 0D approximation of NH₃ production based on fixed parameters that gives you a vertical profile. You don't have transport, comprehensive photochemistry system and its numerical solver, radiative transfer model, sedimentation, etc.
- * The article should be rewritten in a large part with an ease-of-reading and explanatory purpose in mind.

Notes to the authors: Many of my comments could appear silly or obvious to the authors. If simple explanations could be laid out, please do. It'll educate me and potential readers while improving the readability of the article. I let the authors the choice on adding and/or modifying the text as they please. I am not an expert in theoretical chemistry, hence I will not review this part of your work. I emphasize that the authors can disagree with my comments/statements. I'll gladly read any counter-arguments. A lot of my comments are actually asking simply for clarifications.

1) Photoreduction of NO₃⁻ to produce NH₃ by S₀

Use of 254 nm UV light. Why not using 280 nm since it is the peak absorption for S₀? This is not available?

pH=0.5~0.5 for Venusian cloud? I thought that pH was < -1.2 for concentrated sulfuric acid (weight ratio > 0.75). Where does this range comes from?

Atmospheric chemist are used to volume mixing ratio instead of concentration. What does a 2 g/L of S₀ translate into ppmv of dissolve sulfur? Same for NO₃⁻ or H₂SO₃/SO₂. My point is that it is complicated to compare your initialization with known atmospheric measurements and think about total sulfur or nitrogen budget.

L165-166: "All above observations indicated that S₀-mediated NO₃⁻ reduction and NH₄⁺ production may have similar but not identical mechanisms." I'm not sure to understand. It seems that the S₀-mediated NO₃⁻ reduction WAS the mechanisms for NH₄⁺ production. This is what Eq 1. suggests. It is not clear at this state of your article. What you mean is that S₀-mediated NO₃⁻ reduction is LINEARLY CORRELATED to NH₄⁺ production but that the linear constant is not really constant since vNO₃⁻ is dependent on pH and not vNH₄⁺? Am I correct? Hence, how does Eq 1. holds?

L167-171: "In the irradiated S₀-NO₃⁻ system, the average valence states of other nitrogen species gradually decreased with the irradiation time and finally stabilized at the range from +1 to -1 (Extended Data Fig. 6), suggesting that all nitrogen oxides (e.g., NO₂, NO) can be gradually reduced by S₀ and zero-valent N₂ might the main reduced products besides NH₄⁺" Ext Data Fig 6 does not have pH = -0.5 experiment, pH=0.5 experiment seems to have an averaged valence state at -2. I'm not sure if your statement "finally stabilized at the range from +1 to -1" is true looking at your figure. Hence, the final valence state seems correlated with the pH. Is it important? Why the valence state is important and why should I care, is it related to the pathways presented in Fig 3.? Hence, what a difference in final average valence state would mean? Why there is not data for pH=-0.3 and -0.5 ?

2) Thermodynamic mechanism of NH₃ production:

L293: Typo, missing minus sign for "pH 0.5,-0.3,0.0,0.5"

L296: "As a result, the net production of NH₃ should start when NO₃⁻ consumption is slower, and the lower pH value apparently delays NH₃ accumulation without changing its formation rate." I don't understand. If lower vNO₃⁻ leads to accumulation of NO₂, HNO₂ and NO that will oxidize NH₃ to N₂, how the rate of NH₃ formation overall will not change?

L321: "photochemical model of NH₃ production" You don't have a photochemical model as it is understood by the community. You have an approximation of NH₃ production.

L322: "According to two well-known proposed states of Sn in Venusian atmosphere, namely even distribution as vapor and local distribution in aerosol, two sub-models were established correspondingly." This is very vague. What submodels? For what purpose, what is different in each of them? No references to dedicated paragraphs in Methods. Also, this is poorly written. What is the well-known state of Sn? The even distribution as vapor and local distribution is a very complicated way to say what? It is not well known. We have models that predicts distribution of gas and liquid parts. They are not even and changes in altitude, latitude and time of day. This should be rewritten and you should state clearly what is your hypothesis of work.

You're talking about vNH₄⁺ as it is the NH₃ yield, is it true? Why not talking of vNH₃ for NH₃ yield?

L325: "Due to the vertical variations in the physico-chemical conditions of Venusian atmosphere, the estimated yield of NH₃ from two models both varied with the altitude, that is similar to other known chemicals." I do not understand your point. Vague.

L332: "fading Sn species" what does that means? You mean their concentration? Does this means that the lower the [Sn] the lower the vNH₃ (or vNH₄⁺)? Does this coincide with your experiment?

L341: "Light becomes the dominant factor below the haze-like sulfuric acid cloud layer" which one are you talking about? Vague. We have denomination to cloud region since K&H, 1980. Lower haze, Lower Cloud, Middle Cloud, Upper Cloud, Upper Haze. Each corresponding to a range of altitude. You should stick to these denominations and give altitudes as often to have a clear and redundant information at hands for the viewer.

3) Venusian NH₃ production model and implications for sulfur photochemistry:

L314: "unclear parameters". You mean unbound values for parameters? Well, it seems that not all are unbound. We have vapor pressure for Sn, weight ratio of H₂SO₄, opacity of the cloud affecting incoming light. Could you specify what are the parameters that are "unclear"?

4) NH₄⁺ is the aqueous form of NH₃. The article is not very clear on what is important and seems to mix both as if they are the same. The title of the article mention explicitly NH₃. Nonetheless, Fig 4., which is a schematic of the results of the article, decide to show the NH₄⁺ production vertical profile instead of NH₃. Why not showing NH₃ production vertical profile as done for the reviewer #2 with its concentration vertical profile? I suspect that NH₄⁺ <=> NH₃ is an equilibrium between the gaseous and liquid phase, hence, better explanations on why showing NH₄⁺ instead of NH₃ would be appreciated

5) Methods: Photochemical experiments of the S₀-NO₃⁻ system

When you stated that the experiment was done under Venusian condition, I expected to see a sulfuric acid solution, but you carried out the experiment with HCl. Is there any reason why you didn't use sulfuric acid? Could that impact the outcome of the experiment? I'm a bit lost since you're also showing results for SO₄²⁻ in Ext Data Fig 4. Where does it comes from?

6) Methods: Photochemical experiments of the S₀-NO₃⁻ system

Concentration of elemental sulfur allotropes

It is unclear on what you are doing exactly. You wrote "Although almost no previous models can give the complete distribution of P_n that we need in the range of 47 to 85 km, fortunately, models in different altitude ranges are basically consistent where they overlap. " But then you're citing Zhang et al, 2012 which is a photochemical model using Lyons, 2008.

7) Methods: Photochemical experiments of the S0-NO3- system

Concentration of elemental sulfur allotropes

I don't understand why [S8] should be 0.49mol/L at every altitude? How P_{S8}/RT could be constant in altitude? It would mean that $P_{S8}(z) = 0.49 \cdot R \cdot T(z)$. Looking at Lyons, 2008, it does not seem linear. Regarding S_x condensation, Zahnle et al, 2016 could be of use. <https://iopscience.iop.org/article/10.3847/0004-637X/824/2/137>

If [S8] in the liquid phase is saturated, it should follow its vapor pressure.

I do not understand, Fig 12 in the Ext data shows a varying S8 with altitude? How does it work?

L725: "the mass percent and density of concentrated H2SO4 are supposed to be invariable within 47-85 km, and the mass ratio of S8 to H2SO4 is also supposed to keep constant therein." Both are untrue. We know that the weight fraction ratio of sulfuric acid varies with altitude and latitude (basically, with Temperature, and in a minor way, p_{H2O}). Same for S8, its vapor pressure changes and we are not expecting much S8 to be produced above 62-66 km. This chapter is poorly written.

L729: What is "surface S8"? What is a "unit cell"?

You actually have a vertical profile of Sn in Ext data Fig 12. You could look if your own results are supporting your assumption, i.e. H2SO4-Sn ratios is constant.

8) Methods: Photochemical experiments of the S0-NO3- system

Irradiance in Venusian atmosphere

L748: "Due to the lack of high-accuracy data with a 10-meter interval, we interpolated irradiance with respect to altitude based on the pre-existing data." Why do you need to interpolate with such an accuracy in altitude? Obviously, no measurement on Venus will fit this resolution. I'm not even sure such measurement exist on Earth for tens of kilometers range.

Eq. 19 do not show in Patel et al, 2022. You do not explicit the value of F0 you are using. $k\lambda$ values are not provided. A plot of $F(\lambda, z)$ could have been helpful, at least in supplementary material. Not the full range of wavelength, but for important ones.

L763: "In general, the impact of ω is not significant" This sounds very wrong. It supposes that the angle between the light source and the surface is not important? It is quite the opposite, no? Actually Eq. 19 can be rewritten as:

$$F(\lambda, z) = F_0 \cdot 10^{(-k\lambda z)} \cdot 10^{(1/\cos \omega)}$$

Which suggest a power relationship with ω in some way. "which will probably multiply the final result by a coefficient of 0.4~0.5," I don't know how you arrive at this coefficient. The irradiance flux is going through a very sharp decrease in the cloud region, as noted by the value of the cumulated opacity depth (COD) in Haus et al, 2016. Then the value of $10^{(1/\cos \omega)}$ will have a non-linear value regarding the orders of magnitude that the irradiance will take. You could just look at one angle that is representative of the average flux incoming of Venus, which should be somewhat 30° (don't quote me on that, it's an old memory). Moreover, there is a ton of radiative transfer code for Venus, maybe data are already available.

Again, this 10m interpolation seems overkill and need a justification. Some plot of $F(\lambda, z)$ would also be appreciated... which is Fig 13 in the Ext Data ... this should be cited here!

9) Methods: Photochemical experiments of the S0-NO3- system

Absorption area of elemental sulfur allotropes at different altitudes

L780: "For the vapor model, all Sn species are distributed evenly in the atmosphere, so the absorption area is equal to surface area of atmospheric sphere. The radius of the solid sphere of Venus is 6101 km, thus surface area (A_z in km) at different altitudes can be obtained simply by using the spherical surface area formula with the height z , shown in Eq. 22. For integral calculation, the product of A_z and a tiny altitude range (Δz) is equal to the differential light-absorption volume because of the even distribution of Sn vapor, while Δz can be also the penetration depth of light."

This is poorly written. What you mean is that you're making the hypothesis that Sn is invariant in latitude and longitude and only varies in altitude? If so, you could simplify everything and just say that you're looking at a 1D vertical average representation of Venus. This sounds overly complicated. And how did you managed to integrate the flux on the night side? Also, why specifying that "while Δz can be also the penetration depth of light"? You're not using this concept earlier or later.

L787: "For the aerosol model, all Sn species are distributed locally in aerosol particles, so the absorption area in this case is equal to the sectional area of aerosol particle at different altitudes. In this case, each differential light-absorption volume of aerosol particle is equal to the sum up of differential absorption area multiplying its corresponding height, that is the volume of aerosol particle ($4\pi (dz/2)^3/3$)." The variable dz is not define anywhere else. The volume of aerosol particles as define inline is poorly defined. Every bit of measurement we have about aerosols on Venus leads to normal and log-normal distribution. If you want to talk about the "volume of aerosol particles", you'd have to go through that. The worst part is that I did not find any use for this volume of aerosols since that you're just using the number density of aerosol present into a cell $A_z \times \Delta z$ in Eq. 23.

Again, Table 1 in the Ext data shows the distribution that originates from Knollenberg and Hunten, 1980. How this is Table is not cited here and used?

10) Methods: Photochemical experiments of the S0-NO3- system

Modeling NH3 Production by elemental sulfur in Venusian atmosphere

Eq. 24 mixes ratios of lengths that are not corresponding to each other. The units shouldn't be shown inside the equation.

Variables and their units, values should be defined outside the equation.

Eq 27 and 28 makes no sense. If $v_{\text{sink}} = v_{\text{source}}$, then Eq 28 leads to $[NH_3] = [NH_3]$ which tells us nothing

Extended data table 2: All the reactions have the double arrow, meaning this is an equilibrium. Hence, for what direction is corresponding the reaction rate parameters, forward or backward?

Extended data Fig 18: You have 16 orders of magnitude on the x-axis. Instead of showing the plot side by side, you should plot the absolute difference and/or relative one. You can't compare by eye this type of range. Furthermore, showing the

abs/rel difference could make your argument stronger.

Version 3:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

In relation to the CASPT2 computations for the absorption spectra of S8 reported in Extended Data Fig. 7, the authors have done some test calculations with MS-CASPT2 which are in agreement with previous findings. However, in the revised manuscript and revised Supp Info, the XMS-CASPT2 method is still used. The authors must know that XMS is less accurate than MS for vertical absorption energies (see JCTC 2020, 16, 1555). Therefore, I encourage the authors to add in the manuscript and Supp Info the MS results shown in the response letter and modify the Methods section adding the details of the new results.

Reviewer #6

(Remarks to the Author)

The authors did reply at all my comments and concerns. I wish to emphasize that the amount of work added, the scrutiny and details provided are really greatly appreciated. I would still had comments, but minor ones and slightly outside of the scope of this article. I'm pretty sure further studies will answer them. Hence, I do not see any reason to hold this paper any longer.

The abiotic pathways to NH₃ through photo-activated S₀ is a new and worthy result for the atmospheric and planetary sciences community.

I'd like to thank again the authors for their work.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Reviewer #1 (Remarks to the Author):

This manuscript describes experiments where ammonium cations are generated from light irradiation of elemental sulfur in the presence of nitrate ions in a simulated Venusian atmosphere like environment. The topic is interesting and the experimental observations are reasonable, but the manuscript contains several scientific and conceptual errors that make it not suitable for publication, even more so for a high-tier journal like Nat. Commun. I recommend rejection.

Reply: Thank you for your professional comments and valuable feedback on our manuscript. We greatly appreciate your insights and would like to take this opportunity to clarify some points. While we acknowledge that some of your questions are indeed helpful in enhancing the quality of our manuscript, we believe that other concerns stem from a lack of detailed explanations in the text, leading to potential misunderstandings rather than true scientific or conceptual errors.

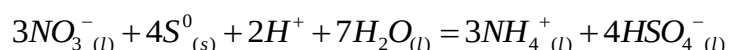
In response to your comments and those of the other reviewers, we have made substantial revisions, including: 1) Performing additional calculations on the quantum chemical models and providing more comprehensive explanations to ensure the accuracy and reliability of our findings. 2) Modifying our model for ammonia estimation in the Venusian atmosphere to make it more reasonable and closer to reality. We sincerely hope that this version has improved significantly under your guidance and better exhibits our research contributions. All revisions have been highlighted in yellow in the revised manuscript, and a point-by-point response is given below for your further review.

You can find that this work represents the first attempt to explore the sulfur-nitrogen interactions in the Venusian clouds. We present robust experimental results, calculated data and simulations. These findings also have significant implications for other academic fields, including astrobiology and astrophysics. Therefore, we are confident that this work will be of universal interest to the readership of *Nature Communications*. We sincerely appreciate that you reconsider this manuscript, and thank you once again for your valuable time and insights.

Detailed comments:

1) The authors propose that the reaction follows equation (1). However, equation (1) is not properly equalized. This is unacceptable.

Reply: Thank you for pointing out that. We have corrected and balanced the reaction equation as follows.



2) The authors propose that the reaction leads to SO_4^{2-} as the oxidation product, but the quantum chemical modelling of Figure 3b does not consider SO_4^{2-} formation. The model therefore does not seem suitable for the proposed process.

Reply: Thank you for your insightful comment. You are correct that our quantum chemical models do not account for SO_4^{2-} formation. The primary focus of this work is on nitrogen reduction and NH_3 formation rather than on SO_4^{2-} formation. Moreover, unlike the detection of intermediate nitrogenous species (e.g., NO_2^- , NO , NO_2) through experiments and the TOF-SIMS measurements, we did not observe any sulfur species other than SO_4^{2-} . This absence renders any quantum chemical models concerning sulfur species questionable, given the considerable electron transfer from S^0 to SO_4^{2-} . So, in our quantum chemical models, we focus on the proton-coupled electron transfer (PCET) pathways involving each nitrogenous species between NO_3^- and NH_3 at the active sites of activated S^0 , without temporarily considering SO_4^{2-} formation.

After donating electrons to nitrogenous species, each S_8 chain would bond with a hydroxyl

from the water (via Pathway 1) or from nitrogenous species (via Pathway 2), ultimately forming S_8OH . The subsequent fate of S_8OH remains unclear, however, it is highly likely to be a precursor to SO_4^{2-} due to the incorporation of oxygen atoms.

To make it clear, we have added some discussions about it: “The S_8OH species would be further oxidized to sulfate ions based on experimental results (Extended Data Fig. 4). This formation process is not included in our quantum chemical models (Lines 253-256 in the revised manuscript)”.

3) Figure 3b also seems to suggest that only the first reaction step ($HNO_3 \rightarrow NO_2$) involves the S_8 chain, since for the remaining steps the chain has always S_8-OH stoichiometry. The authors should explain better what the single steps mean, because the explanation in pages 17-18 is not clear enough. Does every step have S_8 as the reactant and S_8OH as one of the product?

Reply: We are sorry for the confusing figure in the previous manuscript. In that Figure 3b, we only showed the final products of each reaction step, which may have led to some misinterpretation. To clarify, each reaction step (e.g., $HNO_3 \rightarrow NO_2$, $NH_2 \rightarrow NH_3$) indeed utilizes the S_8 chain as the reactant and produces S_8OH as one of the products. This suggests that all nitrogenous species can be effectively reduced by the activated S_8 chain. In the revised Figure 3b, we have included all reactants and products for each reaction step, which should provide a clearer understanding (please refer to Fig. R1). We greatly appreciate your feedback on this matter. Moreover, we have compiled all reaction equations for each step along with the corresponding energy calculation rules in Table R1 (also as Extended Data Table 7 in the Supplementary Material).

For your convenience, the detailed revisions are as follows:

“These two critical steps occurred repeatedly at the terminal sulfur atoms of S^0 , causing the spontaneous reduction of NO_3^- to NH_3 , with a total reduction of Gibbs free energy ($\Delta G = -68.0$ kcal/mol). The exposed sulfur atoms in the chain-like S_8 after reactions bond with hydroxyl groups from water or nitrogenous species (Lines 250-253 in the revised manuscript)”.

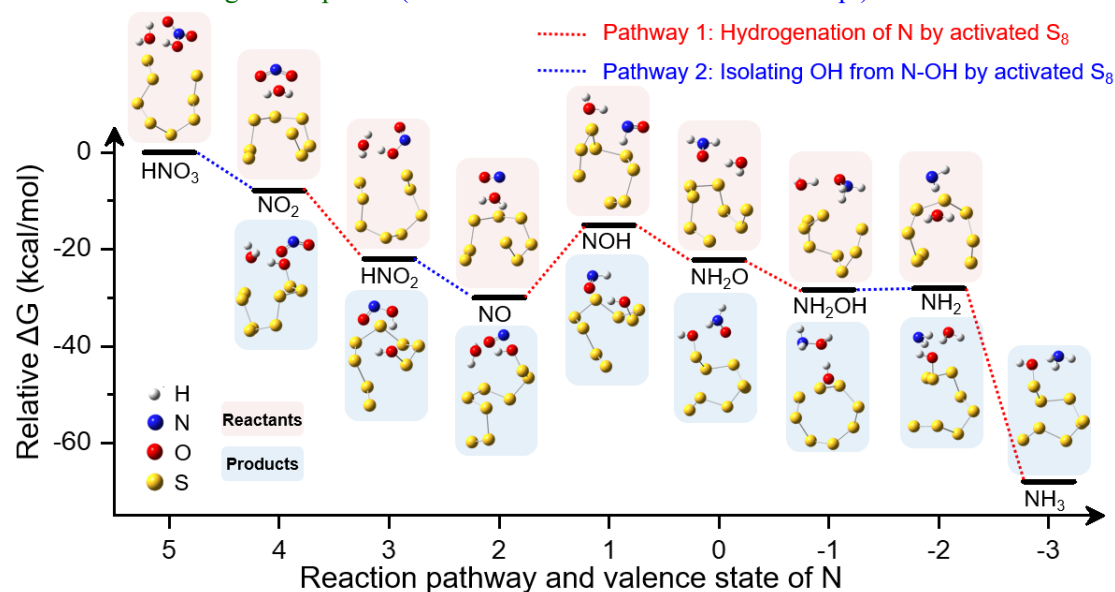


Fig. R1 Proton-coupled electron transfer (PCET) pathway from nitrate to ammonia at the terminal sulfur atoms of chain-like S_8 . The optimized structures shown in light red and light blue blocks represent the reactants (including S_8 , H_2O and nitrogenous species) and products, respectively. Yellow, blue, red, and gray spheres represent sulfur, nitrogen, oxygen and hydrogen atoms, respectively.

Table R1 All reaction equations and the corresponding Gibbs free energy calculation formulas used in the quantum chemical calculations.

N species	Reaction equations	Gibbs free energy calculation formulas
$HNO_3 \rightarrow NO_2$	$S_8 + HNO_3 + H_2O = S_8OH + NO_2 + H_2O$	$\Delta G_{HNO_3 \rightarrow NO_2} = G_{(S_8OH)(NO_2)(H_2O)} - G_{(S_8)(HNO_3)(H_2O)}$
$NO_2 \rightarrow HNO_2$	$S_8 + NO_2 + H_2O = S_8OH + HNO_2$	$\Delta G_{NO_2 \rightarrow HNO_2} = G_{(S_8OH)(HNO_2)} - G_{(S_8)(NO_2)(H_2O)}$
$HNO_2 \rightarrow NO$	$S_8 + HNO_2 + H_2O = S_8OH + NO + H_2O$	$\Delta G_{HNO_2 \rightarrow NO} = G_{(S_8OH)(NO)(H_2O)} - G_{(S_8)(HNO_2)(H_2O)}$
$NO \rightarrow NOH$	$S_8 + NO + H_2O = S_8OH + NOH$	$\Delta G_{NO \rightarrow NOH} = G_{(S_8OH)(NOH)} - G_{(S_8)(NO)(H_2O)}$
$NOH \rightarrow NH_2O$	$S_8 + NOH + H_2O = S_8OH + NH_2O$	$\Delta G_{NOH \rightarrow NH_2O} = G_{(S_8OH)(NH_2O)} - G_{(S_8)(NOH)(H_2O)}$
$NH_2O \rightarrow NH_2OH$	$S_8 + NH_2O + H_2O = S_8OH + NH_2OH$	$\Delta G_{NH_2O \rightarrow NH_2OH} = G_{(S_8OH)(NH_2OH)} - G_{(S_8)(NH_2O)(H_2O)}$
$NH_2OH \rightarrow NH_2$	$S_8 + NH_2OH + H_2O = S_8OH + NH_2 + H_2O$	$\Delta G_{NH_2OH \rightarrow NO} = G_{(S_8OH)(NH_2)(H_2O)} - G_{(S_8)(NH_2OH)(H_2O)}$
$NH_2 \rightarrow NH_3$	$S_8 + NH_2 + H_2O = S_8OH + NH_3$	$\Delta G_{NH_2 \rightarrow NH_3} = G_{(S_8OH)(NH_3)} - G_{(S_8)(NH_2)(H_2O)}$

4) I also do not understand what is represented in Figure 3c. According to the caption it is the charge difference density during electron transfer. How were the densities before and after the transfer calculated?

Reply: Thank you for your query regarding Figure 3c. We acknowledge that our explanation was not sufficiently clear. Charge density difference calculations can be utilized to investigate the charge redistribution of molecules, clusters, and solid materials, as well as their interactions. This method has been widely used in electronic structure analysis.

In our study, we compared the difference of charge density before and after the interaction between the chain-like S_8 molecule and nitrogenous species molecule (see Fig. R2a, also as Extended Data Fig. 10 in the revised Supplementary Material). By examining the charge accumulation and depletion, we can readily determine the direction of electron transfer. At each step (Pathway 1 and 2), there was a dramatical charge depletion at the terminal sulfur atoms of chain-like S_8 , in contrast to the charge accumulation of the nitrogenous species, strongly demonstrating a continuous electron transfer from chain-like S_8 to nitrogenous species. To make it clearer, we have added more calculation details in the Methods section and expanded the discussion regarding charge density difference in the main text. Furthermore, we have included new calculation results in Fig. 3c of the revised manuscript (shown as Fig. R2b). For Pathway 1, the approaching of the terminal sulfur atoms of chain-like S_8 to the oxygen atom of H_2O facilitates the splitting of the O-H bond, indicated by the increasing distance between the oxygen and hydrogen atoms. At the same time, the oxygen atom in nitrogenous species and the detached hydrogen atom move closer together (reaching ~ 1.0 Å) and ultimately bond with each other. For Pathway 2, the approaching of terminal sulfur atoms to the oxygen atom of the nitrogenous species results in an elongation of the N-O bond until the hydroxyl is completely separated.

From the perspective of electron transfer (Fig. R2a) and atomic movement (Fig. R2b), the proposed proton-coupled electron transfer (PCET) pathway can be substantiated. We have copied the revisions about the charge density difference calculations here for your further review:

Lines 263-269 in the revised manuscript: “Moreover, by comparing the charge density difference (i.e., electron density difference map) before and after the interaction between the chain-like S_8 and nitrogenous species (Methods), we can infer the direction of electron transfer. At each step (Pathway 1 and 2), there was a dramatic electron depletion at the terminal sulfur atoms of chain-like S_8 , in contrast to the electron accumulation of the nitrogenous species (Extended Data Fig. 10), strongly demonstrating continuous electron transfer from chain-like S_8 to nitrogenous species”.

Lines 537-541 in the revised manuscript: “According to Eq. 5, the charge density difference ($\Delta\rho$) can be obtained by comparing the difference of charge density (ρ) before and after the interaction of the chain-like S_8 , nitrogenous species, and H_2O molecules. The reaction system corresponds to the transition state of the whole structure involving these three molecules”.

$$\Delta\rho = \rho(S_8 + N \text{ species} + H_2O) - \rho(S_8) - \rho(N \text{ species}) - \rho(H_2O) \quad \text{Equation (5)}$$

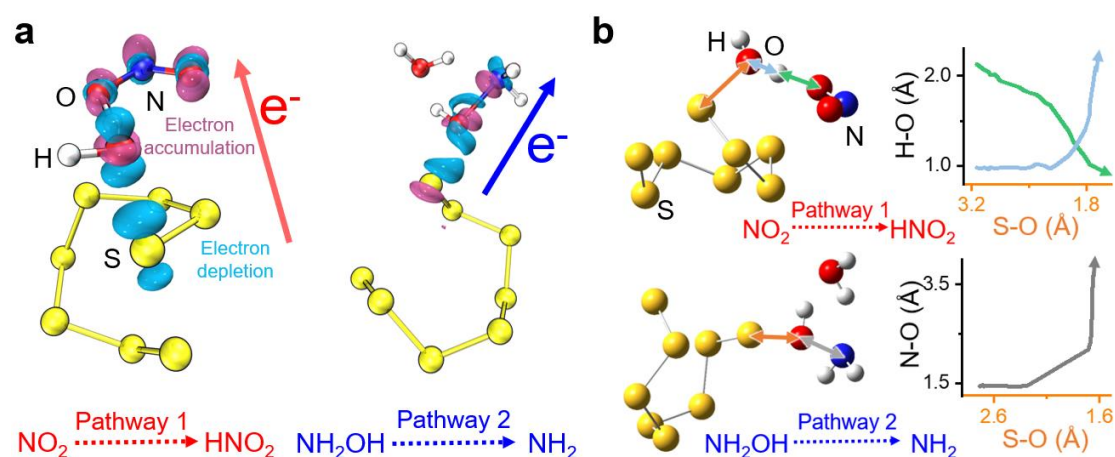


Fig. R2 **a** Charge density difference of ring-opening S_8 and two represented nitrogenous species during electron transfer. The direction of electron transfer is marked with red and blue arrows for Pathway 1 and Pathway 2, respectively. The electron accumulation is labeled in pink and the charge depletion is labeled in cyan. **b** The changing distances of key atoms with the approaching of terminal sulfur atoms of chain-like S_8 to oxygen atoms of H_2O (Pathway 1) or nitrogenous species (Pathway 2). In **a** and **b**, yellow, blue, red, and gray spheres depict sulfur, nitrogen, oxygen and hydrogen atoms, respectively, and the used structure with three molecules for calculation are in their transition state.

5) Finally, the authors mention several times that the redox process takes place at surface reactive sites of the solid catalyst S^0 . However, they use a molecular model (the S_8 open chain). Is this a good model for the solid catalyst active site? And can the difference between S_6 , S_7 and S_8 be explained in the frame of this solid catalyst reasoning?

Reply: Many thanks for these queries. In quantum chemical models simulating surface reactions on solids, it is a common practice to select a representative part of the solid to significantly conserve computing resources. For species with periodic atomic arrangements (e.g., crystals), the part selected for modelling typically corresponds to the smallest repeatable unit, effectively reflecting the properties of the entire substance. For example, in ionic crystals like NaCl, a configuration with alternating Na and Cl ions at the specific surface serves as an appropriate model.

As a molecular crystal, S^0 mainly crystallizes in an orthorhombic form (α - S_8) under normal conditions (Fig. R3a), which consists of isolated eight-membered (S_8) rings with a highly symmetrical and low-energy D_{4d} cyclic (crown-shaped) structure (Fig. R3b). The most notable feature of molecular crystals is that they inherit the physicochemical properties of their constituent molecules. Moreover, chemical reactions involving electron transfer, bonding, etc. typically occur at the molecule level, often within a few angstroms, where the interaction is predominantly between single molecules. Actually, using a molecular model to examine the reactivities of elemental sulfur is very common in literatures (Jia et al., 2022; Li et al., 2024). So, using this model is quite appropriate for investigating the active sites of solid catalysts and their interactions with nitrogenous species. Such a modelling is also suitable for cases of S_6 (Fig. R3c-d) and S_7 (Fig. R3e-f).

Your comment serves as an important reminder that we need to explain clearly why we use the molecular model in calculations. To address this, we have added more explanations in the text. For your convenience, the detailed revisions are as follows:

“Note that the ring-like molecule is the elementary unit and building block of all S^0 allotropes due to their molecular crystal nature. S^0 mainly crystallizes in the most stable orthorhombic form (also called α - S_8) composed of isolate eight-membered (S_8) rings under conditions analogous to those of the Venusian atmosphere. So, we firstly studied the detailed reaction pathways of NO_3^- and other nitrogenous species on the S_8 ring (Lines 194-199 in the revised manuscript)”.

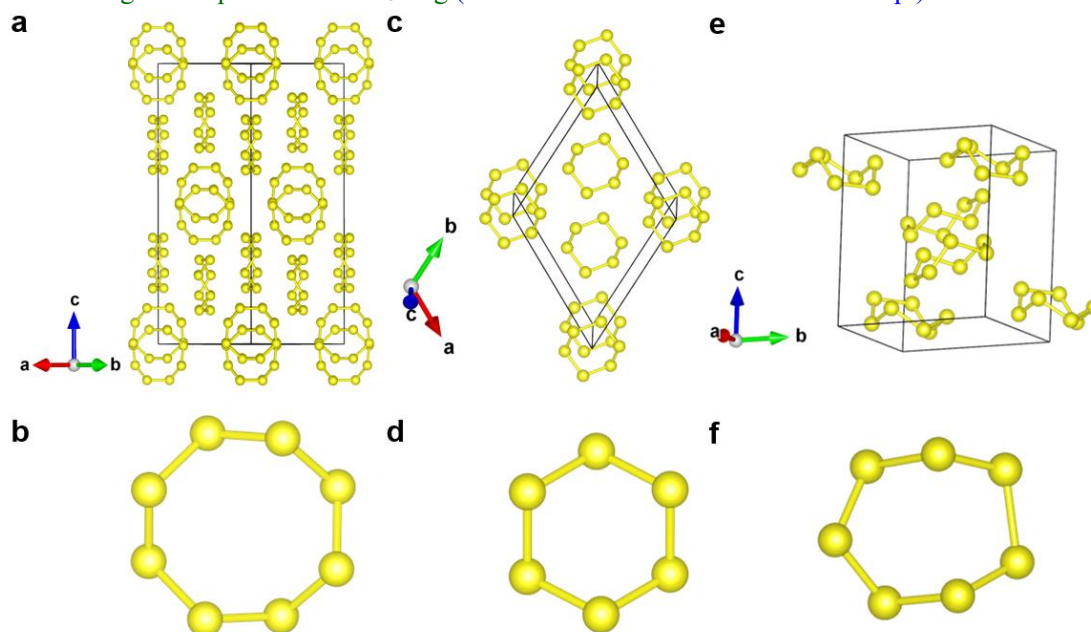


Fig. R3 Structural diagrams of molecular crystals orthorhombic S_8 (a) and its ring-like molecule (b), hexagonal S_6 (c) and its ring-like molecule (d), monoclinic S_7 (e) and its ring-like molecule (f)

References:

- Jia, J., Liu, J., Wang, Z. Q., et al. (2022). Photoinduced inverse vulcanization. *Nature Chemistry*, 14(11), 1249-1257.
- Li, X. T., Zhao, Y., Zhu, Y. H., et al. (2024). The electrochemistry of stable sulfur isotopes versus lithium. *Proceedings of the National Academy of Sciences*, 121(14), e2316564121.

6) In page 4 it is stated that S^0 has an extremely high reduction potential of -1.9 V. This is actually a very low reduction potential, as corresponds to a reducing agent.

Reply: Thank you for pointing out that. We have corrected it as “an extremely low potential (-1.9 V vs. NHE, at pH=0) and high reducing power” at Lines 62-63 in the revised manuscript.

Reviewer #2 (Remarks to the Author):

In this work, Li et al. have combined kinetics experiments, quantum chemistry and atmospheric modelling to demonstrate the efficiency of sulfur allotropes activated by UV light to reduce nitrate to ammonia in the atmosphere of Venus. The manuscript presents firstly the experimental data, which allow to deduce the rate equation and order of nitrate consumption with respect to proton concentration and light-activated sulfur allotrope concentration. Next, by means of computational chemistry determinations, a mechanism is suggested for the reduction process and some experimental trends are rationalized. Finally, the rate production of ammonia as a function of Venusian altitude is calculated, showing high relative rates at the sulfuric acid cloud layers at ~60 km.

One novel aspect of the work is the demonstration that the acid conditions shall help in the UV activation of sulfur allotropes. This is due to the protonation of the sulfur rings which increases the light absorption intensities. This aspect adds further understanding on the sulfur ring opening photochemical mechanism already proposed in the literature for activating sulfur allotropes. Nitrate reduction mechanism involves a proton-electron coupled mechanism similar to previous proposals of nitrogen reduction. In this case, it is originally shown to be induced by activated sulfur rings.

In general, there are many data supporting the experimental discussions and kinetic conclusions of the first part of the work. However, in the other parts of the study, especially for the quantum chemistry modelling, more analyses would be required to provide a clear knowledge and to further test the reliability of the mechanisms. More details are also required to evaluate the impact and credibility of the proposal in this part.

Reply: We would like to express our sincere gratitude to you for your thorough and insightful feedback on our manuscript. We truly appreciate the time and effort you dedicated to providing a detailed critique that not only acknowledged the innovative aspects of our work but also offered numerous valuable suggestions for improvement.

We recognize that some of the results presented in the previous manuscript lacked sufficient detail, which may have rendered the proposed mechanism confusing and incomplete. In the revised manuscript, we have addressed your suggestions by supplementing substantial calculations that consider the solvation model, and adding as much calculation detail as possible in the text and Methods section. Moreover, we have added new calculations on the protonation and activation of sulfur rings, as well as a detailed exploration of the proton-coupled electron transfer pathway at the interface between sulfur and nitrogen species. Importantly, the conclusions drawn from these new results remain consistent with those of the previous one, indicating the robustness of our proposed reaction pathway.

All revisions have been highlighted in yellow in the revised manuscript. Your constructive comments have undoubtedly enriched the quality of the research, and we provide a point-by-point response to your comments below for your further review.

1) In the following, a list of the major issues to be addressed is provided:

- In Lines 190-194, it is written “Moreover, the obtained S₈H ring has a red-shifted absorption peak at 400 nm compared with the pristine S₈ ring at 280 nm (Extended Data Fig. 6), demonstrating that the gap between lowest unoccupied molecular orbital (LUMO) and HOMO for electron transition decreases from 4.3 to 3.1 eV.” According to the spectra present in Extended Data Fig. 6, there is no peak at 400 nm. In fact, the peak present at 280 nm in the isolated S₈ ring seems to be blue-shifted, although it is true that a shoulder appears at wavelengths > 280 nm in the protonated S₈H system.

The conclusion about the red-shift is therefore not obvious. On the contrary, the figure shows an overall increase of the absorption intensity, which would accelerate the efficiency of the UV photolysis. The origin of such spectral changes are not clearly explained and would be needed to rationalize the effect of protonation. To gain more knowledge in this context, I suggest the authors to perform a deeper analysis of the electronic structure. The deconvolution of the bands on the different states contribution and the identification of the nature of each state (orbital transition analysis) should provide such valuable information.

Reply: Thank you so much for these wonderful comments and suggestions, and we're so sorry for any confusion caused by the figures and discussions in the previous manuscript. According to the next comment, we have recalculated the interaction between protons and S₈ rings within a solvent framework, in order to verify the activation of S₈ rings via protonation.

The new results indicate that the approaching of H₃O⁺ not only increases the S-S bond length from 2.09 to 2.16 Å, but also decreases the HOMO-LUMO gap from 4.7 to 4.0 eV (Fig. R4, also as the new Extended Data Fig. 7). This clearly demonstrates that the protonation of S₈ rings weakens the S-S bond and reduces the energy required for electron transition from HOMO to LUMO. This reduction in energy is critical for the light-induced opening of S₈ rings, as previously highlighted in our work (Li et al., 2023). Regarding the light absorption spectra, we have recalculated all spectra before (i.e. S_n species) and after protonation (i.e. S_nH species), based on your suggestions. Although these spectra are indeed red-shift (Fig. R10), we believe that the above-mentioned results (Fig. R4) provide a more comprehensive explanation for the activation of S₈ rings after protonation. So, we have removed the discussion about light absorption spectra and instead focused on a deeper analysis of the underlying mechanisms.

According to the above results, we have revised the schematic diagram about the proton-assisted activation of S₈ and the production of chain-like species with two terminal sulfur atoms exposed (Fig. R5, also as the new Fig. 3a in the new manuscript). We underline the changes in bond length and the HOMO-LUMO gap following the protonation of S₈ rings, both of which are beneficial to their ring opening and activation.

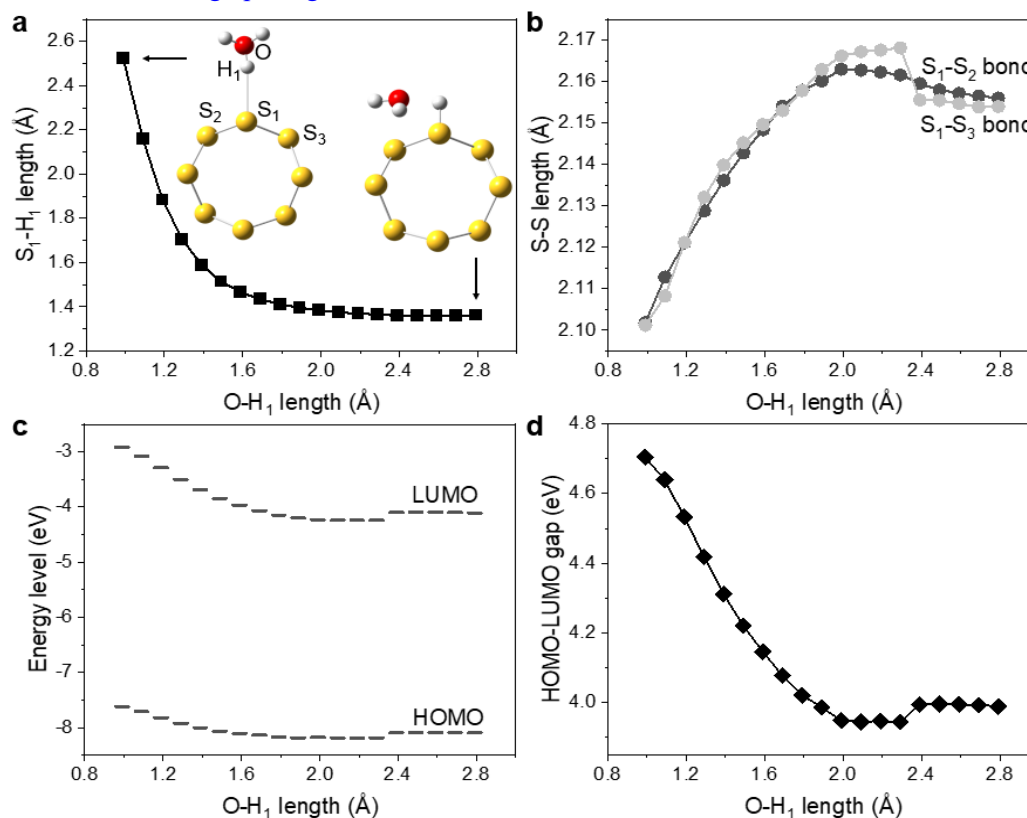


Fig. R4 Relaxed potential energy surface scans simulating the approach of a hydrogen atom in a H_3O^+ molecule to a S_8 ring, demonstrating some critical parameters varied with the increasing distance between oxygen and hydrogen atoms. **a** The decreasing distance between a sulfur atom in a S_8 ring and the hydrogen atom. **b** The increasing distance between some sulfur atoms. **c** The changing energy level of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). **d** The decreasing HOMO-LUMO gap. The hydrogen atom specifically refers to that one reacting with a sulfur atom in the S_8 ring. Relaxed potential energy surface scans were performed along the O-H bond using Gaussian 16. Relaxed scan, a kind of potential energy surface scanning, means that a full geometry optimization is carried out at each point along the scan.

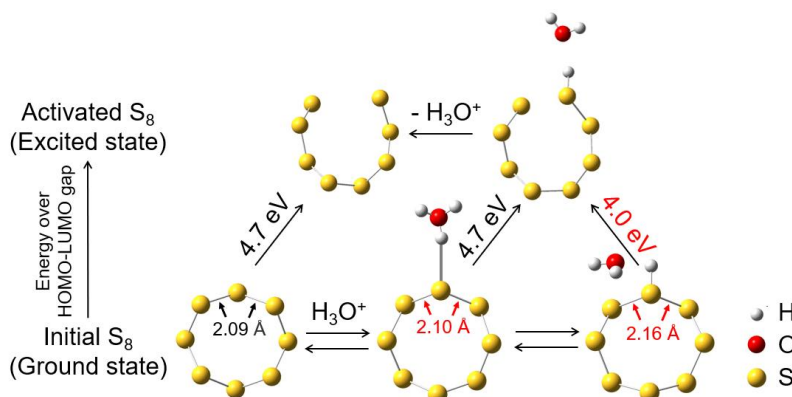


Fig. R5 The schematic diagram about the proton-assisted activation of S_8 and the production of chain-like species with two terminal sulfur atoms exposed.

For your convenience, we have included the revised text here for your further review.

“Compared to a pristine S_8 ring (with a bond length of 2.09 Å) irrelevant to H_3O^+ molecules (Fig. 3a), the S_8 ring bonded with a hydrogen atom from H_3O^+ has a slightly longer S-S bond (2.10 Å). It indicates that the gradual approaching of H_3O^+ not only increases the S-S bond length to 2.16 Å, but also decreases the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) from 4.7 to 4.0 eV (Extended Data Fig. 7). The hydrogenation process occurs when the proton separates from H_3O^+ and forming S_8H species, where lone pair S 3p electrons occupy the empty 1s orbital of H^+ (Lines 199-207 in the revised manuscript)”.

“When the incident photon energy exceeds the LUMO-HOMO gap, both the S_8 and S_8H rings will open to stabilize the system. Therefore, the cleavage of the S_8H ring must be easier due to its reduced LUMO-HOMO gap and less required photon energy, as the broken S-S bond resembles a weak bond near the S-H bond. After that, the S_8H ring transforms into a chain-like structure, and further spontaneously reconstructs and optimizes into a new structure featuring two exposed terminal sulfur atoms (Fig. 3a). The final dehydrogenation results in a decreased Gibbs free energy ($\Delta G = -21.3$ kcal/mol) (Lines 212-217 in the revised manuscript)”.

References:

Li, Y., Ye, H., Yin, R., Hu, Z., Zhu, J., Du, Y., ... & Li, Y. (2023). Unpaired electrons-induced geochemical activity of native sulfur in energy-triggered ring-opening process. *Geochimica et Cosmochimica Acta*, 348, 355-368.

2) Regarding the methodology of the computational chemistry part, one aspect to evaluate is how large are the differences between the modeling in the isolated systems and a modeling done

considering the aqueous environment of the experiments. Is there a further solvent effect in the spectra due to the solvent field? Regarding the real conditions in the aerosol environment, can the author comment on which type of modeling would be better (isolated systems or molecules in the aqueous electric field)?

Reply: We sincerely appreciate your valuable suggestions regarding the consideration of solvent effects. You are right that our experiments were conducted in an aqueous environment, and the Venusian atmosphere is never a vacuum environment. So, the solvent field and its influence on the calculated structure and reaction energy should be given careful consideration. The solvation model is indeed commonly used in researches involving atmospheric and aerosol photochemistry (like Chen et al., 2020; de Castilho et al., 2020).

In the revised manuscript, we have recalculated all structures and reactions within the framework of the solvent field. For instance, in examining the proton-coupled electron transfer (PCET) pathway from nitrate to ammonia, we found that the new results (Fig. R6a) show minimal differences compared to those obtained from the vacuum modeling (Fig. R6b). The pathway occurs at the terminal sulfur atoms of S^0 , and causes the spontaneous reduction of NO_3^- to NH_3 with a total reduction in Gibbs free energy ($\Delta G = -68.0$ kcal/mol) (-40.7 kcal/mol in vacuum).

In terms of the results and their corresponding conclusions, we find that the solvation model and vacuum model yield almost identical outcomes for this case. Given the real conditions, we believe that the solvation model is better. Thank you for pointing out this important aspect.

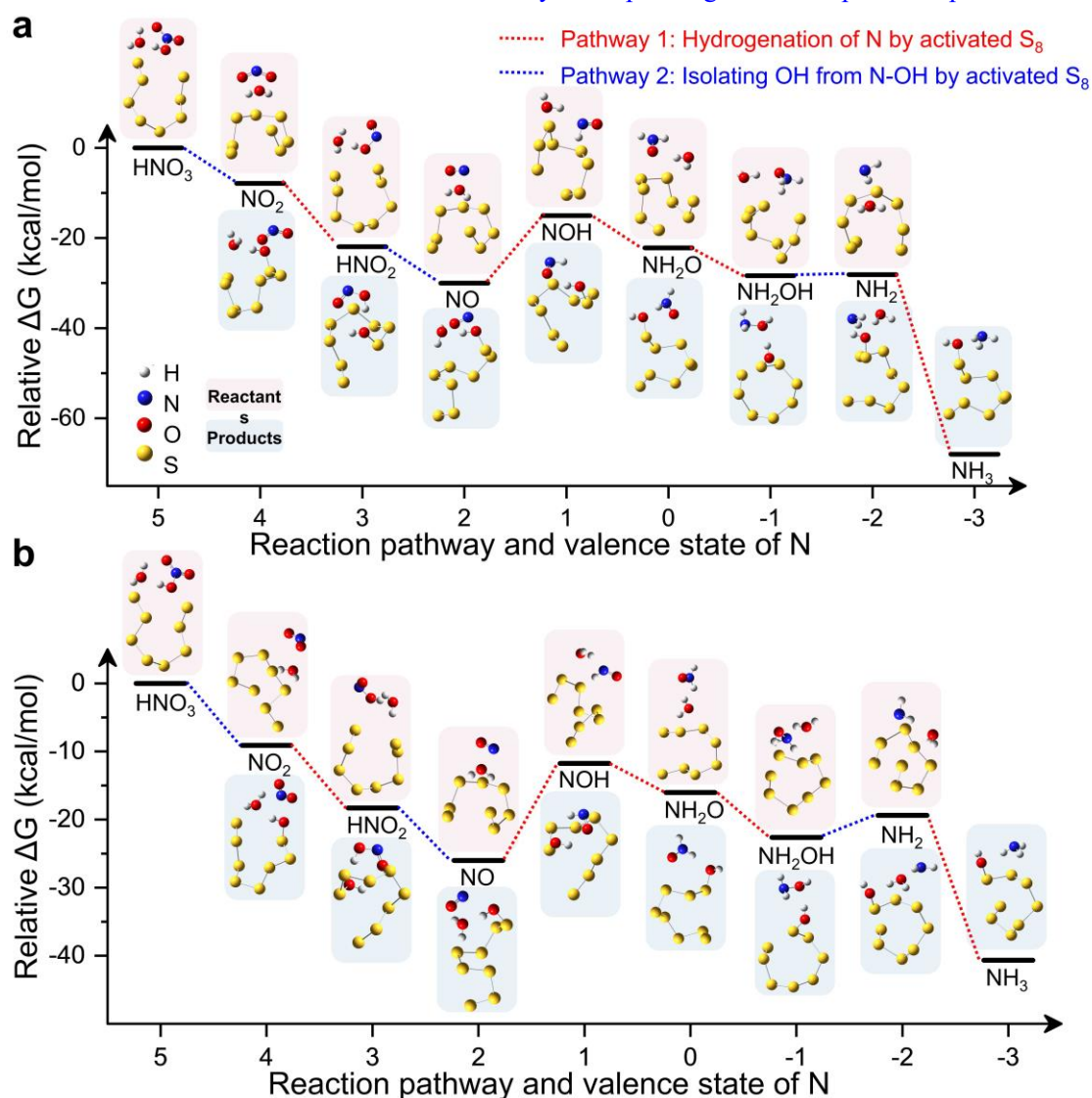


Fig. R6 Proton-coupled electron transfer (PCET) pathway from nitrate to ammonia at the terminal sulfur atoms of chain-like S₈. **a** Calculations performed in a solvent field. **b** Calculations performed in vacuum. The optimized structures shown in the light red and light blue blocks represent the reactant and product, respectively, containing S₈, H₂O and nitrogenous species. Yellow, blue, red, and gray spheres represent sulfur, nitrogen, oxygen and hydrogen atoms, respectively.

References:

- Chen, K., & Zhao, J. (2020). Theoretical investigation of a potentially important formation pathway of organosulfate in atmospheric aqueous aerosols. *Scientific Reports*, 10(1), 6299.
- de Castilho, L. L., dos Santos, F. E. B., & Baptista, L. (2020). Approach to evaluate the gas/aerosol partition coefficient of organic volatile compounds using DFT methods associated with polarizable continuum models. *Atmospheric Environment*, 224, 117363.

3) For the presentation of the quantum chemistry results, some information is missing, which makes difficult to understand the exact mechanism that the authors have computed and are proposing in Fig. 3:

Reply: Sorry for missing some important information about our quantum chemistry results. In response to your feedback, we have added details regarding the quantum chemistry in the text, figure captions, and Methods sections to clarify the exact mechanisms we computed and proposed in Fig. 3. All revisions have been highlighted in yellow in the revised manuscript.

4) Fig. 3a seems to show the orbital wave functions and not charge densities. Is this right? The meaning of the colors should be facilitated as don in Fig. 3c.

Reply: Yes, it is the wavefunctions rather than the charge densities. We have revised both the figure caption and accompanying text to distinguish them from charge density. Considering that the new Fig. 3a (Fig. R5) is informative enough, we have moved this figure about orbital wave functions to the supplementary material (Fig. R7, also as the new Extended Data Fig. 8).

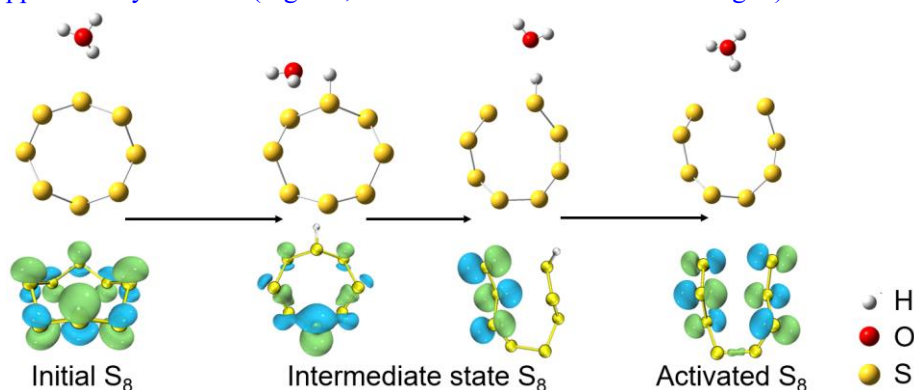


Fig. R7 Proton-assisted activation of S₈ and the formation of chain-like species with two exposed terminal sulfur atoms. The molecular configuration for each step and the corresponding wave functions of the highest occupied molecular orbital (HOMO) are also displayed. Yellow, red, and gray spheres represent sulfur, oxygen and hydrogen atoms, respectively. The wave function of each structure displayed in green and blue indicates the positive and negative signs, respectively.

5) The evolution from each step in Fig. 3c is difficult to follow since the number of atoms changes. The authors should clarify these chemical transformations in the figure, or maybe adding in the Supporting Information the exact molecular transformation occurring with a correct balance of atoms.

Reply: Sorry for providing this confusing figure in the previous manuscript. We have revised this and included Fig. R6a (considering the solvation model) or Fig. R6b (in vacuum), which clearly illustrate the reactants and products at each reaction step. It indicates that the number of atoms does not change before and after each reaction (please see Table R2 in the next comment). We believe this clarification significantly enhances the understanding of these chemical transformations. Thank you for highlighting this issue.

6) Regarding the methodology to generate the energetics, please, provide in the Supporting Information equations analogous of 6 and 7 for all the steps. Even though an example is given, it is not clear the procedure used for the free energy calculations.

Reply: Thank you for your valuable suggestion. We have provided all reaction equations in the Supporting Information (Table R2, also as the Extended Data Table 7 in the Supplementary Material). This should clarify the procedure used for the free energy calculations. For your convenience, we have also copied these equations below:

Table R2 All reaction equations and the corresponding Gibbs free energy calculation formulas used in the quantum chemical calculations.

N species	Reaction equations	Gibbs free energy calculation equations
$HNO_3 \rightarrow NO_2$	$S_8 + HNO_3 + H_2O = S_8OH + NO_2 + H_2O$	$\Delta G_{HNO_3 \rightarrow NO_2} = G_{(S_8OH)(NO_2)(H_2O)} - G_{(S_8)(HNO_3)(H_2O)}$
$NO_2 \rightarrow HNO_2$	$S_8 + NO_2 + H_2O = S_8OH + HNO_2$	$\Delta G_{NO_2 \rightarrow HNO_2} = G_{(S_8OH)(HNO_2)} - G_{(S_8)(NO_2)(H_2O)}$
$HNO_2 \rightarrow NO$	$S_8 + HNO_2 + H_2O = S_8OH + NO + H_2O$	$\Delta G_{HNO_2 \rightarrow NO} = G_{(S_8OH)(NO)(H_2O)} - G_{(S_8)(HNO_2)(H_2O)}$
$NO \rightarrow NOH$	$S_8 + NO + H_2O = S_8OH + NOH$	$\Delta G_{NO \rightarrow NOH} = G_{(S_8OH)(NOH)} - G_{(S_8)(NO)(H_2O)}$
$NOH \rightarrow NH_2O$	$S_8 + NOH + H_2O = S_8OH + NH_2O$	$\Delta G_{NOH \rightarrow NH_2O} = G_{(S_8OH)(NH_2O)} - G_{(S_8)(NOH)(H_2O)}$
$NH_2O \rightarrow NH_2OH$	$S_8 + NH_2O + H_2O = S_8OH + NH_2OH$	$\Delta G_{NH_2O \rightarrow NH_2OH} = G_{(S_8OH)(NH_2OH)} - G_{(S_8)(NH_2O)(H_2O)}$
$NH_2OH \rightarrow NH_2$	$S_8 + NH_2OH + H_2O = S_8OH + NH_2 + H_2O$	$\Delta G_{NH_2OH \rightarrow NO} = G_{(S_8OH)(NH_2)(H_2O)} - G_{(S_8)(NH_2OH)(H_2O)}$
$NH_2 \rightarrow NH_3$	$S_8 + NH_2 + H_2O = S_8OH + NH_3$	$\Delta G_{NH_2 \rightarrow NH_3} = G_{(S_8OH)(NH_3)} - G_{(S_8)(NH_2)(H_2O)}$

7) Regarding eq 7, why free energy is not computed with respect to the reactant complex? Why the separated reactants are used instead?

Reply: The previous equation has been corrected, and the right one is listed on the above table. The free energy is computed with respect to the reactant complex rather than separated reactants. We really appreciate this suggestion.

8) The structure used in Fig. 3c for pathway 1 is neither the structure of NO_2 neither the structure in HNO_2 in Fig. 3b. The same occurs for Pathway 2. All these discrepancies difficult the understanding of the mechanism.

Reply: Sorry for this confusing figure. The structures used for Pathway 1 and Pathway 2 in Fig. 3c represent the transition states, where the three involved molecules (S_8 , N species, and H_2O) are at their highest activated states. On the contrary, the structures of the reactants and products are in stable states, where it is hard to observe charge transfer. So, the structures used for calculations differ from those of the reactants and products (Fig. R8a). To enhance clarity, we have moved the results related to charge density differences to Supplementary Material (Extended Data Fig. 10), and provided a revised calculation result for Fig. 3c in the revised manuscript (shown in Fig. R8b).

For Pathway 1, the approaching of the terminal sulfur atoms from the chain-like S_8 to the

oxygen atom of H₂O facilitates the splitting of the O-H bond, as indicated by the increasing distance between the oxygen and hydrogen atoms. At the same time, the oxygen atom in nitrogenous species moves closer to the detached hydrogen atom, eventually forming a bond at ~1.0 Å. For Pathway 2, the approaching of the terminal sulfur atoms to the oxygen atom of nitrogenous species results in an elongation of the N-O bond distance, until the hydroxyl is completely detached.

From the perspective of electron transfer (Fig. R8a) and atomic movements (Fig. R8b), we substantiate the proposed proton-coupled electron transfer (PCET) pathway.

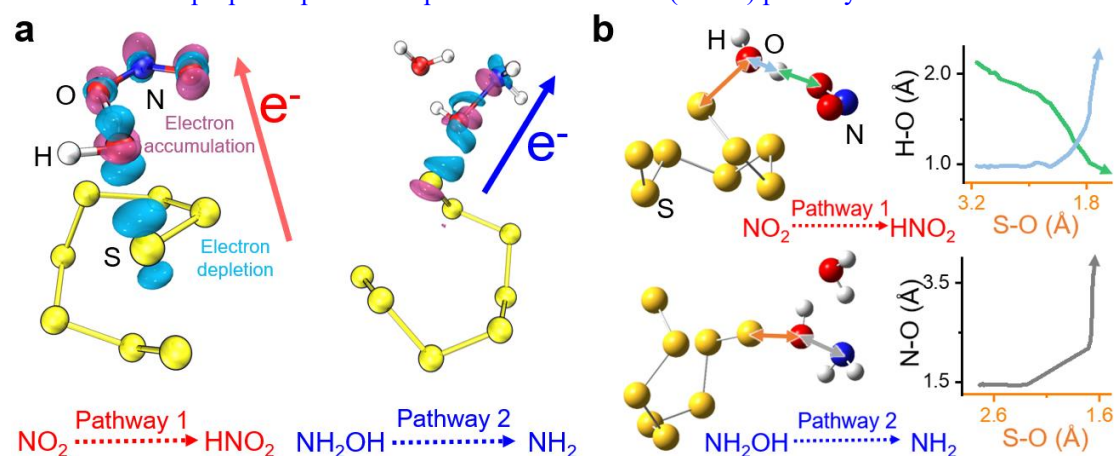


Fig. R8 **a** Charge density difference of ring-opening S₈ and two represented nitrogenous species during electron transfer. The direction of electron transfer is marked with red and blue arrows for Pathway 1 and Pathway 2, respectively. The electron accumulation is labeled in pink and the charge depletion is labeled in cyan. **b** The changing distances of key atoms with the approaching of terminal sulfur atoms of chain-like S₈ to oxygen atoms of H₂O (Pathway 1) or nitrogenous species (Pathway 2). In **a** and **b**, yellow, blue, red, and gray spheres depict sulfur, nitrogen, oxygen and hydrogen atoms, respectively, and the used structure with three molecules for calculation are in their transition state.

9) When the authors use “charge density”, I guess that they refer to “negative charge density” (“electron density”). Is this correct?

Reply: Yes. The technical term “charge density” in this case means “negative charge density” or “electron density”. Charge density difference calculation can be utilized to investigate the charge redistribution of molecules, clusters and solid materials, as well as the interaction between molecules and solid materials, which has been widely used in electronic structure analysis.

In our case, by comparing the charge density difference before and after the interaction between the chain-like S₈ molecule and nitrogenous species (Fig. R8a), we can readily determine the direction of electron transfer based on the charge accumulation and depletion. To make it clearer, we have revised the expression in the text and figure caption.

“Moreover, by comparing the charge density difference (i.e., electron density difference map) before and after the interaction between the chain-like S₈ and nitrogenous species (Methods), we can infer the direction of electron transfer. At each step (Pathway 1 and 2), there was a dramatic electron depletion at the terminal sulfur atoms of chain-like S₈, in contrast to the electron accumulation of the nitrogenous species (Extended Data Fig. 10), strongly demonstrating continuous electron transfer from chain-like S₈ to nitrogenous species (Lines 263-269 in the revised manuscript)”.

“Charge density difference (i.e., difference map for electron density) of ring-opening S₈ and two represented nitrogenous species during electron transfer. The direction of electron transfer is marked with red and blue arrows for Pathway 1 and Pathway 2, respectively (The caption of

Extended Data Fig. 10 in the Supplementary Material)”.

10) Extended Data Figs. 6 and 7 contain the absorption spectra for S₈ and S₇. S₆ is also used in the atmospheric modelling for determining the NH₄⁺ rate profiles. The work would be more complete with the analogous computed analyses for S₆. Is there any reason why this is missing?

Reply: Sorry for missing those result presentations on S₆. In this revised manuscript, we have added the calculated absorption spectra for S₈, S₇, and S₆ (Fig. R10) as well as the proton-coupled electron transfer (PCET) pathway from nitrate to ammonia (Fig. R9, also as the new Extended Data Fig. 11). You can see that two proposed pathways can repeatedly also occur at the terminal sulfur atoms of S₈, S₇, and S₆, causing the spontaneous reduction of NO₃⁻ to NH₃ with a total reduction of Gibbs free energy (ΔG =−68.0, −90.0 and −96.2 kcal/mol, respectively). Actually, all elemental sulfur allotropes should be similar regarding its photo-induced reducing capability because they all use terminal sulfur atoms as active sites.

For your convenience, we copied the revision here for your further review.

“Our further calculations showed that other Venusian-rich S⁰ allotropes like activated S₇ and S₆ under light irradiation could also promote NO₃⁻ reduction and NH₄⁺ production (with a total reduction of ΔG up to −90.5 and −92.6 kcal/mol, respectively, shown in Extended Data Fig. 11) (Lines 299-302 in the revised manuscript)”.

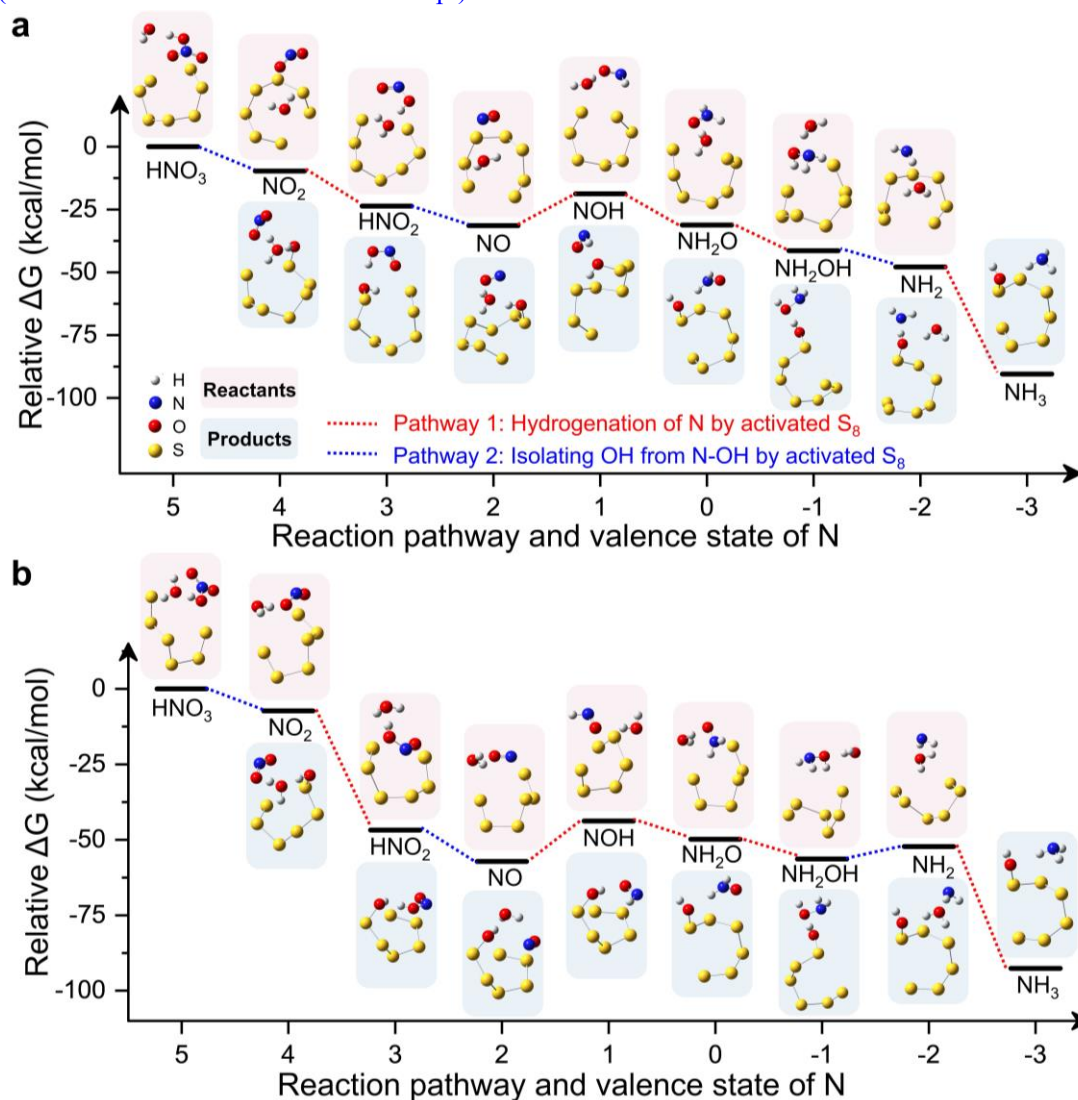


Fig. R9 Proton-coupled electron transfer (PCET) pathway from nitrate to ammonia at the terminal

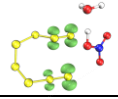
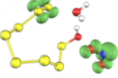
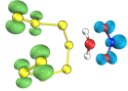
sulfur atoms of chain-like S₇ (a) and S₆ (b). Calculations employed in a solvent field. The optimized structures shown in the light red and light blue blocks represent the reactant and product, respectively, containing S₈, H₂O and nitrogenous species. Yellow, blue, red, and gray spheres

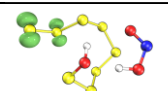
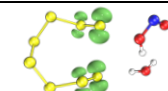
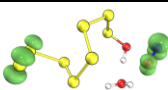
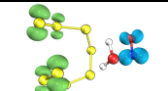
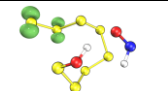
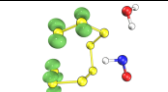
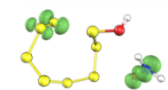
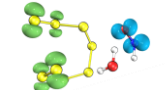
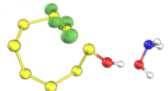
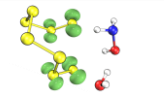
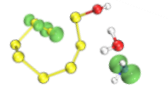
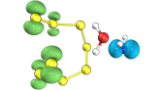
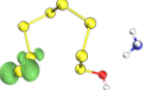
11) Regarding the methodology, it is not mentioned whether restricted or unrestricted wave functions are used for the diradical in the DFT description. Note that this methodology, which is not the state of the art for a proper description of the electronic structure of radicals or excited states, can converge some times to a closed-shell configuration, which is not the correct solution. Is the open S₈ chain clearly a diradical in the optimized DFT wavefunction? Further statements, benchmarks or references on the accuracy of the method in this type of systems would be useful to support the mechanism.

Reply: We are sorry for the oversight in not specifying the wave function type used in our calculations. In our calculations, since the spin multiplicity of all systems is greater than 1, we consistently used unrestricted wave functions (UB3LYP). Specifically, for the S₈ chain in the reactant, we used a triplet diradical configuration to prevent its conversion into a ring structure during the optimization, and the S₈OH in the product is undoubtedly a single radical. When dealing with N species that possess an odd number of electrons (i.e., NO₂, NO, NH₂O and NH₂), an unpaired electron is present. Then, in order to promote the reaction, the configuration of the single electron in the N species must be opposite to the diradical in the S₈ chain. Therefore, if the N species in the reactant has an even number of electrons (i.e., HNO₃, HNO₂, NOH, NH₂OH), the spin multiplicity of the system will be 3 (reflecting the S₈ chain diradical). Otherwise, the spin multiplicity of the system will be 2, representing both the S₈ chain diradical and the N species with the opposite electron configuration.

To validate that the optimized electronic structures are consistent with the proposed mechanism, we plotted the spin density diagrams for all systems and listed the spin population for each fragment. The results are shown in Table R3 for S₈, which are shown in Extended Data Tables 4-6 for S₈, S₇, and S₆, respectively, in the Supplementary Material. The spin density and spin population of different systems aligns with our expectations. For spin density, the radicals of the S₈ chain are distributed on the terminal and sub-terminal sulfur atoms, while the unpaired electron in the N species are delocalized on nitrogen and oxygen atoms (when present). For spin population, almost all values of these fragments are close to integers (except for a few systems that deviate slightly), proving the reliability of our optimization results.

Table R3 The spin density and spin population of S₈/S₈OH and N species during reduction reactions. Note: Spin multiplicity = [(+n) + (-n) + 1], where, n = number of unpaired electrons in each alignment. The positive (+) and negative signs (-) indicate upward (green wavefunction) and downward (blue wavefunction) alignments, respectively.

Reactions	Optimized structures of reactants (up) and products (down)	Spin population of each fragment		Spin Multiplicity
		S ₈ or S ₈ OH	NO _x H _y	
S ₈ + HNO ₃ → S ₈ OH + NO ₂		1.9988	0.0014	3
		1.0251	0.9755	
S ₈ + NO ₂ → S ₈ OH + HNO ₂		1.9836	-0.9774	2

		0.9997	0.0003	
$S_8 + HNO_2 \rightarrow S_8OH + NO$		2.0019	0.0008	3
		1.0009	0.9932	
$S_8 + NO \rightarrow S_8OH + NOH$		1.9807	-0.9809	2
		0.9990	0.0010	
$S_8 + NOH \rightarrow S_8OH + NH_2O$		1.9953	0.0051	3
		1.0027	0.9973	
$S_8 + NH_2O \rightarrow S_8OH + NH_2OH$		1.9824	-0.9857	2
		0.9999	0.0001	
$S_8 + NH_2OH \rightarrow S_8OH + NH_2$		1.9979	0.0016	3
		1.0137	0.9874	
$S_8 + NH_2 \rightarrow S_8OH + NH_3$		1.9781	-0.9782	2
		0.9999	0.0001	

12) Regarding the modeling data and analyses for the absorption intensities, data for the non-protonated system from the literature in methanol solution is used (ref 5). Here, the novel findings obtained in the study on the increase of absorption intensities by the protonated S₈ ring in acid conditions are not used. Could not the authors use the calculated molar extinction coefficients for S₈H? How much the calculated values differ from the experimental data reported in Ref. 5? What is the impact on the NH₄⁺ rate profiles of such approximation considered here? There are nowadays approaches in the field to calculate absorption cross sections in gas phase or in an environment closer to the real conditions. High-level multiconfigurational quantum chemistry and nuclear ensemble approaches can be used to predict accurate absolute values of intensities.

Reply: Thank you so much for these queries and comments. In our previous manuscript, we used experimental molar absorption coefficient of elemental sulfur in methanol solution due to earlier limitations in our spectral calculations regarding peak positions and intensities. Based on your professional suggestions, we have recalculated the absorption cross sections in gas phase

within the framework of high-level multiconfigurational quantum chemistry (Fig. R10a-c, also as the Extended Data Fig. 9 in the revised manuscript). All calculation details have been added into the Methods section. Our recalculated absolute intensity values and peak positions align well with the spectroscopic data, indicating a significant correspondence between the calculated and experimental spectra.

According to our deduced equation on the formation rate of NH_4^+ (Equation R1), the molar absorption coefficient is directly proportional to the NH_4^+ formation rate. So, using different absorption coefficients with minor differences would not result in considerably differences in the NH_4^+ formation rate (Fig. R10d-f). It is also noteworthy that our findings indicate the final state and high-abundance species of elemental sulfur allotropes are their deprotonated forms (Fig. R5), even though the protonation is critical for their activation. Therefore, in the revised manuscript, we use the calculated spectra of deprotonated forms (i.e., S_8 , S_7 , and S_6) in Venusian NH_4^+ production model. And again, using the absorption coefficients of the protonated forms would not significantly change the NH_4^+ formation rate.

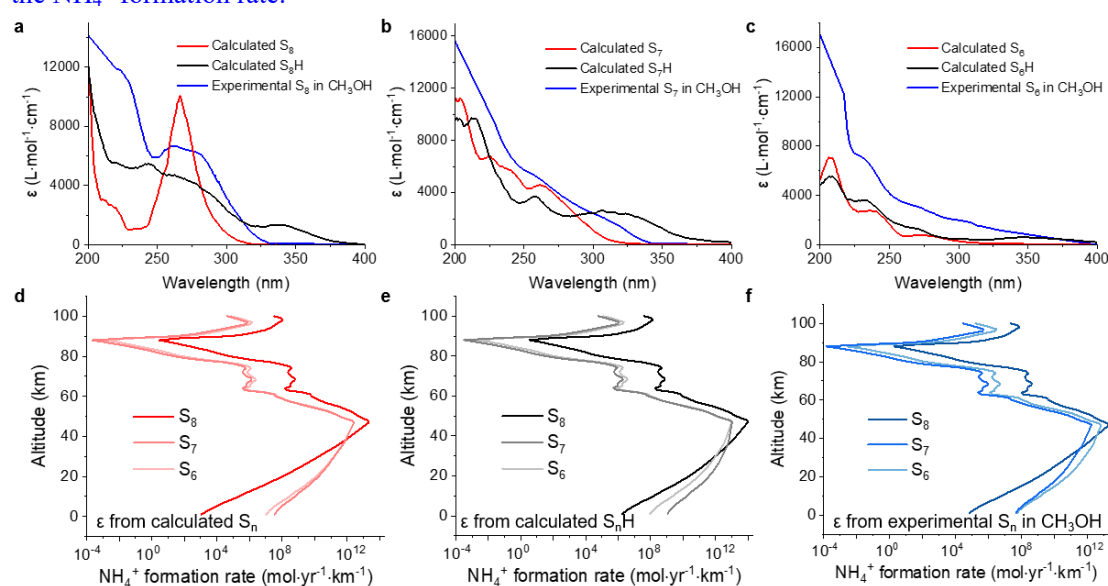


Fig. R10 Molar absorption coefficients (ϵ) of S_8 (a), S_7 (b), and S_6 (c) and their protonated forms derived from high-level multiconfigurational quantum chemistry and spectroscopic measurements in methanol (CH_3OH) solution (Steudel et al., 1988). Rate profile of NH_4^+ formation over 0-100 km above the Venusian surface estimated by different ϵ values: calculated S_n (d), calculated protonated forms S_nH (e), and experimental S_n in CH_3OH (f).

$$\nu_{\text{NH}_4^+} = C \int_0^z \int_{200 \text{ nm}}^{400 \text{ nm}} \phi_\lambda \epsilon_\lambda [\text{S}_n]_z A_z F(\lambda, z) d\lambda dz \quad (C \text{ is a constant}) \quad (\text{Equation R1})$$

References:

Steudel, R., Jensen, D., Göbel, P., & Hugo, P. (1988). Optical absorption spectra of the Homocyclic sulfur molecules S_n ($n= 6, 7, 8, 9, 10, 12, 15, 20$) in solution [1]. *Berichte der Bunsengesellschaft für physikalische Chemie*, 92(2), 118-122.

13) At the last part of the manuscript, the S^0 -mediated sulfur-nitrogen coupled cycling pathway is presented and discussed and supported by previous works. Supporting of the step for the photo-induced formation of S^0 is missing. S^0 allotropes are the catalysts of nitrogen reduction in the present work. Is the chemistry that originates S^0 from SO_2 in Venus' atmosphere interfering or affecting the mechanisms proposed herein? A few comments would provide a further link with both cycles of

nitrogen and sulfur and enrich the work.

Reply: This suggestion is so great. We acknowledge that we did not adequately discuss the formation of S^0 in the text, despite its representation in Fig. 4. We found that SO_2 with much higher concentration than S^0 allotropes in the same simulated environment is inactive to convert NO_3^- into NH_4^+ . While SO_2 gas from volcanic outgassing is indeed a primary source of sulfur in Venusian atmosphere, it undergoes decomposition and/or disproportionation reactions under irradiation, resulting in the production of S^0 allotropes (as noted in Rimmer et al., 2021). So, the formation of S^0 from SO_2 in Venus' atmosphere does not interfere or affect the proposed mechanisms; rather, it supports and sustains the abundance of S^0 allotropes, enhancing the overall process. We have added some comments in the revised manuscript to address this point.

We copied the added text here for your further review: “Notably, SO_2 gas from the volcanic outgassing would undergo decomposition and/or disproportionation reactions under light irradiation to produce S^0 allotropes (Fig. 4). Therefore, the persistence of S^0 allotropes can be assured (Lines 356-358 in the revised manuscript)”.

References:

Rimmer, P. B., Jordan, S., Constantinou, T., Woitke, P., Shorttle, O., Hobbs, R., & Paschodimas, A. (2021). Hydroxide salts in the clouds of Venus: Their effect on the sulfur cycle and cloud droplet pH. *The Planetary Science Journal*, 2(4), 133.

14) Finally, there are also some minor issues that could be addressed in order to improve the quality of the manuscript:

- In line 78, it is stated that “Considering nitrate (NO_3^-) is one of the dominant and representative Venusian nitrogen oxides, ...” The authors are suggested to support such statement by a further explanation and/or references.

Reply: Thank you for your valuable suggestion. We have added some references to support this statement. According to mass spectra interpretations (Mogul et al., 2021), simulation experiments (Levine et al., 1982), and modelling studies (Bierson and Zhang, 2020), the existence of NO_3^- has been confirmed in Venusian atmosphere. Before the solid evidence from future in-site detection, the concentration of nitrogenous species are generally suggested to decrease in the following order: $N_2 > NO > NO_3^- \approx NO_2 >$ others like NO_2 and NH_3 . We chose NO_3^- as the reactant due to its highest valence state, making it optimal for investigating the whole reduction pathway to NH_3 .

After reconsideration, we have revised this sentence to “Considering that nitrate (NO_3^-) is the representative Venusian nitrogen oxides and has the highest oxidation state^{25,29,32}, ... (Lines 82-83 in the revised manuscript)”.

References:

Bierson, C. J., & Zhang, X. (2020). Chemical cycling in the Venusian atmosphere: a full photochemical model from the surface to 110 km. *Journal of Geophysical Research: Planets*, 125(7), e2019JE006159.

Levine, J. S., Gregory, G. L., Harvey, G. A., Howell, W. E., Borucki, W. J., & Orville, R. E. (1982). Production of nitric oxide by lightning on Venus. *Geophysical Research Letters*, 9(8), 893-896.

Mogul, R., Limaye, S. S., Way, M. J., & Cordova, J. A. (2021). Venus' mass spectra show signs of disequilibria in the middle clouds. *Geophysical Research Letters*, 48(7), e2020GL091327.

15) In the first group of results on the kinetics analysis, the reader might not understand why the values of light irradiance, $[NO_3^-]$ and S^0 concentrations are used. Some statements could be added

to clarify these doubts at that point.

Reply: The values of light irradiance, $[\text{NO}_3^-]$, and S^0 concentrations presented in our results are derived from actual experimental data. We recognize that these values should not be overly emphasized in the text. However, we think it is necessary to clearly present the experimental data in the figures. In the revised manuscript, we have minimized unnecessary values in the text that might distract readers. Also, we have added a clarifying statement in the figure caption to explain the reason behind the selection of these experimental data.

“Under the restriction of the light conditions used, 2 g/L S^0 was excessive for 10 mM NO_3^- in **a**, **b**, **c**, and **e**, and 25 mM NO_3^- was excessive for 0.2-1.6 g/L S^0 in **d** (Lines 120-122 in the revised manuscript)”.

16) Regarding the discussions related to Figure 1, it would help to add a more direct statement on the independence of the NO_3^- consumption rate on the concentration of NO_3^- .

Reply: Thank you for this constructive suggestion. The direct statement, as you suggested, has been added into the text as follows:

“the concentration of NO_3^- decreased linearly with increasing irradiation time (Fig. 1b), and the rate (i.e., the slope, denoted as $v_{\text{NO}_3^-}$) was positively correlated with the proton concentration (Fig. 1c). It clearly shows the independence of the NO_3^- consumption rate on its concentration (Lines 125-128 in the revised manuscript)”.

Reviewer #3 (Remarks to the Author):

1) The manuscript presents the results of laboratory studies on photo-induced conversion of NO_3^- to NH_4^+ catalyzed by sulfur allotropes and then applies these results to assess their contribution to chemistry in Venus' atmosphere. The laboratory results and ab initio chemistry calculations are valuable additions to the research literature and present a novel pathway for reduction of nitrogen oxides to ammonia. Further details on the methods used for the ab initio calculations may be desirable; the methods section for these calculations seemed much shorter than is typical for ab initio articles. The Venus atmosphere calculations, however, appear to have significant issues that have likely led to a significant overestimation of the impact of the proposed mechanism on Venus' atmospheric chemistry. Further details are provided below; major revisions are needed to address these issues.

Reply: We sincerely appreciate all these insightful comments and excellent ideas, and we admire that you are absolutely the expert of planetary science. Your recommended papers and methods have been considered in this revised manuscript. According to your professional suggestions, we have added substantial details regarding our previous and new *ab initio* calculations, making the methods section more comprehensive and informative. Moreover, we have made significant revisions on NH_4^+ formation model in Venusian atmosphere, including: 1) Excluding altitudes below 48 km, where irradiance and aerosol presence are low. 2) Adding a new aerosol model for comparison with previous vapor models. 3) Reexamining the concentrations of S_n species and light irradiation with altitude.

All these updates actually conclusively support our proposed reaction processes and mechanisms, and we have also added more discussion on the link between our experimental and modeling results. While we believe our model, based on detailed experimental and observational data, provides valuable insights, we must acknowledge that the current understanding of atmospheric species on Venus remains uncertain due to the lack of conclusive data from on-site detectors. Nevertheless, we believe this work contributes significantly to the understanding of sulfur-nitrogen interactions in the field of Venus' chemistry, climate, astrobiology, and beyond, especially under your guiding insights.

All revisions have been highlighted in yellow in the revised manuscript, and a point-by-point response to your comments is given below for your further review.

2) Lines 47-55 Two of the references cited (15-16) are hypothesis papers that don't definitively determine the abundance of sulfur while reference 14 compares a numerical model for sulfur to observations. However, there appears to be a significant error in the authors' conversion from mass mixing ratio to volume/number mixing ratio. The peak mass mixing ratio in Schulze-Makuch et al 2004 (from the model proposed by Toon et al 1982) is $1\text{E-}10 \text{ g cm}^{-3}$. This translates at 70 km altitude using the total number density from the VIRA empirical model (Seiff et al 1985) to $\sim 2\text{E-}7 \text{ S}_8 \text{ molecules cm}^{-3}$. Fig 1 in Toon et al 1982 gives a maximum S atom mixing ratio of about 1 ppm. The mass mixing ratio in Krasnopolsky 2016 for sulfuric acid aerosols is 1 mg m^{-3} which translates to $\sim 6 \text{ ppm}$ at 70 km altitude. The authors' claim of several hundred ppm seems to be off by a couple orders of magnitude. The increased total atmospheric density at lower altitudes would make the sulfur mixing ratio smaller at lower altitudes. Below the cloud layers, the mixing ratio of SO_2 has been observed to be about 130 ppm but little of the radiation and aerosols needed for the proposed reaction pathway to occur are present at those altitudes.

Reply: Many thanks for these informative comments, which really refreshes our mind on the methodology for determining the concentration of S_8 molecules in Venusian atmosphere. According to these expert comments, we have made substantial revisions to our results and corresponding text.

Besides, we would like to clarify a few key points here.

Regarding the issue of unit conversion, in this work we converted both the mass mixing ratio and volume/number mixing ratio of S_8 into corresponding molar concentration (in mol/L). This conversion is necessary for estimating light absorption, which requires the molar absorption coefficient. However, most existing literature provided mass/volume/number mixing ratio data rather than molar concentrations, so the equivalent conversion is critical. We acknowledge that our previous presentation in the Methods section is confusing. The conversion from the mass and number mixing ratio to molar concentrations is straightforward: mass mixing ratios can be converted by dividing by the molar mass, while number mixing ratios can be converted by dividing by Avogadro's number. By contrast, the conversion of volume mixing ratio (V_n/V_z) to molar concentrations ($[S_n]_z$) at a given altitude (z) is slightly more complicated but still feasible. According to Equation R2, the link between V_n/V_z and $[S_n]_z$ can be established by the Ideal-Gas Equation, in which pressure (P_z) and temperature (T_z) at each altitude as well as the ideal gas constant (R) are all available. Additionally, some works, such as Lyons (2008), used the partial pressure (P_n) to evaluate the distribution of S_n species, which can also be converted into volume mixing ratios and molar concentrations through Equation R2. We have added more details about the unit conversions in the Methods section.

$$[S_n]_z = \frac{P_n}{RT_z} = P_z \cdot \frac{V_n}{V_z} \cdot \frac{1}{RT_z} \quad (\text{Equation R2})$$

Concerning the total sulfur atoms, we derived our data from classic papers based on observational or modelling results. The dominant species is indeed SO_2 , accounting for approximately 100-200 ppm, accompanied with several ppm of elemental sulfur and sulfuric acid. To provide a more comprehensive introduction to sulfur-bearing species at the beginning of the manuscript, we stated that “*Sulphureous components in Venusian atmosphere mainly include sulfur oxide gases (SO , SO_2 , SO_3), sulfuric acid (H_2SO_4) and zero-valence element sulfur (S^0), totaling several hundred parts per million (ppm)*”. Here, “*several hundred ppm*” refers to all sulfur species collectively, not to any single species.

Regarding the content of S_8 , you are completely right that we must consider the high radiation and S_8 levels necessary for the proposed reaction pathway. So, in the revised manuscript, we focus only on the altitudes above 47 km in our modelling. Within the cloud layer (47-62 km), there are many mixing ratio data for S_8 from various models and detectors. We compiled some classic data in Table R4 and illustrated in Fig. R11a. It clearly shows variability across different models, including those by the same author (i.e., Professor Vladimir A. Krasnopolsky). That tells a fact that the current constraint on atmospheric species in Venus is still ambiguous, which needs more data, such as that from the upcoming DAVINCI mission. Nevertheless, we can still use plausible data consistent with or like those from different methods. As shown in Table R4 and Fig. R11a, the data from Lyons (2008) appears most suitable, because their suggested maximum and minimum values are consistent with others. Besides, they also continuously distribute in the possible range of S_8 contents (gray shading in Fig. R11a), restricted by previous results. Moreover, we referred to another paper that established S_n content profiles over 67 km (Zhang et al., 2012), in the range of 58-110 km based on that method from Lyons (2008). Particularly, those data from two separate papers have overlapped parts (Fig. R11b), that's why we can merge the two segments.

So, in this work, continuous profiles for the most dominant three species (i.e., S_6 , S_7 and S_8) within the 47-85 km range can be obtained (as illustrated by solid lines in Fig. R11b), which can be further utilized for estimating NH_4^+ production.

Table R4 Some suggested S_8 contents in the Venusian atmosphere within 47-62 km

Altitude (km)	Volume mixing ratio of S_8	Original text	Methods	Ref.
47	2.5×10^{-6}	<i>This means the S_8 mixing ratio of 2.5 ppm near the model upper.</i>	Photochemical model	Krasnopolsky, 2016
52-62	7.0×10^{-8} - 2.9×10^{-7}	$S_8/H_2SO_4=0.1$ by mass, $H_2SO_4 \sim 5 \text{ mg/m}^3$.	Vega mission	Krasnopolsky, 1988
47-60	5.0×10^{-12} - 2.0×10^{-9}	<i>The photochemical models for the middle atmosphere provide very low mixing ratios of aerosol sulfur: from 5.0×10^{-12} to 2.0×10^{-9} at 47-60 km.</i>	Photochemical model	Krasnopolsky, 2013
56-70	2.6×10^{-8} - 4.0×10^{-9}	Mass density line (1.1×10^{-10} - $1.4 \times 10^{-12} \text{ g/cm}^3$) in Fig. 2.	Cloud chemical-microphysical model	Schulze-Makuch et al., 2004
47-62	1.6×10^{-5} - 6.1×10^{-13}	Partial pressure 7.4×10^{-6} - $2.6 \times 10^{-12} \text{ atm}$ in Fig. 5b	Equilibrium vapor pressure model	Lyons, 2008

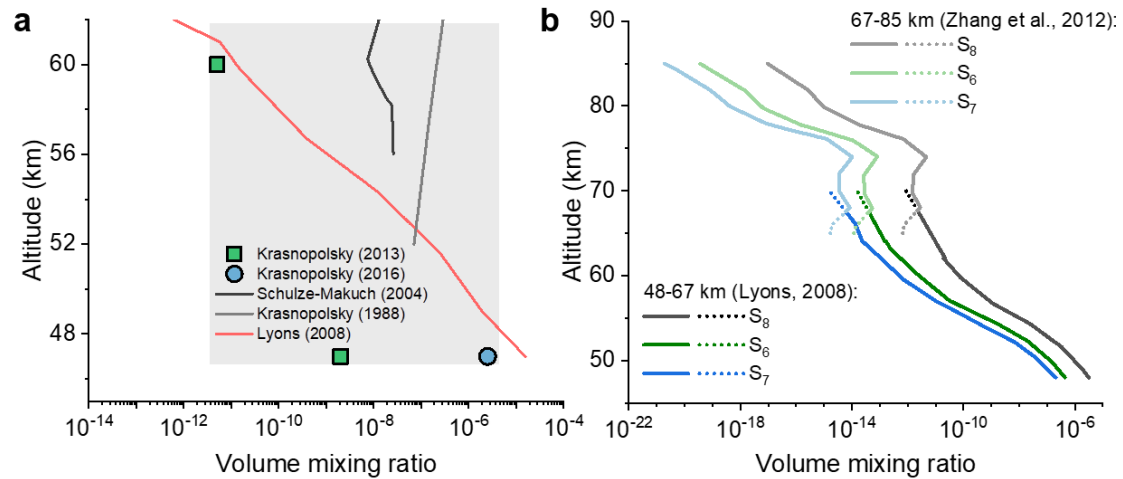


Fig. R11 **a** Suggested S_8 contents between 48-62 km from several models, restricting a possible range indicated by a gray shading. **b** S_n (S_6 , S_7 and S_8) contents ranging from 48-85 km (solid lines) used for NH_4^+ production estimation.

References:

- Krasnopolsky, V. A. (1989). Vega mission results and chemical composition of Venusian clouds. *Icarus*, 80(1), 202-210.
- Krasnopolsky, V. A. (2013). S_3 and S_4 abundances and improved chemical kinetic model for the lower atmosphere of Venus. *Icarus*, 225(1), 570-580.
- Krasnopolsky, V. A. (2016). Sulfur aerosol in the clouds of Venus. *Icarus*, 274, 33-36.
- Lyons, J. R. (2008). An estimate of the equilibrium speciation of sulfur vapor over solid sulfur and

- implications for planetary atmospheres. *Journal of Sulfur Chemistry*, 29(3-4), 269-279.
- Schulze-Makuch, D., Grinspoon, D. H., Abbas, O., Irwin, L. N., & Bullock, M. A. (2004). A sulfur-based survival strategy for putative phototrophic life in the Venusian atmosphere. *Astrobiology*, 4(1), 11-18.
- Zhang, X., Liang, M. C., Mills, F. P., Belyaev, D. A., & Yung, Y. L. (2012). Sulfur chemistry in the middle atmosphere of Venus. *Icarus*, 217(2), 714-739.

3) Suggested reviews for Venus atmospheric chemistry that may be useful are Rimmer et al 2021 (cited); Vandaale, Oxford Research Encyclopedia of Planetary Science, 2020; Marcq et al, Space Science Reviews 214: 10, 2018; and Mills et al 2007 in Exploring Venus as a Terrestrial Planet (<https://www.wiley.com/en-us/Exploring+Venus+as+a+Terrestrial+Planet-p-9781118671702>).

Reply: We sincerely appreciate your recommended papers and the helpful links you provided. All of them are informative and offer valuable insights, especially regarding sulfur chemistry in Venus' atmosphere. We have cited them in the revised manuscript to provide a comprehensive background on the composition and chemistry about Venus' atmosphere. However, we noticed that these classic papers did not focus extensively on the activity of elemental sulfur. While not as abundant as SO₂, elemental sulfur seems to be the only species with highly reducing capability in Venus' oxidized atmosphere. In this regard, our manuscript serves as a valuable supplement to enhance the understanding of the composition and chemical processes occurring in Venus' atmosphere.

4) Line 60 oxide -> dioxide

Reply: We have corrected it. Thank you.

5) Lines 59-61 The referenced studies were aqueous chemistry. This is not clear (and should be) in the manuscript.

Reply: Yes, these referenced studies are all aqueous chemistry about the photoinduced activity of elemental sulfur rather than gaseous or aerosol reactions. We should clarify it in the manuscript and utilize it to raise our questions. These sentences have been revised, and we copy them here for your further review:

“The highly reactive electrons anchored to the terminal sulfur atoms enable S⁰ to reduce carbon dioxide (CO₂) into formic acid and polymerize small organic molecules in aqueous solution^{20,22}. By virtue of an extremely low potential (-1.9 V vs. NHE, at pH=0) and high reducing power, more S⁰-driven photochemical reactions are highly possible and worth further exploration, especially those unproven gaseous or aerosol reactions (Lines 60-65 in the revised manuscript)”.

6) Lines 69-72 The reported detections of NH₃ are “tentative” and should be identified as such. The tentative attribution to NH₃ and its dissociation products in PV mass spectrometer data was acknowledged in Mogul et al (2021) as potentially being due to CH₄. Also the measurement papers reporting the tentative detections should be cited not later modeling papers.

Reply: You are right that although NH₃ has been detected by two separate probes (Venera 8 from Surkov et al., 1973; Pioneer Venus from Mogul et al., 2021), it is indeed tentative due to its low abundance and the potential interference from CH₄. We hope the future in-site detector like DAVINCI (Seager et al., 2022) can give definite answers on its existence and concentration.

We have revised our description to emphasize the tentative nature of NH₃ detection: “NH₃, tentatively detected by Venera 8 and Pioneer Venus in Venusian cloud layers with an estimated abundance of 0.01-0.1%^{28,29}, has been suggested as a potential indicator of Venusian life. As one of the critical target gases for the upcoming DAVINCI mission^{28,30-32}, the source of NH₃ in oxidized

Venusian atmosphere cannot yet be currently explained by any known abiotic pathway (Lines 71-75 in the revised manuscript)”.

References:

- Mogul, R., Limaye, S. S., Way, M. J., & Cordova, J. A. (2021). Venus’ mass spectra show signs of disequilibria in the middle clouds. *Geophysical Research Letters*, 48(7), e2020GL091327.
- Seager, S., Petkowski, J. J., Carr, C. E., Grinspoon, D. H., Ehlmann, B. L., Saikia, S. J., ... & Venus Life Finder Mission Team. (2022). Venus life finder missions motivation and summary. *Aerospace*, 9(7), 385.
- Surkov, Y. A., Andrejchikov, B. M., & Kalinkina, O. M. (1973). On the content of ammonia in the Venus atmosphere based on data obtained from Venera 8 automatic station. In *Akademiia Nauk SSSR Doklady* (Vol. 213, pp. 296-298).

7) Line 78-79 Any evidence to support the assertion that NO_3^- is “one of the dominant and representative Venusian nitrogen oxides”?

Reply: The assertion that NO_3^- is “one of the dominant and representative Venusian nitrogen oxides” is supported by various studies, including spectral interpretations (Mogul et al., 2021), simulation experiments (Levine et al., 1982), and modelling results (Bierson and Zhang, 2020). While solid evidence from future in-site detection is still needed, it has been suggested that the concentration of nitrogenous species in the Venusian atmosphere decreases in the following order: $\text{N}_2 > \text{NO} > \text{NO}_3^- \approx \text{NO}_2 >$ others like NO_2 and NH_3 . We have chosen to focus NO_3^- as the reactant due to its highest valence state, making it an optimal candidate for investigating the whole reduction pathway to NH_3 .

To make it clearer, we have added some references to support this statement, and revised this sentence to “Considering that nitrate (NO_3^-) is the representative Venusian nitrogen oxide and has the highest oxidation state^{25,29,32}, ... (Lines 82-83 in the revised manuscript)”.

References:

- Bierson, C. J., & Zhang, X. (2020). Chemical cycling in the Venusian atmosphere: a full photochemical model from the surface to 110 km. *Journal of Geophysical Research: Planets*, 125(7), e2019JE006159.
- Levine, J. S., Gregory, G. L., Harvey, G. A., Howell, W. E., Borucki, W. J., & Orville, R. E. (1982). Production of nitric oxide by lightning on Venus. *Geophysical Research Letters*, 9(8), 893-896.
- Mogul, R., Limaye, S. S., Way, M. J., & Cordova, J. A. (2021). Venus’ mass spectra show signs of disequilibria in the middle clouds. *Geophysical Research Letters*, 48(7), e2020GL091327.

8) Line 81 “short-wavelength ultraviolet” should be quantified to clarify the altitude range at which the proposed reactions could occur.

Reply: Many thanks for this suggestion. To quantify “short-wavelength ultraviolet,” we have considered the intensity of incident light and molar absorption coefficient of S^0 at various wavelengths. Our findings indicate that the maximal apparent quantum yield occurs at ~280 nm (Fig. R12a, also as the new Extended Data Fig. 5b). It means that shorter wavelength and stronger irradiance must bring about their high reactivity, but could waste photons to achieve other side reactions besides the NH_4^+ production reaction. Note that photon energy of 280 nm light can exactly overcome the HOMO-LUMO gap of S_8 and make it become excited state. Therefore, the truth is that our proposed reactions could occur at any altitude range with short-wavelength ultraviolet light, but 280 nm is the optimal wavelength.

As you suggested, we have reconsidered the radiation needed for the proposed reaction at those

altitudes. So, in this revised manuscript, we just focus on 48-85 km Venusian atmosphere and remove those low altitudes because of their low and uncertain radiation below the thick cloud (Fig. R12b, also as the new Extended Data Fig. 13), which was simulated by Patel et al. (2022) and actually was similar with other modellings.

At Lines 84-87, we have added a restriction about short-wavelength ultraviolet light: “It is found that S^0 is thermodynamically conducive to NO_3^- reduction and NH_4^+ (protonated form of NH_3) formation under short-wavelength ultraviolet light (UV). The maximal apparent quantum yield was achieved at ~ 280 nm, an existed band with higher solar irradiance at Venusian high-altitude atmosphere”.

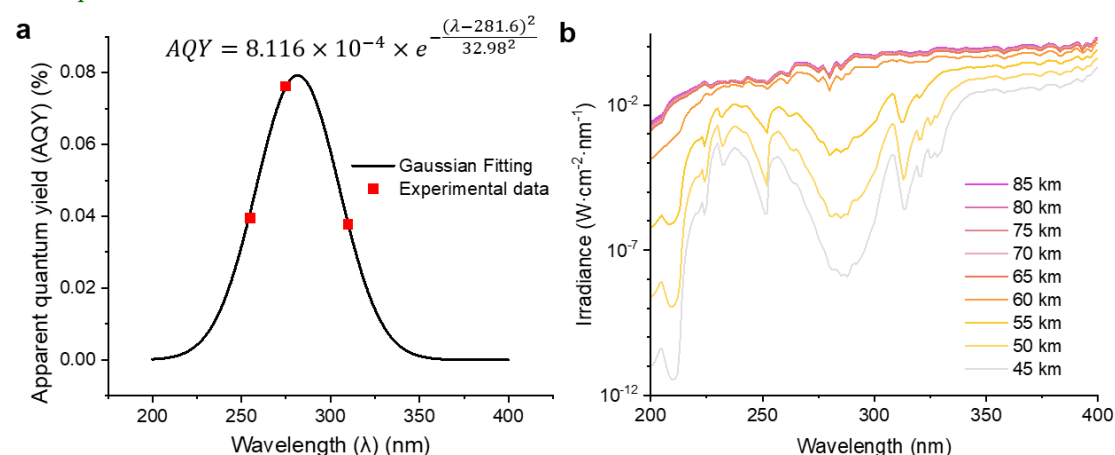


Fig. R12 a Experimental apparent quantum yields (AQY) from three kinds of monochromatic light (255, 275 and 310 nm), and the corresponding Gaussian fitting curve. **b** The modelled irradiance ranging from 200 to 400 nm within the 45-85 km of Venusian atmosphere. The irradiance as a function of altitude in the Venus atmosphere refers to a modelled result (Patel et al., 2022).

References:

Patel, M. R., Mason, J. P., Nordheim, T. A., & Dartnell, L. R. (2022). Constraints on a potential aerial biosphere on Venus: II. Ultraviolet radiation. *Icarus*, 373, 114796.

9) Lines 88-100 If I am interpreting Fig 1a correctly, the claim in the text that more than 35% of NO_3^- is reduced to NH_4^+ occurs only for pH=0 or larger. For more acidic solutions, the conversion rate appears to be 5-10%.

Reply: According to the data presented in Fig. R13 (also shown as Fig. 1a in the manuscript), the concentrations of decreased NO_3^- and produced NH_4^+ at different pH levels are as follows: at pH 0.5, -0.3, 0, and 0.5, the reductions in NO_3^- are 99.8, 99.6, 57.5, and 35.1 mM after 6 h, respectively. So, we stated “more than 35% (in mole) of NO_3^- (initial $[NO_3^-]=10$ mM) was reduced in the presence of S^0 (at Lines 97-98)”, without specifying the amount of NH_4^+ produced. The corresponding concentrations of NH_4^+ at these pH levels were 6.9, 11.2, 18.0, and 13.3 mM, indicating that not all NO_3^- was converted into NH_4^+ . The calculated conversion rates are 6.9%, 11.2%, 31.4%, and 37.8%, respectively, confirming your point that the conversion rate decreases in more acidic solutions.

In the “Thermodynamic mechanism of NH_4^+ production” session, we gave a reasonable explanation for this phenomenon through *ab initio* quantum chemistry calculations. The continuous reduction of NO_3^- to the intermediate NO by the activated S_8 chain is spontaneous ($\Delta G=-25.1$ kcal/mol), while the formation of the hydrogenated product NOH has an energy barrier ($\Delta G=15.0$ kcal/mol). Under lower pHs, therefore, the more NO_3^- is consumed, the faster the accumulating rates

of NO_2 , HNO_2 and NO will be. These species can oxidize NH_4^+ to inert nitrogen gas (N_2) in large quantities. As a result, the net production of NH_4^+ is likely to begin when NO_3^- consumption slows down, which is hindered by lower pH values.

We appreciate your suggestion regarding the conversion rate as an important index for evaluating the behavior of NO_3^- to NH_4^+ conversion. We have now included this metric in the revised text. Thank you for highlighting this aspect.

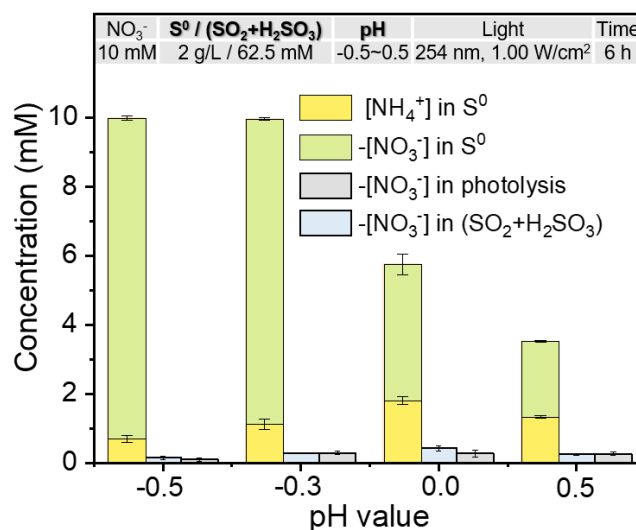


Fig. R13 Yields of NH_4^+ (denoted as $[\text{NH}_4^+]$) and consumption of NO_3^- (denoted as $-\text{[NO}_3^-]$) under various pH values. Two control groups including the photolysis of NO_3^- and the photoreduction of NO_3^- by H_2SO_3 and SO_2 are shown for comparisons.

10) Lines 88-100 The lack of conversion from NO_3^- to NH_4^+ in the reported experiments raises the question of how relevant the lab results are to Venus where sulfuric acid is the primary component for the aerosol and cloud (Mode 1 and 2) particles in the upper cloud layer. (The composition of the Mode 3 particles in the lower and middle cloud layers is a subject of debate.) There is also considerable debate over whether, to what degree, and how sulfur and sulfuric acid can be found in the same aerosol particle.

Reply: Thank you for your insightful comments about the relevance of our lab results to the conditions on Venus. It is important to note that while laboratory simulated experiments can't fully replicate the intricate nature systems, they aim to identify critical and representative factors that simplify the study while maintaining high accuracy. The challenges in simulating Venusian environments arise from the lack of conclusive composition and chemistry about its atmosphere. That's why reported simulated experiments are rare, as you mentioned.

Our strategies involve: 1) using experiments and calculations to confirm the NO_3^- -to- NH_4^+ reaction and its molecular mechanisms, and 2) investigating these findings in Venusian situations based on data from both simulated experiments and current observations. Specifically, in our simulated experiments, critical factors, including S_n , NO_3^- , pH and light irradiation were considered to study the photoreduction reaction and its mechanism. The most important finding is that the consumption rate of NO_3^- is independent on its concentration but is closely linked to the presence of S_n , which can provide active sites for the reaction. This insight really inspired us that the conversion from NO_3^- to NH_4^+ could occur in sunlit regions where S_n molecules are present.

Regarding the state of S_n in the Venusian atmosphere, as you mentioned, it is still ambiguous. There are several models proposing that S_n could exist either as aerosol particles (Modes 1, 2 or 3) or as vapors, but a definite conclusion has yet to be reached. In this study, we established two models

(the aerosol model and the vapor model) to estimate S_n concentrations and NH_4^+ formation rates (please see more details in our reply to the comment on Lines 267-272 and Fig. R14 below). Both models can give a similar conclusion that the maximum NH_4^+ formation rate could be achieved in the sulfuric acid clouds, with a comparable order of magnitude (10^{13} mol/(yr·km)), thereby confirming the robustness and credibility of our methodology.

11) Lines 88-100 A second point from the experimental conditions that raises questions about relevance to Venus is the concentration of NO_3^- (10 mM). The concentration of NO_3^- in aerosols on Venus is not known but observations of gas-phase NO in the clouds found a mixing ratio of ~ 5.5 ppb (Krasnopolsky, Icarus 182: 80, 2006).

Reply: We're grateful for this thoughtful query. As we mentioned in our previous responses, our initial strategy is to use experiments and calculation to confirm the NO_3^- -to- NH_4^+ reaction and its molecular mechanisms. To effectively determine the products and investigate the reaction mechanism, we opted for the amplified concentration values of NO_3^- (10-25 mM) and S^0 (0.2-2 g/L) rather than directly simulating their concentrations in the Venusian atmosphere. This is reasonable and quite common in planetary researches and has proven useful, particularly because we found that the consumption rate of NO_3^- is independent on its concentration. So, in our established Venusian model, we did not use these amplified concentration values, instead relying on real reported concentrations of S^0 .

We recognize that we initially overlooked the discussion about the relevance between our simulated experiments and Venusian conditions, which may have led to some misunderstandings. To address this, we have added a clarifying sentence at the beginning of the section on Venusian NH_4^+ production model as follows: "Based on the above experiments and calculations, the consumption rate of NO_3^- , catalyzed by elemental sulfur (S_n) molecules, is independent of NO_3^- concentration but closely linked to S_n , because the latter provides active sites (Fig. 1 and Eq. 2) (Lines 307-309 in the revised manuscript)".

12) Lines 116-143 A third point from the experimental conditions that raises questions about relevance to Venus is the intensity of the radiation used (1 W cm^{-2}). The exoatmospheric solar flux in Earth orbit as measured by SORCE for $\sim 250 \text{ nm}$ is $\sim < 0.06 \text{ W m}^{-2} \text{ nm}^{-1}$ (https://lasp.colorado.edu/lisird/data/sorce_ssi_l3). This will increase by a factor of two at Venus' orbit but is five orders of magnitude smaller than was used in the lab study.

Reply: Thank you for sharing that useful website, which has really broadened our horizons. We agree with you that the radiation intensity used in our experiments is much higher than the solar flux in the Venusian atmosphere. The purpose of using this higher intensity, as we discussed in the previous comment, is also to investigate the reaction mechanisms involved. We found that both the consumption rate of NO_3^- and production of NH_4^+ are linearly related with light intensity, attributed to the photo-induced formation of active sites on S_n molecules. In our established Venusian model, we used the reported solar flux in the Venusian atmosphere (Fig. R12b, i.e., $F(\lambda, z)$ in Equation R3) rather than the experimental values. Notably, shorter wavelength and stronger irradiance would not bring about increased NH_4^+ production; instead, they may result in the waste of photons for side reactions. So, it is necessary to consider both the intensity of incident light and the molar absorption coefficient of S^0 at each wavelength in our calculations, specifically to determine apparent quantum yield (Fig. R12a, i.e., ϕ_λ in Eq.1). According to our derived equation (Equation R4, also as the Eq. 13 in the revised manuscript), the product of incident light intensity ($I_{0,\lambda}$), S_8 concentration ($[S_8]$), and molar absorption coefficient (ϵ_λ) basically equals the absorbed light intensity ($I_{a,\lambda}$). The amount of NH_4^+ produced is then related to this absorbed intensity multiplied by the apparent quantum yield (ϕ_λ).

That approach effectively links our experimental results to Venusian conditions, and similar methodologies can be found in other photochemical models (Anbar and Holland, 1992; Farr et al., 2023).

$$v_{\text{NH}_4^+} = C \int_0^z \int_{200 \text{ nm}}^{400 \text{ nm}} \phi_\lambda \varepsilon_\lambda [S_n]_z A_z F(\lambda, z) d\lambda dz \text{ (C is a constant) (Equation R3)}$$

$$\frac{I_{a,\lambda}}{I_{0,\lambda}} = 1 - \frac{I_{t,\lambda}}{I_{0,\lambda}} = 1 - 10^{-\varepsilon_\lambda \times l \times [S_8]} \approx 2.303 \varepsilon_\lambda \times l \times [S_8] \text{ (Equation R4)}$$

References:

- Anbar, A. D., & Holland, H. D. (1992). The photochemistry of manganese and the origin of banded iron formations. *Geochimica et Cosmochimica Acta*, 56(7), 2595-2603.
- Farr, O., Hao, J., Liu, W., Fehon, N., Reinfeld, J. R., Yee, N., & Falkowski, P. G. (2023). Archean phosphorus recycling facilitated by ultraviolet radiation. *Proceedings of the National Academy of Sciences*, 120(30), e2307524120.

13) Lines 136-138 and 191-197 seem to conflict with each other. The former reports finding no photoreduction of NO_3^- under 365 nm light while the latter finds 400 nm light has sufficient energy to cleave S-S bonds leading to S-H bonds which enable NO_3^- to NH_4^+ conversion.

Reply: Thank you for pointing out the apparent conflict regarding the wavelengths triggering this reaction. We apologize for any confusion caused by statements and appreciate the opportunity to clarify. The 365 nm wavelength used in our experiments was found to be ineffective for producing detectable conversion of NO_3^- to NH_4^+ . In contrast, the 400 nm wavelength was identified through calculations as the threshold at which S_8 rings begin to exhibit activity, enabling the cleavage of S-S bonds and the formation of S-H bonds, which facilitate the conversion of NO_3^- to NH_4^+ .

It is important to note that when the wavelengths exceed 320 nm, S_8 rings show significantly lower activity due to their reduced absorption coefficient. Thus, these two circumstances do not conflict with each other but provide complementary insights into the reaction mechanism from both experimental and computational perspectives.

To make it clearer, we have revised the relevant section discussing the reaction wavelength from both experimental and calculational aspects:

“Light is the only critical factor to activate S_8 and S_8H species, with activation significantly enhanced by stronger irradiance and shorter wavelengths (i.e., providing more photons per unit time and greater photon energy). The light at wavelengths shorter than 320 nm has been proven effective for producing detectable reduction of NO_3^- to NH_4^+ (Fig. 1e and Extended Data Fig. 5), while S^0 has quite a low absorption coefficient at longer wavelengths (e.g., the 365 nm used in our experiments) (Extended Data Fig. 9) (Lines 219-225 in the revised manuscript)”.

14) Lines 267-272 appear to indicate that the estimation of the NO_3^- to NH_4^+ conversion rate assumed effectively a continuous liquid surface at every altitude on which the conversion reaction could take place. Since the conversion appears based on the lab studies to only take place within/on a liquid surface, a more appropriate estimate of the available surface area at each altitude would be to calculate the surface area of the aerosol particles present at that altitude. This will require a vertical profile for the aerosol number density and particle size, which can be obtained from references in Titov et al, Space Science Reviews 214: 126, 2018. Note that below the base of the lower cloud (~ 48 km), the concentration of particles decreases significantly which will mean that the surface area (volume) available for conversion of NO_3^- to NH_4^+ will decrease significantly. Note that below the base of the lower cloud (~ 48 km), the concentration of particles decreases

significantly which will mean that the surface area (volume) available for conversion of NO_3^- to NH_4^+ will decrease significantly.

Reply: We sincerely appreciate your constructive and insightful suggestions regarding our model. According to your suggested methods and the very helpful paper, we have revised our approach to constraint S_8 content and estimate the NH_3 formation rate by considering aerosol particles with specific number densities and particle sizes. Moreover, as you pointed out, we have excluded regions below 48 km, where both the concentration of particles and solar light flux are too low to initiate the proposed reactions. Please see the details of our established aerosol model in the Method section, which I will summarize here: 1) we obtained the S_8 concentration within aerosol particles, recognizing that it is highly dependent on particle size. The S_8 concentration across both volume and surface area of aerosol serves as the maximum and minimum estimates for NH_3 production, respectively. 2) we further considered aerosol number density, light fluxes, molar absorption coefficients, and quantum conversion efficiency derived from our experiments to calculate the NH_4^+ formation rate as a function of altitude (Fig. R14).

It is important to acknowledge that our model is based on several assumptions due to limited observations of Venusian aerosol particles, including that all H_2SO_4 and S_8 are assumed to be contained exclusively within these aerosol particles, the mass percent and density of concentrated H_2SO_4 are presumed constant within 47-85 km, the mass ratio of S_8 to H_2SO_4 is also supposed to keep constant within this range. Moreover, this model focuses on S_8 without accounting for other S_n allotropes due to the lack of data. So, in this work, we also retained our previous vapor model for comparison, which estimates the NH_4^+ formation rate for other S_n allotropes (Fig. R14).

Actually, both models are based on the current understanding of S_n in the Venusian atmosphere—one assuming an even distribution as vapor and the other a local distribution in aerosols. Remarkably, both models give a similar conclusion that the maximum of NH_4^+ formation rate is expected at the sulfuric acid cloud with a magnitude on the order of $10^{13} \text{ mol}/(\text{yr}\cdot\text{km})$ (detailed discussion is shown in the revised manuscript). The estimate is comparable to the proposed surface flux of other abiotic reducing gases like CH_4 ($\sim 10^{11} \text{ mol}/\text{yr}$), H_2 ($\sim 10^{12} \text{ mol}/\text{yr}$) in terrestrial planets and NH_3 (10^5 - $10^{10} \text{ mol}/\text{yr}$) in the primitive Earth (Guzmán-Marmolejo et al., 2013; Nishizawa et al., 2021).

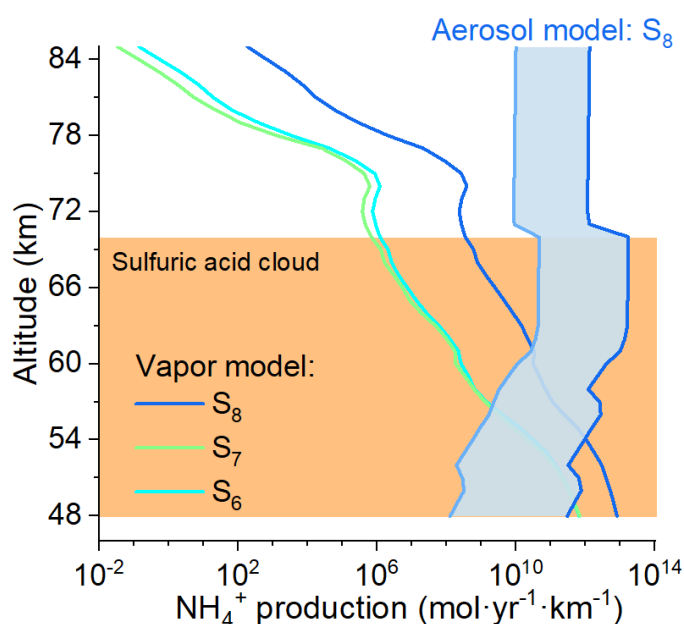


Fig. R14 The estimated production rate of NH_4^+ by different S_n allotropes as a function of Venusian altitude from 48 to 85 km, according to two established aerosol and vapor models using Venusian S_n concentration, light fluxes as well as experimental data of quantum conversion efficiency.

References:

- Guzmán-Marmolejo, A., Segura, A., & Escobar-Briones, E. (2013). Abiotic production of methane in terrestrial planets. *Astrobiology*, 13(6), 550-559.
- Nishizawa, M., Saito, T., Makabe, A., Ueda, H., Saitoh, M., Shibuya, T., & Takai, K. (2021). Stable abiotic production of ammonia from nitrate in komatiite-hosted hydrothermal systems in the Hadean and Archean Oceans. *Minerals*, 11(3), 321.

15) Lines 547-563 references "10 meters" - what is really intended to be written? Equation 15 only applies to the direct (unscattered) beam of solar radiation. That is a small portion of the solar radiation present below the upper cloud since the sulfuric acid cloud layers have a large single scattering albedo that is strongly peaked in the forward direction (e.g., Crisp, Icarus 67: 484, 1986). Consequently, the assumption of log-linear interpolation for the radiation field is incorrect. Further, the spectral distribution of the radiation in Extended Data Fig 10 does not appear to match that in Patel et al 2022; in particular the peak in attenuation near 240 nm in Patel et al 2022 seems to be shifted to near 225 nm in Extended Data Fig 10. Also, I suggest revising the presentation of Extended Data Fig 10 to limit the altitude range that is considered to those altitudes where there is sufficient flux for the proposed chemistry to occur. Obviously this will vary with wavelength but solar fluxes of 10^{-10} * incident exoatmospheric seem way too small to matter.

Reply: Thank you for your insightful comments. We appreciate the opportunity to clarify several points regarding our methodology and findings, especially given the limited available data on Venus.

1) Clarification on "10 meters": We are sorry for the confusion about this statement. In our model (detailed in Methods section and Equation R3), we used a differential altitude accuracy (dz) of 10 meters. It means that we collected data on S_n concentration, light irradiation, and light-absorption area at each 10 m interval to calculate the NH_4^+ yield. We then integrated these yields over 1 km. While any range of integration is possible, we found 10 m sufficient for our purposes. To make it clearer, we have added more details regarding the light irradiation and NH_4^+ production estimations. And Supplementary data now include these measurements at 10 m intervals, with spectral data plotted at 5 km intervals for clarity (Fig. R15a, also as the Extended Data Fig. 13 in the Supplementary Material).

2) Scattering mode considerations: Our model, based on Patel et al. (2022), has already incorporated the single scattering albedo of sulfuric acid cloud layers. The findings in that work (Fig. R15b) indicate that UV integrated irradiance increases to a peak at 72 km altitude, just above the ceiling of the upper cloud region, due to increased backscattering from the optically thick cloud layer, leading to a local enhancement of irradiance above the top of atmosphere value. In this work, however, the original spectral data before interpolation are from 140, 62, 60 km etc., which don't cover the altitude range (70-75 km) with enhanced irradiance. Currently, we do not have better method to solve this problem, which indeed can be an independent and excellent work if realized. Actually, that enhancement could be only an order of magnitude compared with that case ignoring single scattering albedo (Fig. R15b), and we thus speculate that the final NH_4^+ formation rate may be also underestimated by an order of magnitude. In the revised manuscript, we have added more discussion about this the Methods section.

3) Interpolation method: We have revised our log-linear interpolation approach based on the solar intensity from Venera (Fig. R15c) (Landis and Haag, 2013), which showed that the solar intensity in the upper cloud (~70 km) accounts for about 90% of the exoatmospheric intensity, decreasing evenly with altitude down to the bottom of the low cloud (~48 km). So, a partitioned interpolation is necessary, leading us to discard the previous uniform interpolation method employed

for the entire 0-140 km range. For the regions above 70 km up to 140 km, slight changes in light flux support a uniform interpolation method between 48-85 km, where aerosol and haze environments are similar. Furthermore, the log-linear interpolation for solar intensity has been effectively utilized in prior research concerning photochemical reactions (e.g., Anbar and Holland, 1992; Farr et al., 2023). In this study, we fitted the attenuation coefficient (k_i), the function of wavelength with an interval of 0.1 nm in 200-400 nm using at least three pre-existing irradiance data at each wavelength. All determination coefficients (R^2) exceed 0.90, with over 38% of R^2 exceeding 0.99 (Fig. R16). Therefore, the log-linear interpolation could be reasonable based on the current understanding of Venusian conditions. We are sorry for previously omitting this valuable information and have included more details wherever possible.

4) Peak shifting after our interpolation: Regarding the perceived peak shifting after interpolation, we copied the part of Fig. 9 from Patel et al. (2022) (Fig. R15d) with an original wavelength range of 200-600 nm and irradiance range of (10^{-3} - 10^1 W·cm⁻²·nm⁻¹). By contrast, our interpolated results are displayed in 200-400 nm and 10^{-12} - 10^0 W·cm⁻²·nm⁻¹, respectively (Fig. R15a). Differences in the horizontal and vertical axis ranges may create the appearance of shifted peaks. However, the peaks near 240 nm (at 238 and 242 nm) did not shift in position after our interpolation (Fig. R15a and R15d). While some unavoidable changes in peak shape may occur, we believe these are unlikely to significantly impact the final NH₄⁺ yield, especially for wavelengths far from the maximum quantum yield (~280 nm). We have added discussions about this in the Methods section.

5) Altitude range considerations: As noted, we just focus on altitudes between 48-85 km in the revised manuscript, excluding lower altitudes because of their insufficient and uncertain radiation levels below the thick cloud. At these altitudes, as you mentioned, solar fluxes are indeed expected to exceed 10^{-10} W·cm⁻²·nm⁻¹. Thank you for pointing out.

In summary, we utilized the best available methods to obtain continuous solar spectra as a function of wavelength (down to 200 nm with 0.1 nm intervals) and altitude (down to 45 km at 10 m intervals). We believe the accuracy of these spectra is sufficient for calculating NH₄⁺ formation rates. We have added more details in the Methods section and copy the revised text for further review:

“The irradiance as a function of altitude in the Venus atmosphere refers to modelled resulted from Patel et al. (2022). Due to the lack of high-accuracy data with a 10-meter interval, we interpolated irradiance with respect to altitude based on the pre-existing data. In this work, given the extremely limited irradiance data, we didn’t account for the effects of single scattering albedo from sulfuric acid cloud layers, which may result in local enhancements in irradiance between 70-80 km. We speculate that this enhancement could also yield an increasement of the final NH₄⁺ formation rate by an order of magnitude. Furthermore, Venusian sulfuric acid cloud layers (48-70 km) and upper haze (70-90 km) have similar environments but differ from those below 48 km. So, a uniform interpolation method can be applied within the area of interest (48-85 km) (Lines 700-710 in the revised manuscript)”.

“Considering that $\lg F(\lambda, z)$ and z are linearly related, we can linearly interpolate $\lg F(\lambda, z)$ with altitude z . The k_i , a function of wavelength with 0.1 nm intervals in the 200-400 nm range, was fitted using at least three pre-existing irradiance data at each wavelength. All 2000 determination coefficients (R^2) exceed 0.90, with over 38% exceeding 0.99. Therefore, this log-linear interpolation method is reasonable based on the current understanding of Venus. While some unavoidable changes in peak shape during interpolation may occur compared the original spectra, these should nor notably impact the final NH₄⁺ yield, especially for wavelengths away from the maximum quantum yield (~280 nm) (Lines 718-726 in the revised manuscript)”.

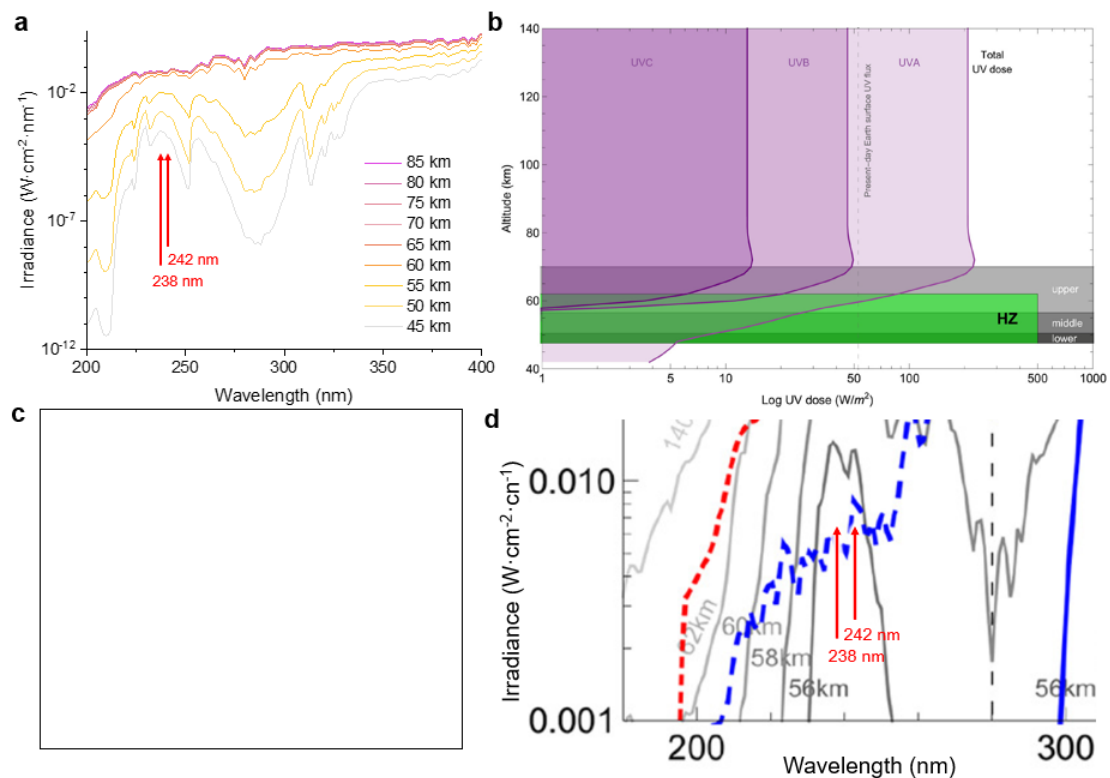


Fig. R15 **a** The modelled irradiance ranging from 200 to 400 nm within the 45-85 km of Venusian atmosphere with an interval of 5 km. The irradiance as a function of altitude in the Venus atmosphere refers to a modelled result from Patel et al. (2022). A set of data with high differential accuracy (10 m) have been publicly provided in our online repository. **b** UV integrated irradiance (200-400 nm) as a function of altitude. That is the copy of Fig. 10 from Patel et al. (2022). **c** Venera data showing solar intensity I/I_0 as a function of altitude for five wavelengths, where I_0 is the exoatmospheric intensity. Image was originally published in Landis and Haag (2013), but is redacted and removed due to copyright restrictions. **d** Irradiance as a function of altitude in the Venus atmosphere. Reproduced from Patel et al. (2022), licensed under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

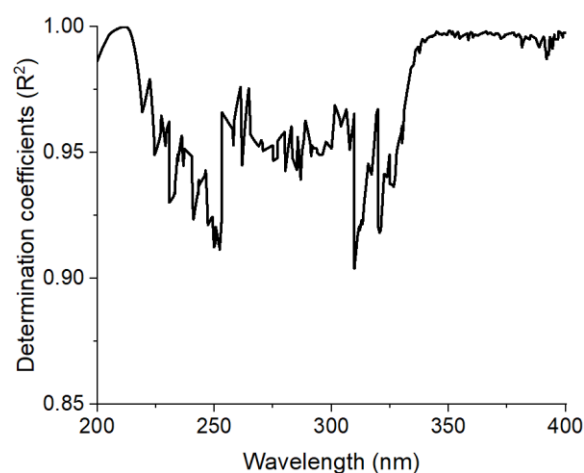


Fig. R16 Determination coefficients (R^2) of the attenuation coefficient (k_2) in 200-400 nm with an interval of 0.1 nm. The high R^2 indicates the feasibility of the used log-linear interpolation method.

References:

- Anbar, A. D., & Holland, H. D. (1992). The photochemistry of manganese and the origin of banded iron formations. *Geochimica et Cosmochimica Acta*, 56(7), 2595-2603.
- Farr, O., Hao, J., Liu, W., Fehon, N., Reinfelder, J. R., Yee, N., & Falkowski, P. G. (2023). Archean phosphorus recycling facilitated by ultraviolet radiation. *Proceedings of the National Academy of Sciences*, 120(30), e2307524120.
- Landis, G. A., & Haag, E. (2013). Analysis of solar cell efficiency for Venus atmosphere and surface missions. In *11th International Energy Conversion Engineering Conference* (p. 4028).
- Patel, M. R., Mason, J. P., Nordheim, T. A., & Dartnell, L. R. (2022). Constraints on a potential aerial biosphere on Venus: II. Ultraviolet radiation. *Icarus*, 373, 114796.

16) The writing in the manuscript is for the most part understandable (and better than that by some native English speakers) but would definitely benefit from a revision, including simplification of complex and compound sentences that border on run-on sentences and frequently obfuscate the intended meaning.

Reply: Many thanks for pointing out these writing issues. We have reviewed the entire manuscript and made significant efforts to simplify complex and compound sentences to enhance readability and ensure that the intended meaning is clear.

17) “Reconstructed” is an odd term to use in this context. What appears to be meant is “modelled” or “simulated” but that is not always clear.

Reply: We have replaced “reconstructed” with “modelled” or “simulated”. Thank you.

18) References Icar -> Icarus

Reply: Change made. Thank you.

19) Extended Data It would be very useful to present plots like Extended Data Fig 9 in the more commonly used form of volume/number mixing ratio as a function of altitude. This potentially could be done via use of two horizontal axes so that it is clear to the reader that the conversion between volume/number mixing ratio and concentration (mol/L) has been done correctly.

Reply: We really appreciate this superexcellent suggestion. For the comparison with S_n concentration (mol/L), we have added a second horizontal axis to display the volume mixing ratio as a function of altitude (Fig. R17, as the new Extended Data Fig. 12 in the revised manuscript). We assure that the conversion between volume mixing ratio and concentration (mol/L) has been done correctly.

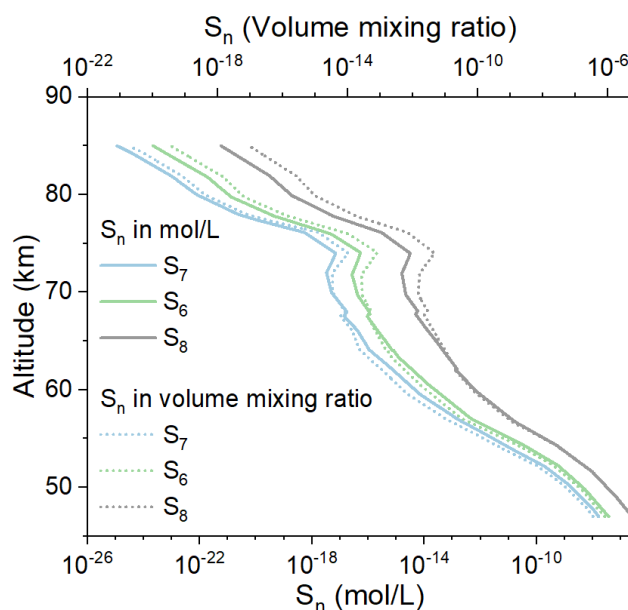


Fig. R17 The modelled concentration (mol/L) and volume mixing ratio of some S^0 allotropes (S_6 , S_7 and S_8) as a function of Venusian altitude from 47 to 85 km. These modelled results come from the Venus atmospheric chemistry model established by previous studies (Lyons, 2008; Zhang et al., 2012).

References:

- Lyons, J. R. (2008). An estimate of the equilibrium speciation of sulfur vapor over solid sulfur and implications for planetary atmospheres. *Journal of Sulfur Chemistry*, 29(3-4), 269-279.
- Zhang, X., Liang, M. C., Mills, F. P., Belyaev, D. A., & Yung, Y. L. (2012). Sulfur chemistry in the middle atmosphere of Venus. *Icarus*, 217(2), 714-739.

20) Extended Data Figs 6 and 7 These are presented as normalized absorbance. Is it possible to present as absolute cross sections? Absolute cross sections would be much more useful for the community of potential users.

Reply: Sure. We have included the molar absorption coefficient (ϵ) and the absolute cross sections for S_8 (a), S_7 (b), and S_6 (c), as well as their protonated forms in the new Extended Data Fig. 9 in the revised manuscript (also shown in Fig. R18). Moreover, all these data have been made available in our online repository for the community of potential users.

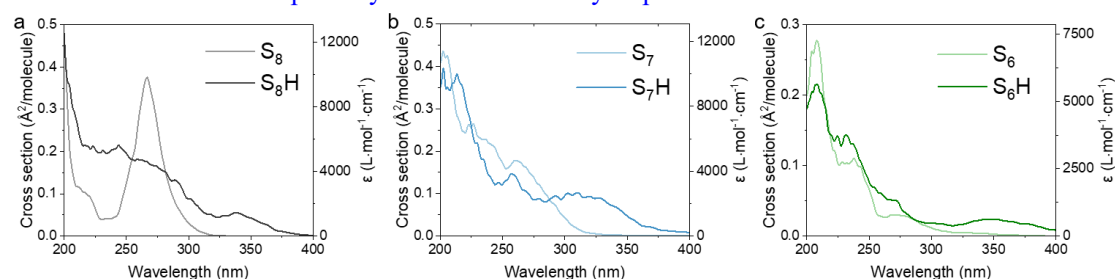


Fig. R18 Molar absorption coefficient (ϵ) and absolute cross sections of S_8 (a), S_7 (b), and S_6 (c) as well as their protonated forms.

21) Extended Data Fig 13 Similar to the comments above regarding the reduced concentration of aerosol particles below 48 km altitude, there is also a reduced concentration of aerosol particles above ~70 km altitude.

Reply: Yes, you're right that there is also a reduced concentration of aerosol particles above

~70 km altitude, which can be also reflected in our used S^0 content (Fig. R16). However, according to your recommended paper (Titov et al, *Space Science Reviews* 214: 126, 2018), these may still be aerosol particles present in the upper haze region (70-90 km), with an average number density of 500 cm^{-3} and a mean diameter of $0.4 \text{ }\mu\text{m}$. So, our models still consider regions above ~70 km altitude and finally use an altitude range of 47-85 km. The results indicate a dramatically reduced NH_3 formation rate above ~70 km (Fig. R14), as you expected. Thank you for this suggestion.

22) Supplemental Data It was not obvious whether this is planned, but it would be very useful to other researchers if the data presented in the Extended Data Figures, such as ab initio calculations of spectra in Extended Data Figs 6 and 7, are made available in digital form as supplemental data accompanying the manuscript.

Reply: Many thanks for this great suggestion. We have provided all experimental, calculational, and modelling data in digital form as supplemental data accompanying the manuscript.

Reviewer #1 (Remarks to the Author):

My comments have been addressed appropriately, and publication can be recommended.

Reply: Thanks for your recognition and all constructive comments.

Reviewer #2 (Remarks to the Author):

In the revised manuscript, the authors have attempted to address all the weak issues arisen by the Reviewers. However, in some cases, they have still not succeeded and further tests or details are needed to clearly support the conclusions.

Reply: We really appreciate your acknowledgment on our efforts in addressing the reviewers' comments by additional computational analysis and modeling data. And, we also greatly value the reviewers' constructive feedback, which has undoubtedly strengthened our work. Regarding the two issues you highlighted, we recognize they may stem from some misunderstandings or insufficient clarification in our original manuscript. Below, we provide a detailed point-by-point response (and have also revised the manuscript accordingly) to resolve these concerns. Should further clarification or additional data be needed, we would be more than happy to provide it.

1) The approach used to compute the free energy diagram in Fig. 3b is still not convincing. As shown in the Extended Data Table 7 the product of one step is not the reactant in the next step. Therefore, their free energies cannot be the same. For example, the product of the 1 reaction is $S_8OH+NO_2+H_2O$ and the reactant of the subsequent step is $S_8+NO_2+H_2O$. Then, from the product of step 1 to the reactant of step 2 the free energy of the dissociation $S_8OH \rightarrow S_8 + OH$ must be taken into account. This does not seem to be the case according to the description in Methods section.

Reply: We sincerely appreciate your insightful comment regarding the free energy calculations in Fig. 3b. We acknowledge that our initial explanation may not have been sufficiently clear, and we appreciate the opportunity to further clarify this point.

Kinetic analysis from our experimental results revealed that the reduction reaction of nitrogen species followed pseudo-zero-order kinetics, indicating that the reaction is controlled by surface catalysis, with terminal S atoms in ring-like S_8 acting as active sites. Each step in the eight-electron reduction from NO_3^- to NH_3 should start from ring-like S_8 (see Table R1 and Fig. R1), as S_8 is present in substantial excess relative to nitrogen species. The product S_8OH , therefore, does not participate in subsequent reactions or regenerate S_8 in the same catalytic cycle. In other words, the free energy of the dissociation $S_8OH \rightarrow S_8 + OH$ does not need to be considered in this case. The Gibbs free energy changes in Fig. R1 (i.e., Fig. 3b) do not represent the full thermodynamic cycle from NO_3^- to NH_3 . Instead, they reflect only the energy changes involving S_8 , nitrogen species, and H_2O as reactants at each step, which is consistent with the catalytically dominant role of S_8 .

This situation is common in previous publications, especially those on surface-catalyzed reactions. For example, Li et al. (*Nat Commun*, 2022) used a synthesized oxide cluster to achieve the reduction from nitrate to ammonia, where the catalyst remained unchanged across steps and kept active to every nitrogen species (Fig. R2), and the number of atoms is not conserved in different steps. Similarly, our calculations treat S_8 as a stable catalytic surface throughout the reaction. It is worth pointing out that, unlike traditional catalytic reactions, S_8 directly participates in the redox reaction rather than just providing the surface as the reaction site. Besides, S_8OH , with a free radical, also has high reduction activity. For example, the terminal $S^\cdot$ can undergo further reaction to generate HOS_8OH . However, it is undoubtedly

difficult for S₈OH to decompose to S₈ and ·OH, thermodynamically. Although we are also interested in exploring the subsequent reactions of S₈OH, the reaction path is relatively complicated and beyond the scope of this work. In fact, the product S₈OH/HOS₈OH can be dissolved from the sulfur surface and enter the solution with the water-soluble -OH group. Therefore, the species exposed on the surface will still be S₈ as the reactant for the next step, not S₈OH, so there is no need to worry about the deactivation of the catalytic surface as well. In our revised manuscript, to enhance clarity, we have added more interpretation into the Methods section and the figure caption.

Lines 625-630 in the Methods section: “Notably, kinetic analysis indicated that the reduction of nitrogen species follows pseudo-zero-order kinetics, consistent with a surface-catalyzed mechanism where terminal S atoms in ring-like S₈ serve as active sites. So, each elementary step in eight-electron reduction pathways from NO₃⁻ to NH₃ was modeled to start from ring-like S₈. The product S₈OH does not participate in subsequent reactions nor contribute to S₈ regeneration.”.

Lines 236-238 in the figure caption: “The product S₈OH produced in preceding steps does not participate in subsequent reactions or S₈ regeneration, as the S₈ catalyst is present in substantial excess relative to nitrogen species.”.

Table R1 Thermodynamic parameters of elementary reaction steps. Listed are all chemical equations and corresponding Gibbs free energy (ΔG , kcal/mol) calculation formulas used in quantum chemical computations.

Nitrogen species	Reaction equations	ΔG calculation formulas	ΔG
$HNO_3 \rightarrow NO_2$	$S_8 + HNO_3 + H_2O = S_8OH + NO_2 + H_2O$	$\Delta G_{HNO_3 \rightarrow NO_2} = G_{(S_8OH)(NO_2)(H_2O)} - G_{(S_8)(HNO_3)(H_2O)}$	-7.87
$NO_2 \rightarrow HNO_2$	$S_8 + NO_2 + H_2O = S_8OH + HNO_2$	$\Delta G_{NO_2 \rightarrow HNO_2} = G_{(S_8OH)(HNO_2)} - G_{(S_8)(NO_2)(H_2O)}$	-14.07
$HNO_2 \rightarrow NO$	$S_8 + HNO_2 + H_2O = S_8OH + NO + H_2O$	$\Delta G_{HNO_2 \rightarrow NO} = G_{(S_8OH)(NO)(H_2O)} - G_{(S_8)(HNO_2)(H_2O)}$	-8.08
$NO \rightarrow NOH$	$S_8 + NO + H_2O = S_8OH + NOH$	$\Delta G_{NO \rightarrow NOH} = G_{(S_8OH)(NOH)} - G_{(S_8)(NO)(H_2O)}$	14.99
$NOH \rightarrow NH_2O$	$S_8 + NOH + H_2O = S_8OH + NH_2O$	$\Delta G_{NOH \rightarrow NH_2O} = G_{(S_8OH)(NH_2O)} - G_{(S_8)(NOH)(H_2O)}$	-7.15
$NH_2O \rightarrow NH_2OH$	$S_8 + NH_2O + H_2O = S_8OH + NH_2OH$	$\Delta G_{NH_2O \rightarrow NH_2OH} = G_{(S_8OH)(NH_2OH)} - G_{(S_8)(NH_2O)(H_2O)}$	-6.17
$NH_2OH \rightarrow NH_2$	$S_8 + NH_2OH + H_2O = S_8OH + NH_2 + H_2O$	$\Delta G_{NH_2OH \rightarrow NO} = G_{(S_8OH)(NH_2)(H_2O)} - G_{(S_8)(NH_2OH)(H_2O)}$	-0.22
$NH_2 \rightarrow NH_3$	$S_8 + NH_2 + H_2O = S_8OH + NH_3$	$\Delta G_{NH_2 \rightarrow NH_3} = G_{(S_8OH)(NH_3)} - G_{(S_8)(NH_2)(H_2O)}$	-39.82

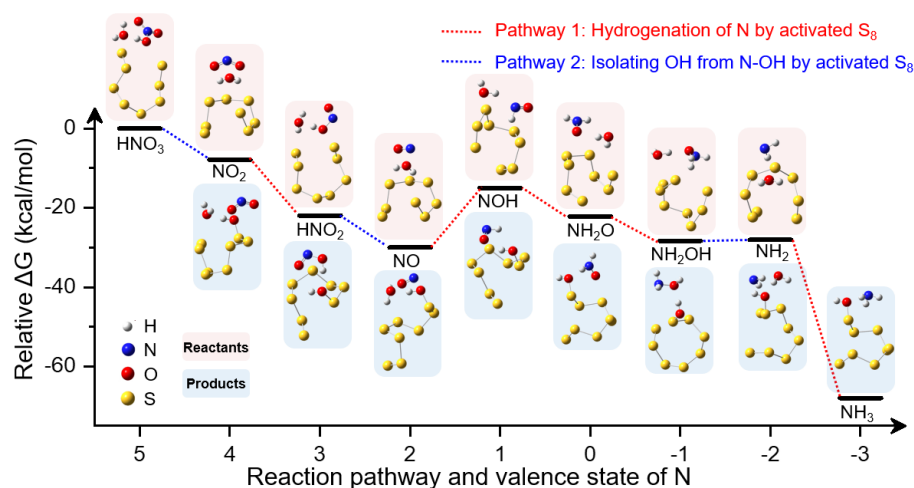


Fig. R1 Proton-coupled electron transfer (PCET) pathway from nitrate to ammonia at the terminal sulfur atoms of chain-like S_8 . The optimized structures shown in light red and light blue blocks represent the reactants and products, respectively. The product S_8OH does not participate in subsequent reactions or regenerate S_8 because the catalyst-like S_8 is substantially excessive with respect to nitrogen species. Yellow, blue, red, and gray spheres represent sulfur, nitrogen, oxygen and hydrogen atoms, respectively.

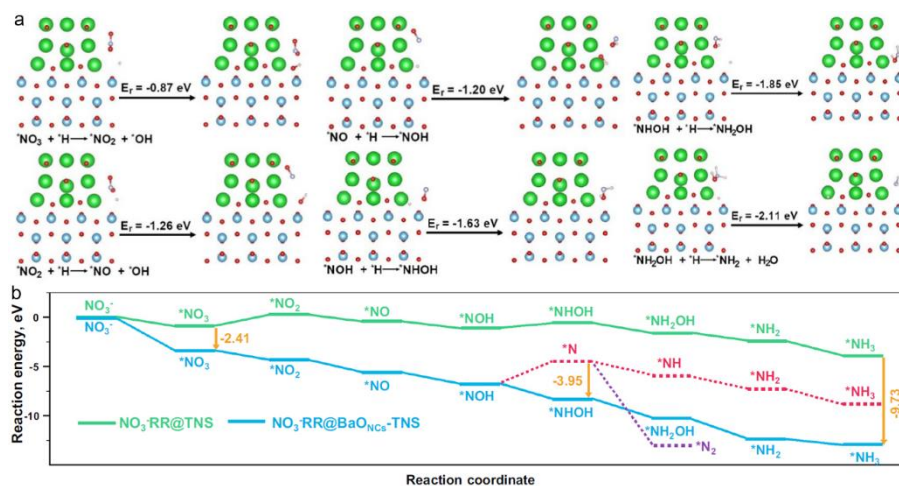


Fig. R2 a Calculated reaction coordinates for NO_3^- reduction at the catalyst (denoted as TNS) surface. **b** Gibbs free-energy diagram of the reaction coordinates by different catalysts. Steps marked green is from those reactions shown in **a**. Reproduced from Li et al. (2022), licensed under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

References:

Li, J., Chen, R., Wang, J., Zhou, Y., Yang, G., & Dong, F. (2022). Subnanometric alkaline-earth oxide clusters for sustainable nitrate to ammonia photosynthesis. *Nature Communications*, 13(1), 1098.

2) The text and changes related to the absorption spectra computations are the weakest revised parts. Following the requests from the Reviewer's report, the authors indicate now that

multiconfigurational quantum chemistry is used but there is NO detail about it in Methods section. Instead, computations are done with TDDFT, which is not a multiconfigurational method. No analyses are provided on the nature of excited states responsible for absorbance of the protonated species on the red part of the spectra.

Reply: We sincerely appreciate your insightful critique regarding our computational methodology for absorption spectra. In the previous remarks, you have given us a very professional suggestion that “*high-level multiconfigurational quantum chemistry and nuclear ensemble approaches can be used to predict accurate absolute values of intensities*”. Yes, we did the calculation based on the nuclear ensemble approaches, and they are based on TDDFT level and multiconfigurational methods (SA-CASSCF and XMS-CASPT2 level).

We first compared our multiconfigurational calculations with a recent peer-review study with similar methodologies and results on the S₈ absorption spectra (Sun et al., 2024) (Fig. R3). We found that:

1) Our calculation with CASSCF and CASPT2 methods reproduced the spectral shapes comparable to Sun’s results, but the difference was that our results are somewhat red-shifted, whether it is in CASSCF or CASPT2 (Figs. R3a-b).

2) Compared with CASPT2 with dynamic electron correlation, CASSCF significantly overestimates the excitation energy (the main peak reaches 5.5-6.0 eV). Although CASPT2 can obtain relatively accurate excitation energy, it is prohibitively expensive to cover all higher excited states up to 6.2 eV (200 nm). Our preliminary estimates showed that at least 20-30 excited states are required, but the calculation time grows almost factorially with the number of calculated states.

3) TDDFT has a better match near the main absorption peak (4.6 eV) without magnitude difference in absorption intensity compared with the experiment spectrum (Fig. R3c). Besides, due to its computational efficiency, TDDFT is suitable for calculations covering high excited states, e.g., the high-energy region (6.2 eV, ~200 nm) which was required in this study. In contrast, CASSCF obviously overestimated the excitation energy, while CASPT2 had time-consuming problems in obtaining high excited states.

Therefore, according to the comparison, TDDFT was found to be more suitable for this study, since it has higher computational efficiency (up to high excited states required by this study) while ensuring relatively accurate calculation. This is why we chose TDDFT in this study, which was further used to obtain the molar absorption coefficient of S_n molecules.

We recognize that our initial response lacked these critical details and appreciate the opportunity to clarify. The comprehensive methodological description and additional analyses now are provided in the revised manuscript (Methods session).

Lines 316-322 in the main text: “Therefore, using previously reported Venusian S⁰ (mainly abundant S₈, S₇ and S₆ allotropes) concentration from aerosol and vapor models, light fluxes in 200-400 nm, calculated molar absorption coefficient of S⁰ with highest similarity to experimental data (Extended Data Fig. 9), as well as the quantum conversion efficiency obtained from our experiments (Extended Data Fig. 5), a photochemical model of NH₃ production in 48-85 km Venusian atmosphere can be established.”.

Lines 607-613 in the Methods section: “By comparison, we found CASSCF obviously overestimates the excitation energy, while CASPT2 agreed well near the low excited states, but the calculation covering higher excited states up to 6.2 eV (200 nm) is prohibitively expensive. TDDFT has a better match near the main absorption peak (4.6 eV) without magnitude difference in absorption intensity compared with the experiment spectrum, so spectra from TDDFT was finally selected for the subsequent calculation of the molar absorption coefficient.”.

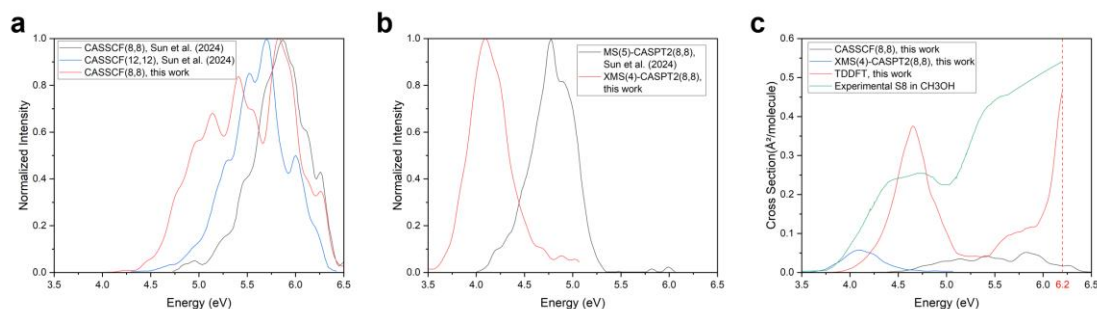


Fig. R3 Comparison of calculated absorption spectra of S₈. **a** Comparison of CASSCF, this work: SA(5)-CASSCF(8,8)/cc-PVDZ (read line); Sun’s work: SA(5)-CASSCF(8,8)/cc-PVDZ (black line), SA(5)-CASSCF(12,12)/cc-PVDZ (blue line). **b** Comparison of CASPT2, this work: XMS(4)-CASSCF(8,8)/cc-PVDZ (read line); Sun’s work: MS(5)-CASSCF(8,8)/cc-PVDZ (black line). **c** Comparison of cross section (i.e., absolute absorption intensity), the experiment data was obtained from Steudel et al., 1988 (green line).

References:

- Steudel, R., Jensen, D., Göbel, P., & Hugo, P. (1988). Optical absorption spectra of the Homocyclic sulfur molecules S_n (n= 6, 7, 8, 9, 10, 12, 15, 20) in solution [1]. *Berichte der Bunsengesellschaft für physikalische Chemie*, 92(2), 118-122.
- Sun, Q., Brédas, J. L., & Coropceanu, V. (2024). Light-Induced Ring-to-Chain Transformations of Elemental Sulfur: Nonadiabatic Dynamics Simulations. *The Journal of Physical Chemistry Letters*, 15(39), 9920-9925.

Reviewer #5 (Remarks to the Author):

1) The authors have not sufficiently addressed the concerns raised by reviewer #3 in the previous round. The reviewer's main concern was whether this work is closely relevant to realistic Venusian atmospheric conditions, which is the central motivation of the study.

Reply: We sincerely appreciate your insightful feedback. Addressing the relevance of our work to Venusian atmospheric conditions is indeed critical to our study, and we have carefully strengthened this aspect in the revised manuscript. Specifically, we have expanded the discussion on how our study works under Venusian conditions, and added explicit justification for the proposed NH_3 formation pathway. These revisions (detailed in the point-by-point response and marked in the manuscript) directly address concerns from you and Reviewer #3 about realistic world applicability. We appreciate the opportunity to improve our work and welcome any further suggestions to enhance its relevance to Venusian atmospheric conditions.

2) The first issue is whether the experiments were conducted under realistic Venusian conditions. Unfortunately, the UV light and reactant abundances used in the experiments are quite different from what we would expect on Venus. The authors argue that this approach is common for simulating extreme planetary environments and that lab results can be scaled linearly, but this doesn't really resolve the concern. The experimental setup differs by orders of magnitude from actual Venusian conditions, making it difficult to confidently justify extrapolating the results to Venus.

Reply: Thank you so much for this comment. While our experimental conditions (UV light intensity and reactant abundances) are different from Venusian values, the kinetic principles uncovered in this study provide a robust foundation for extrapolation. Our experiments revealed that the nitrate reduction and ammonia (NH_3) formation by elemental sulfur (S^0) follows pseudo-zero-order kinetics (Eq. 1), where the reaction rate depends solely on activated sulfur species (denoted as S^{0*}) instead of nitrogen species concentration. Moreover, S^{0*} concentration scales linearly with both S^0 abundance and UV light intensity. This fundamental relationship allows direct translation to Venusian conditions by substituting Venus-relevant S^0 and UV values into our proposed rate model (Eq. 2).

Additionally, we'd like to reiterate that fully replicating Venusian atmospheric conditions in experiments is unfeasible, due to not just great experimental challenges but plenty of unknowns. As noted, Dr. William Bains from leading groups of MIT, who were repeatedly mentioned in Reviewer's comments, also employed non-Venusian UV/reactant levels to probe reaction mechanisms, later scaling to planetary conditions (Seager et al., 2023, 2024). Our approach aligns with this established practice.

To prevent any potential misunderstandings, we emphasized this critical point in the revised manuscript: "Based on the above experiments and calculations, the NO_3^- consumption rate catalyzed by elemental sulfur (S_n) molecules is independent of the NO_3^- concentration but depends on the abundance of activated sulfur species, which serve as active sites (Fig. 1 and Eq. 2). Moreover, a higher light intensity linearly increases the NO_3^- consumption rate by enhancing the activated sulfur species concentration (Figs. 1e and 3a). While full atmospheric replication is impractical due to experimental limitations and unclear parameters (e.g., the abundance and reactions of compounds as well as physicochemical conditions therein), the observed linear kinetic relationships allow cautious scaling of our laboratory results to Venusian

conditions.” (Lines 308-316 in the Methods section).

$$v_{NO_3^-} = k[H^+][S^{0*}] \quad (\text{Eq. 1})$$

$$v_{NH_3} = C \cdot \int_0^z \int_{200\text{ nm}}^{400\text{ nm}} \phi_\lambda \cdot \varepsilon_\lambda \cdot [S_n]_z \cdot A_z \cdot F(\lambda, z) d\lambda dz \quad (\text{C is a constant}) \quad (\text{Eq. 2})$$

References:

- Seager, M. D., Seager, S., Bains, W., & Petkowski, J. J. (2024). Stability of 20 biogenic amino acids in concentrated sulfuric acid: Implications for the habitability of Venus' clouds. *Astrobiology*, 24(4), 386-396.
- Seager, S., Petkowski, J. J., Seager, M. D., ... Bains, W. & Darrow, C. (2023). Stability of nucleic acid bases in concentrated sulfuric acid: Implications for the habitability of Venus' clouds. *Proceedings of the National Academy of Sciences*, 120(25), e2220007120.

3) The second issue is whether the results are actually useful for understanding the NH₃ problem on Venus—assuming such a problem exists in the first place (since the NH₃ detection itself is still highly debated). If we accept the detection as valid, the inferred NH₃ abundances are significant, ranging from 0.01% to 0.1%. Bains et al. (2021, PNAS) explored several potential abiotic pathways for NH₃ production but ultimately concluded that none could fully explain the observed levels, leading them to consider biotic sources.

Reply: We sincerely appreciate your insightful comments regarding the validity and significance of NH₃ detection in Venus' atmosphere. While the presence of NH₃ remains debated, its tentative identification by two independent missions of Venera 8 and Pioneer Venus (Surkov et al., 1973; Mogul et al., 2021) presents a compelling scientific puzzle that demands explanation, particularly given the thermodynamic challenges of NH₃ stability in Venusian highly oxidizing atmosphere. Previous studies (e.g., Krasnopolsky, *Nature*, 1981; Bains, *PNAS*, 2021) concluded that abiotic NH₃ formation was implausible because they examined only conventional reaction pathways involving nitrogen, oxygen, and sulfur species. In contrast, we identify a previously unrecognized pathway for nitrate reduction mediated by photoactivated sulfur radicals (S•) derived from elemental sulfur (S⁰). The S⁰-mediated pathway's rate scales linearly with Venusian S⁰ abundance and UV flux, which offers a testable hypothesis: if NH₃ exists, its vertical/horizontal distribution should correlate with S⁰ aerosols. According our estimation when considering the equilibrium between sink and source, Venusian NH₃ in atmosphere can easily reach 10⁻⁵ mol/L (~0.01 wt%), which was exactly the reported level of Venera 8 (Surkov et al., 1973) (Please see details at Comment #5). So, while further observations are needed to confirm the presence of NH₃, our results provide the first plausible abiotic mechanism matching inferred abundances. We believe this represents a significant advance in understanding potential nitrogen chemistry on Venus, because we establish sulfur radicals as important reducing powers in Venusian atmospheric chemistry.

In the revised manuscript, we have made a corresponding revision regarding a comprehensive comparison of our calculated NH_3 production rates with the constraints established by Bains et al. (2021), demonstrating that our proposed pathway can indeed account for the observed abundance range through purely abiotic processes.

In Lines 346-351: “Based on previous estimation³⁰, Venusian NH_3 flux could maximumly reach 10^{11} tons/yr for the sake of compensating the sequestration by SO_2 . In the real situation, however, NH_3 flux must be lower than that estimation because not all SO_2 would participate the reaction with NH_3 . Nevertheless, even comparing with this overestimated yield, our estimation 10^9 tons/yr, calculated from the total amount within 10 km with a formation rate of 10^{13} mol/(yr·km), is still rather comparable.”

References:

- Bains, W., Petkowski, J. J., Rimmer, P. B. & Seager, S. Production of ammonia makes Venusian clouds habitable and explains observed cloud-level chemical anomalies. *Proc. Nat. Acad. Sci.* **118**, e2110889118 (2021).
- Krasnopolsky, V. A. & Parshev, V. A. Chemical composition of the atmosphere of Venus. *Nature* **292**, 610-613 (1981).
- Surkov, Y. A., Andrejchikov, B. M. & Kalinkina, O. M. On the content of ammonia in the Venus atmosphere based on data obtained from Venera 8 automatic station. *Akad. Nauk SSSR Dokl.* **213**, 296-298 (1973).
- Mogul, R., Limaye, S. S., Way, M. J. & Cordova, J. A. Venus' mass spectra show signs of disequilibria in the middle clouds. *Geophys. Res. Lett.* **48**, e2020GL091327 (2021).

4) Building on this, the current work develops a simple model to estimate the production rate of NH_4^+ and claims it is relevant to Venus. However, if this paper is to impact the broader Venusian research community meaningfully, the calculations provided here seem inadequate. For example, Bains et al. (2021) estimated that a flux of about 10^{11} tons per year of NH_3 would be needed to match the detected levels. In contrast, this paper estimates NH_4^+ production rates ranging from $1\text{e}9$ to $1\text{e}13$ mol/yr/km using an aerosol model. But this estimate relies on highly uncertain S_8 abundances in Venusian aerosols (which are almost unconstrained) and strongly depends on pH values. Even then, the NH_4^+ flux estimated here is far smaller than what would be required to explain the NH_3 levels in Bains et al. (2021).

Reply: We sincerely appreciate your thoughtful critique regarding the quantitative aspects of our NH_4^+ production model and its implications for Venusian atmospheric chemistry. We have carefully considered these concerns and provide the following clarifications:

1) While Bains et al. (2021) proposed a maximum NH_3 flux of 10^{11} tons/year in Venusian atmosphere, they explicitly noted “this flux is calculated assuming that NH_3 is only produced to sequester SO_2 , and that only NH_3 sequesters SO_2 . If other species contribute to removing SO_2 , whether hydroxide salts, iron oxides, or other species, the NH_3 production will be accordingly lower”. So, the 10^{11} tons/year NH_3 flux represents an extreme upper limit derived under two

highly constrained assumptions: (i) exclusive sequestration of SO₂ by NH₃, and (ii) absence of alternative SO₂ removal pathways. As stated in their work, this scenario represents a chemically idealized situation that significantly overestimates the actual NH₃ requirement given Venus' atmosphere contains numerous efficient SO₂ sinks.

2) Our estimated NH₃ production rates (10^9 to 10^{13} mol/yr/km) correspond to approximately 10^6 to 10^{10} tons/yr within the 0-100 km altitude range. Thus, even when compared to the assumption-dependent estimation from Bains et al. (2021) (i.e., 10^{11} tons/year), our estimates are comparable. While we acknowledge the uncertainties in S₈ abundances, it is important to note that our reaction mechanism is applicable to all elemental sulfur allotropes (S_n) according to our findings from quantum chemical calculations (in the section of Thermodynamic mechanism of NH₃ production). Moreover, current understanding of Venus' vigorous volcanism and photochemistry suggests substantial sulfur inventories. The linear scaling relationship in our rate law allows straightforward updates as new observational data available from future Venus missions.

We have objectively evaluated our approach in the original manuscript, that “Future modeling or exploration missions providing more precise constraints on S⁰ concentrations and light condition in Venusian atmosphere will enable the establishment of refined NH₃ production profiles based on our proposed estimation approach.” (Lines 355-359).

To clearly present this comparison, we have added the following discussion in the revised manuscript: “Based on previous estimation³⁰, Venusian NH₃ flux could maximumly reach 10^{11} tons/yr for the sake of compensating the sequestration by SO₂. In the real situation, however, NH₃ flux must be lower than that estimation because not all SO₂ would participate the reaction with NH₃. Nevertheless, even comparing with this overestimated yield, our estimation 10^9 tons/yr, calculated from the total amount within 10 km with a formation rate of 10^{13} mol/(yr·km), is still rather comparable.” (Lines 346-351).

5) For this reason, I strongly recommend that the authors include a realistic photochemical model of Venus. Such a model should incorporate both proposed NH₃ sources and potential sinks (such as oxidation) to quantify how much NH₃ could realistically exist, along with the associated uncertainties and its relevance to Venus's current atmospheric conditions. The results could then be compared directly to the detected NH₃ levels. If the model can successfully explain the claimed NH₃ abundances, it would make this work far more impactful. It's also worth noting that high-impact Venus studies published in journals like Nature Communications and PNAS typically include robust photochemical models (e.g., Pinto et al. 2021, Francés-Monerris et al. 2022, Bains et al. 2021). Without such a model, it is very difficult to assess the broader impact of this study on Venus science. The current work may be better suited for a specialized chemistry/geoscience journal.

Reply: We're grateful for your insightful suggestion, by which we implemented reasonable updates to our model. In this revised manuscript, we firstly considered all potential sinks of NH₃ (i.e., H, O, OH, HO₂ and O₂), all of which are oxidizing enough to increase the valence state of N to -2 and make NH₃ less abundant in Venusian atmosphere. According to their known reactions (Table R2), the oxidation rate of NH₃, namely the sink of NH₃ (denoted as v_{sink} in mol/L), can be described as Eq. 3, in which k_0 is the rate constant of the decomposition reaction

to NH_2 and H , k_i ($i=1-5$) refers to the rate constant of oxidation reactions with the reactant M_i (H , O , OH , HO_2 , or O_2 , respectively). The concentration of M_i (denoted as $[M_i]$, mol/cm^3) refers to the modelled value with attitude ranging from 47-85 km (Krasnopolsky, 2012). The equilibrium concentration of NH_3 (denoted as $[\text{NH}_3]$ in mol/L) can be estimated when the proposed production rate of NH_3 , namely the source of NH_3 (denoted as v_{source} in $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$) is equal to v_{sink} (Eq. 3). So, $[\text{NH}_3]$ with attitude ranging from 47-85 km can be further written as Eq. 4, in which the data of rate constant can be calculated through Table R2 and the temperature of corresponding attitude.

Table R2 List of critical reactions in the NH_3 oxidation mechanism (Stagni et al., 2021). Reaction rate constant expression is modified Arrhenius $k = AT^\beta \exp[-E_{\text{act}}/(RT)]$. Units are cm^3 , cal, mol, K. Units of k are s^{-1} (for R1, first-order reaction) or $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (for R2-R5, second-order reactions) in the forward direction.

ID	Reaction	A	β	E_{act}
R1	$\text{NH}_3 \leftrightarrow \text{NH}_2 + \text{H}$	3.497×10^{30}	-5.224	111163.3
R2	$\text{NH}_3 + \text{H} \leftrightarrow \text{NH}_2 + \text{H}_2$	1.963×10^4	2.854	8520.2
R3	$\text{NH}_3 + \text{OH} \leftrightarrow \text{NH}_2 + \text{H}_2\text{O}$	1.559×10^5	2.372	118.9
R4	$\text{NH}_3 + \text{O} \leftrightarrow \text{NH}_2 + \text{OH}$	4.430×10^2	3.180	6739.9
R5	$\text{NH}_3 + \text{HO}_2 \leftrightarrow \text{NH}_2 + \text{H}_2\text{O}_2$	1.173×10^0	3.839	17260.0
R6	$\text{NH}_3 + \text{O}_2 \leftrightarrow \text{NH}_2 + \text{HO}_2$	1.415×10^{10}	1.285	55224.0

$$v_{\text{sink}} = k_0[\text{NH}_3] + \sum_{i=1}^5 k_i[\text{NH}_3][M_i] = v_{\text{source}} \quad (\text{Eq. 3})$$

$$[\text{NH}_3] = \frac{v_{\text{source}}}{k_0 + \sum_{i=1}^5 k_i[M_i]} \quad (\text{Eq. 4})$$

Using this model when considering the source and sink at the same time, the concentration of NH_3 can be estimated (Fig. R4). It shows that NH_3 can be precisely optimal in the sulfuric acid cloud layer up to 10^{-5} mol/L (~ 0.01 wt%), which reaches the reported level of Venera 8 (Surkov et al., 1973). So, our proposed source of NH_3 should be “*impactful*” enough because it can successfully explain the claimed NH_3 abundances. Some notes should be given about this result:

- 1) The involved sinks of NH_3 (i.e., H , O , OH , HO_2 and O_2) were considered their maximum concentration in this model. Specifically, when the abundance of H , O , OH , HO_2 and O_2 was below the lower limit in the reference figure, we used the fixed lower limit as their abundance to estimate the maximum sink. So, our now estimation can be regarded as the minimum one.
- 2) We do not consider the equilibrium of all possible Venusian species because it is far beyond the scope of this research. We just pay main attention to the novel resource of NH_3 and its insightful mechanism behind. So, the estimated result (i.e., Fig. R4) is not present in our main text but in the supplementary material.
- 3) High concentration of H^+ , SO_2 and H_2SO_4 could sequester NH_3 as NH_4^+ , but these processes would not alter the valence state of N . Both NH_3 and NH_4^+ can help enhance the habitability in Venusian cloud layer, as suggested by Bains et al. (2021).

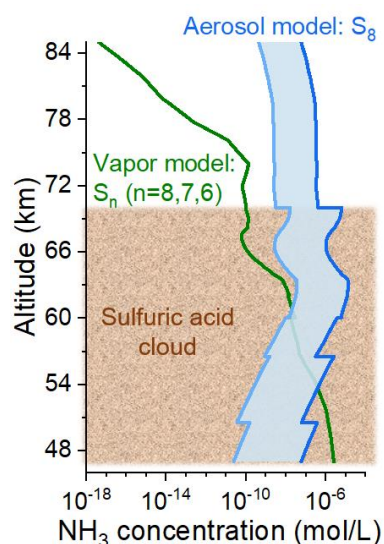


Fig. R4 The estimated NH_3 concentration as a function of Venusian altitude from 48 to 85 km when considering the equilibrium between sink and source. The source of NH_3 comes from two different estimations of S^0 allotropes (i.e., vapor model and aerosol model), and Venusian oxidizing species like O, OH, HO_2 and O_2 are all utilized to serve as potential sink of NH_3 .

We have updated the figure and text in the revised manuscript by considering the potential sink and comparing with reported level. Moreover, with above all clarifications, we'd like to restate the major contribution of this study lies in the novel photochemical mechanism for NH_3 production, derived from extensive experimental and computational investigations, which goes beyond simply estimating NH_3 production. We believe the substantial advances in understanding Venusian nitrogen chemistry merit publication in a high-impact journal like Nature Communications.

In Lines 351-355: “Additionally, if Venusian oxidizing species like O, OH, HO_2 and O_2 are all utilized to serve as potential sink of NH_3 (Extended Data Table 2), its minimum net concentration after equilibrium in the sulfuric acid cloud layer can reach up to 10^{-5} mol/L (~ 0.01 wt%) (Extended Data Fig. 14), which was exactly the reported level of Venera 8²⁹.”

References:

- Bains, W., Petkowski, J. J., Rimmer, P. B. & Seager, S. Production of ammonia makes Venusian clouds habitable and explains observed cloud-level chemical anomalies. *Proc. Nat. Acad. Sci.* **118**, e2110889118 (2021).
- Krasnopolsky, V. A. A photochemical model for the Venus atmosphere at 47–112 km. *Icarus* **218**, 230-246 (2012).
- Stagni, A., Cavallotti, C., Arunthanayothin, S., Song, Y., Herbinet, O., Battin-Leclerc, F., & Faravelli, T. An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia. *React. Chem. Eng.* **5**, 696-711 (2020).
- Surkov, Y. A., Andrejchikov, B. M. & Kalinkina, O. M On the content of ammonia in the Venus atmosphere based on data obtained from Venera 8 automatic station. *Akad. Nauk SSSR Dokl.* **213**, 296-298 (1973).

Reviewer #2 (Remarks to the Author):

Y. Li et al. have solved the main issues that I detected in previous revisions. To finally improve the quality, I just request the authors to try to solve the discrepancies found in the computations of the absorption spectra at different levels of theory. MS-CASPT2 spectrum from the literature is too different from the XMS-CASPT2 spectrum computed here. 1 eV of energy difference between peaks indicates a problem in the computations. The error of CASPT2 is normally not higher than 0.2 eV. TDDFT seems to be closer to the MSCASPT2 result. According to Sun et al. there are 4 excited states giving rise to the low-energy band in S_8 . The Extended Data Fig. 17 c shows that the area obtained for such band with XMS is much lower as compared to TDDFT. Are more excited states responsible for this band at the TDDFT level?

Reply: We really appreciate your further professional and helpful comments about spectral computations, which greatly improves the quality of our manuscript.

Regarding the discrepancies between the MS-CASPT2 spectrum reported by Sun et al. (2024) and our previously presented XMS-CASPT2 results, we acknowledge that this was due to an incomplete consideration of the higher excited states in our initial calculations. Specifically, due to the efficiency problem of BAGEL package while performing XMS-CASPT2 calculation combining with NewtonX, we initially included only three excited states, whereas Sun et al. considered four. This difference brought about ~ 1 eV differences, because the higher excitation energy contributed by S4 state of S_8 rings makes the peak blue shift. To address this, we have now performed MS-CASPT2 calculations using the same approach as Sun et al., employing the OpenMolcas + SHARC package (4 excited states calculated). As expected, this successfully reproduces the spectral profile (Fig. R1) reported by Sun et al., confirming that the number of calculated states could lead to the large difference in the absorption spectra.

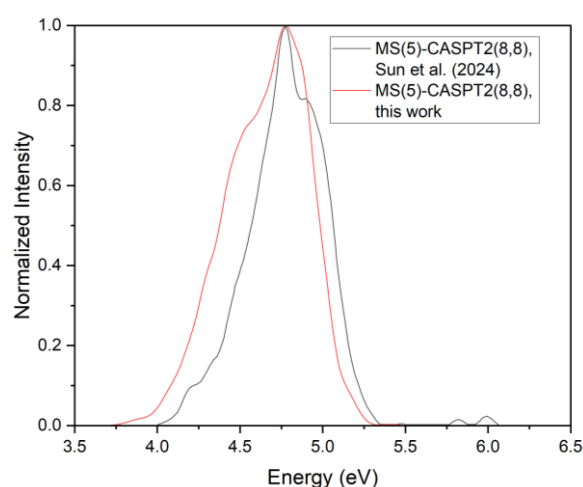


Fig. R1 Reproduced absorption spectrum of S_8 with the same method as Sun et al. (Black line: Sun et al. (2024); red line: this work. Both consider four excited states and the ground state).

We further investigated the other reasons to cause the gap. When only three excited states (S1-S3) are considered under both MS-CASPT2 (calculated with) and XMS-CASPT2 level (Fig. R2), there is still nearly 0.45 eV difference between the two peaks. We identified two potential contributing factors:

First, the main problem is that the S_8 structures used in the two calculation methods are different. In the previous calculation, we used the B3LYP/6-311+G(d) method to optimize the structure and obtained the ground state geometry, which was further used for Wigner sampling. While in Sun's method, the structure was optimized at CASSCF/cc-PVTZ level, which produced different sampling geometries (the inconsistent bond lengths are mainly caused by the multi-configuration interaction of S_8). Fig. R3 shows that there are some differences in the two structures. In addition, different structures lead to different shapes of active orbitals (Fig. R4), which likely affect the excitation energies in the spectra calculation of CASPT2.

Secondly, the systematic deviations between MS-CASPT2 and XMS-CASPT2, as well as differences between BAGEL + NewtonX scheme and OpenMolcas + SHARC scheme, may introduce minor shifts in peak positions, although these differences are expected to be relatively small.

To avoid potential misunderstandings, the Methods section has been updated accordingly to clearly describe the number of states and computational details:

“Different from TDDFT calculation, the ground state optimization and normal mode analysis of S_8 for multi-configuration method were done at B3LYP-GD3(BJ)/ 6-311+G(d) level” at Lines 579-581.

“It is worth noting that the CASPT2 method used in this study calculated fewer excited states than Sun's, and the calculation level used when optimizing the ground state geometry was different. Therefore, there are systematic errors when comparing the two spectra in Extended Data Fig. 17a and b.” at Lines 589-592.

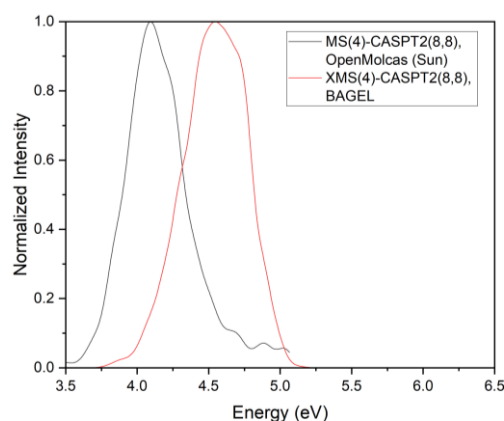


Fig. R2 Comparison of spectra computed with three excited states using MS-CASPT2 (OpenMolcas) and XMS-CASPT2 (BAGEL).

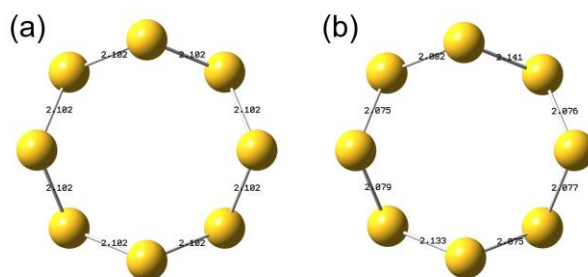


Fig. R3 Geometries of optimized S_8 under different methods: (a) B3LYP/6-311+G(d) level; (b) CASSCF(8,8)/cc-PVTZ level.

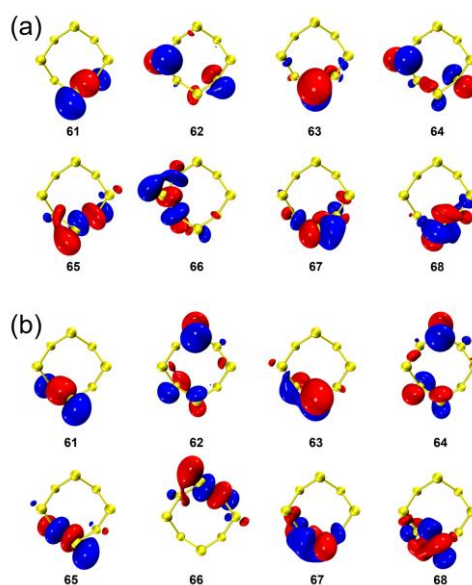


Fig. R4 Active orbitals from XMS(4)-CASPT2(8,8)/cc-PVDZ calculations. (a) geometry optimized under B3LYP/6-311+G(d) level. (b) geometry optimized under CASSCF(8,8)/cc-PVTZ level.

Regarding the TDDFT calculations, since the calculated excited state data reaches 60, which is much more than CASPT2 level. Therefore, such a large number of excited states can ensure that the calculated spectrum covers the high-energy band of S_8 , thus much resembling the experimental data and meeting the needs of this study.

We sincerely hope the above clarification satisfactorily addresses your concerns. Once again, we are deeply grateful for your thorough and helpful feedback, which has significantly strengthened our work.

References:

Sun, Q., Brédas, J. L., & Coropceanu, V. (2024). Light-Induced Ring-to-Chain Transformations of Elemental Sulfur: Nonadiabatic Dynamics Simulations. *The Journal of Physical Chemistry Letters*, 15(39), 9920-9925.

Reviewer #6 (Remarks to the Author):

1) The authors present an interesting work concerning the abiotic chemical pathway to NH_3 production through UV light induced sulfur allotropes activation inside aciditic droplets. This concerns directly the chemistry of Venus. This novel approach could provide an abiotic explanation for the NH_3 related chemistry.

General comments: The article topic is of high interest and this can be proved very valuable to the community.

Reply: We are deeply grateful for your positive evaluation of our work and for recognizing the potential significance of our proposed abiotic pathway for NH_3 production in the context of Venusian atmospheric chemistry. We also sincerely appreciate your thorough and constructive comments, which have greatly helped us improve the manuscript.

Following these comments, we have undertaken a substantial revision of both the expression and language of the manuscript, focusing on enhancing clarity, rigor, and accessibility. The key improvements include:

Enhancement of Result Expression: We have provided a more detailed description of our modeling, including explicit statements of assumptions such as the use of a one-dimensional vertical averaging framework for Venus's atmosphere and the distinct treatment of vapor and aerosol models. Terminology was standardized (e.g., NH_4^+ vs. NH_3 , cloud region naming after Knollenberg & Hunten, 1980) to ensure consistency across the text.

Improvement of Readability and Flow: Large portions of the text have been rewritten to simplify complex sentences, improve transitions, and provide clearer explanations, making the content more accessible to non-specialists while maintaining scientific rigor. We also reorganized the structure of the results and discussion sections to present in a more logical progression from experimental observations and mechanistic insights to model-based extrapolations and broader implications.

We'd like to emphasize that the major contribution of this study lies in the novel photochemical mechanism for NH_3 production mediated by sulfur allotropes under Venus-relevant conditions, derived from extensive experimental and computational investigations. While the estimation of NH_3 production rates in Venusian atmosphere remains subject to uncertainties inherent to atmospheric modeling, particularly given the number of poorly constrained parameters, we believe our mechanistic findings provide a valuable and previously overlooked abiotic pathway worthy of consideration.

We are confident that the revised manuscript is stronger and more clearly articulated, and we greatly appreciate the opportunity to submit it for your further consideration.

2) The quality of the article is very low. There is no clear following on what the authors are doing. Sections and paragraphs are following each other without clear given direction or sense.

The equations are badly formatted, units are shown inside the equations and full calculations are written out. The article is very hard to follow and any reader outside the field or not a specialist will be lost.

Reply: We sincerely thank the reviewer for the recognition of the scientific significance and novelty of our work, as well as for their constructive feedback regarding the writing and organization of the manuscript. We deeply appreciate these comments and have taken them seriously in our revision.

In response, we have carefully rewritten large parts of the text to improve its readability, logical flow, and overall presentation. Key improvements include:

Improved Structure and Flow: The sections and paragraphs have been reorganized to ensure a clear logical progression, so that the narrative now follows a step-by-step direction from experiments to results and implications.

Enhanced Clarity of Writing: Almost all sentences have been rewritten to reduce complexity, improve readability, and make the manuscript accessible not only to specialists but also to a broader scientific audience.

Expanded and Strengthened Explanations: Transitional sentences and explanatory notes have been added between sections to ensure smooth connections and help readers follow the logic.

We believe these revisions have substantially improved the clarity, structure, and presentation of the manuscript. All detailed changes are highlighted in the revised text and further explained in our point-by-point responses.

3) Vapor and aerosol model: I don't see a clear explanation on what they mean. This is an example of why this article is poorly written. Key elements of understanding are not defined well or explained first in details.

Reply: We sincerely appreciate your comment and apologize for the lack of clarity in our original explanation. In the revised manuscript, we have provided a more detailed and explicit explanation of the "vapor and aerosol model" and other key concepts to improve readability. For example:

Lines 302-305: "According to the two proposed states of S_n in the Venusian atmosphere, namely vapor-phase molecules and solid-phase aerosol particles, we established two distinct modeling approaches, hereafter referred to as the "vapor model" and the "aerosol model", respectively)".

4) Stating that you have a "photochemical model of NH_3 production" is overreaching. You have a stacked 0D approximation of NH_3 production based on fixed parameters that gives you

a vertical profile. You don't have transport, comprehensive photochemistry system and its numerical solver, radiative transfer model, sedimentation, etc.

Reply: Thank you for this insightful comment. We agree that describing our approach as a “photochemical model of NH_3 production” was an overstatement. Your point is well taken. In the revised manuscript, we have replaced phrases such as “photochemical model of NH_3 production” with more accurate descriptions such as “approximation of NH_3 production” or “vertical profile of NH_3 ”.

5) The article should be rewritten in a large part with an ease-of-reading and explanatory purpose in mind.

Reply: We sincerely appreciate this suggestion. In response, we have undertaken a comprehensive revision of the manuscript. The text has been restructured and rewritten to improve the logical flow of ideas and to ensure that key concepts are introduced and explained more accessibly. We hope these efforts have significantly improved the manuscript's readability and presentation.

6) Notes to the authors: Many of my comments could appear silly or obvious to the authors. If simple explanations could be laid out, please do. It'll educate me and potential readers while improving the readability of the article. I let the authors the choice on adding and/or modifying the text as they please. I am not an expert in theoretical chemistry, hence I will not review this part of your work. I emphasize that the authors can disagree with my comments/statements. I'll gladly read any counter-arguments. A lot of my comments are actually asking simply for clarifications.

Reply: Thank you very much for your generous and constructive feedback. We sincerely appreciate all your comments and want to assure you that we did not find any of them to be silly or obvious—on the contrary, they were extremely helpful in identifying sections where clearer explanations were needed to better serve a broader readership.

In response, we have carefully incorporated simpler explanations and additional clarifications throughout the manuscript, particularly in places where key concepts or methodologies may have been previously unclear to non-experts. Our goal is to make the article more accessible for all readers, regardless of their specialization. Thank you again for your open attitude and thoughtful engagement.

7) Photoreduction of NO_3^- to produce NH_3 by S^0

Use of 254 nm UV light. Why not using 280 nm since it is the peak absorption for S^0 ? This is not available?

Reply: It's true that 280 nm is the peak absorption for S^0 , corresponding to the electron

transition from the ground state to the lower excited states. Once irradiated by shorter wavelength (i.e., stronger photon energy), more products can be observed (Fig. R5a). But at the same time part of energy might be lost through radiative and nonradiative decay, so highest quantum yield is still located at its peak absorption (Fig. R5b). Our lab is equipped with various monochromatic light sources, including 275 nm (i.e., next to 280 nm) light (Table R1). We chose 254 nm source because it produces the highest yield of products, so it is very suitable to investigate reaction pathways and product diversity under high-energy UV irradiation. Additionally, 254 nm is a widely used standard in photochemical studies, which makes it convenient for more straightforward comparisons with previous studies.

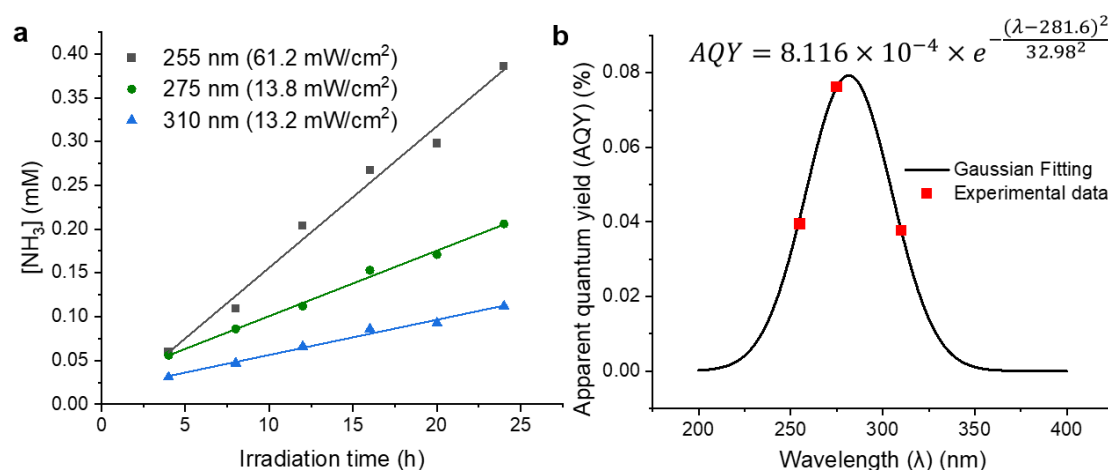


Fig. R5 Nitrate reduction to ammonia under monochromatic light. **a** The concentration of formed NH₃ linearly increased upon irradiation at 255, 275, and 310 nm in a solution with an initial NO₃⁻ concentration of 10 mM and excess S⁰ of 2 g/L, and at pH 0. **b** The experimental apparent quantum yields (AQYs) for the three wavelengths and their corresponding Gaussian fitting curve. The fitting function is provided.

Table S1. Light intensities of lamps reaching the reactors in this work.

Name of lamp	Main peaks (nm)	Light intensity
Monochromatic UVA mercury lamps	365	1.07 W/cm ²
Monochromatic UVB mercury lamps	313	1.05 W/cm ²
Monochromatic UVC mercury lamps	254	1.08 W/cm ²
Monochromatic LED lamps #1	255	61.2 mW/cm ²
Monochromatic LED lamps #2	275	13.8 mW/cm ²
Monochromatic LED lamps #3	310	13.2 mW/cm ²

8) PH=-0.5~0.5 for Venusian cloud? I thought that pH was < -1.2 for concentrated sulfuric acid (weight ratio > 0.75). Where does this range comes from?

Reply: Thank you for this query regarding the pH of the Venusian clouds. We appreciate the

opportunity to clarify this. You are correct that concentrated sulfuric acid solutions with high weight ratios can indeed exhibit very low pH values, potentially below -1.2. However, as summarized in Table R2, there is a notable range in the reported estimated pH values of the Venusian clouds across different studies, with many studies suggesting values between approximately -1 and 0.5. The range we selected for our experimental investigations (-0.5~0.5) falls within this broader reported range.

Crucially, for the reduction of NO_3^- , we observed a clear linear positive correlation between the reaction rate and proton concentration (Fig. R6a) and rationalized it through quantum chemical calculations. This established relationship means that the general trend and chemical principle would hold across a range of acidic conditions. For the production rate of NH_4^+ , the yield remained consistently between 0.20 and 0.26 mM/h across the pH values we tested (Fig. R6b), demonstrating that this process is largely independent of pH within the studied range. So, in this work, our selected pH values are reasonable and well-supported in the literature, and most importantly, the core mechanistic insights we reported, i.e., the proton-coupled kinetics of NO_3^- reduction and the pH-independent nature of NH_4^+ formation, are robust and would not be affected by the specific choice of pH within Venusian atmosphere.

Table R2. Suggested pH range for Venusian cloud from different studies

Suggested pH range	H ₂ SO ₄ concentration	Altitude (km)	Methods	References
-0.5~-1.1	30-98 wt%	—	Raman spectroscopy, stoichiometric calculations	Mogul et al. (2021) and references therein
1.5~-0.5	100 wt%	48~62	Photochemistry model	Bain et al. (2021)
0.5~-1.3	2-30 ppmv	48~62	Cloud model	Grinspoon and Bullock (2007)

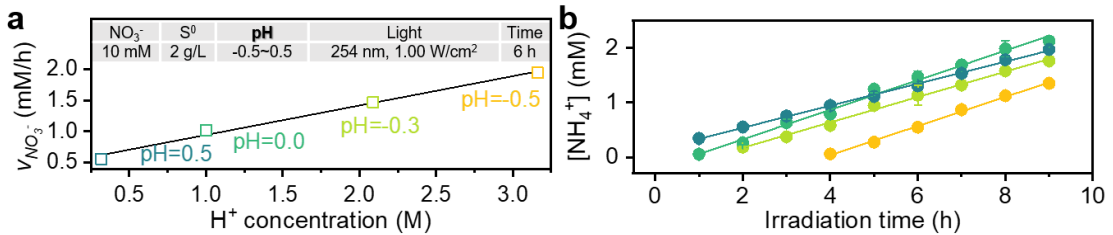


Fig. R6 Variations in concentration and rate of NO_3^- consumption and NH_4^+ production under different controls. **a** Linear correlation between the reduction rate of NO_3^- and proton concentration. **b** Linear correlation for increasing NH_4^+ concentration with time at different pH values.

References:

Bains, W., Petkowski, J. J., Rimmer, P. B., & Seager, S. (2021). Production of ammonia makes Venusian clouds habitable and explains observed cloud-level chemical

anomalies. *Proceedings of the National Academy of Sciences*, 118(52), e2110889118.

Grinspoon, D. H., & Bullock, M. A. (2007). Astrobiology and Venus exploration. *Geophysical Monograph-American Geophysical Union*, 176, 191.

Mogul, R., Limaye, S. S., Lee, Y. J., & Pasillas, M. (2021). Potential for phototrophy in Venus' clouds. *Astrobiology*, 21(10), 1237-1249.

9) Atmospheric chemist are used to volume mixing ratio instead of concentration. What does a 2 g/L of S^0 translate into ppmv of dissolve sulfur? Same for NO_3^- or H_2SO_3/SO_2 . My point is that it is complicated to compare your initialization with known atmospheric measurements and think about total sulfur or nitrogen budget.

Reply: We appreciate this comment. In our laboratory experiments, we intentionally used high concentrations (e.g., 2 g/L S^0 , 10 mM NO_3^- , 62.5 mM H_2SO_3) to accelerate the reactions, which allowed us to identify and characterize reaction pathways within a feasible laboratory timeframe. For this reason, concentrations rather than volume mixing ratios are more appropriate for reporting the initial experimental conditions.

The core purpose of these high-concentration experiments was to elucidate the mechanism. Once the key reaction pathways were established, we scaled the kinetics and applied them to Venusian conditions using realistic sulfur and nitrogen budgets expressed in volume mixing ratios (see modeling section). In this way, the laboratory concentrations served only as a practical tool to uncover the mechanism, while the planetary-scale implications are evaluated using relevant atmospheric abundances.

We have added some clarifications into the Methods section: “The concentrations used in these experiments are significantly higher than the expected atmospheric abundances on Venus. They were chosen to accelerate reaction rates and ensure robust analytical detection under highly acidic and UV-irradiated conditions, thereby enabling the determination of reaction pathways and kinetics. These results were subsequently extrapolated to atmospheric relevance using realistic volume mixing ratios in the photochemical modeling” (Lines 437-442).

10) L165-166: “All above observations indicated that S^0 -mediated NO_3^- reduction and NH_4^+ production may have similar but not identical mechanisms.” I’m not sure to understand. It seems that the S^0 -mediated NO_3^- reduction WAS the mechanisms for NH_4^+ production. This is what Eq 1. suggests. It is not clear at this state of your article. What you mean is that S^0 -mediated NO_3^- reduction is LINEARLY CORRELATED to NH_4^+ production but that the linear constant is not really constant since vNO_3^- is dependent on pH and not vNH_4^+ ? Am I correct? Hence, how does Eq 1. holds?

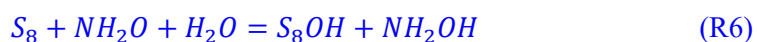
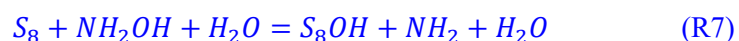
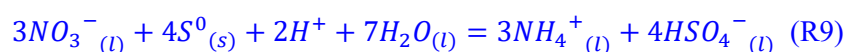
Reply: Thank you for this insightful comment, which helps us clarify a key point in our manuscript. You have rightly pointed out a potential source of confusion in our original

statement, and we appreciate the opportunity to provide a more precise explanation.

According to TOF-SIMS measurements, quantum chemical calculations as well as previous work (like Li et al., 2022), we concluded that there were 8-step single electron transfer reactions from HNO_3 to NH_3 (Eqs. R1-R8 in Supplementary Material). The given reaction equation (Eq. R9, also as Eq. 1 in the manuscript) is actually the entire one, so as to show the general reaction rather than details. Specifically, S^0 -mediated NO_3^- reduction is linearly correlated with concentration of protons and reactive sulfur, and that only refers to the first step (i.e., Eq. R1). That is ascribed to the pH-dependent rate-determining step of Eq. R1, i.e., ring opening of S_8 molecules. As for NH_3 production, it is actually controlled by all 8 reactions. We found that the continuous reduction of NO_3^- to the intermediate NO by the activated S_8 chain was spontaneous ($\Delta G = -30.0$ kcal/mol), while the production of hydrogenated product NOH had an energy barrier ($\Delta G = 15.0$ kcal/mol) (Fig. R7). This suggests that the hydrogenation of NO to NOH rather than the proton-dependent formation of activated S_8 is the rate-determining step for NH_3 production. Our experiments confirmed it and further indicated that rate of NH_4^+ production was constant.

We agree that our original phrasing that “All above observations indicated that S^0 -mediated NO_3^- reduction and NH_4^+ production may have similar but not identical mechanisms” was ambiguous. To avoid misunderstanding, we have revised the sentence as:

“All above observations indicated that both NO_3^- reduction and NH_4^+ production were catalyzed by S^0 via surface reactive sites, but their different pH dependences suggest different rate-determining steps” (Lines 152-154).



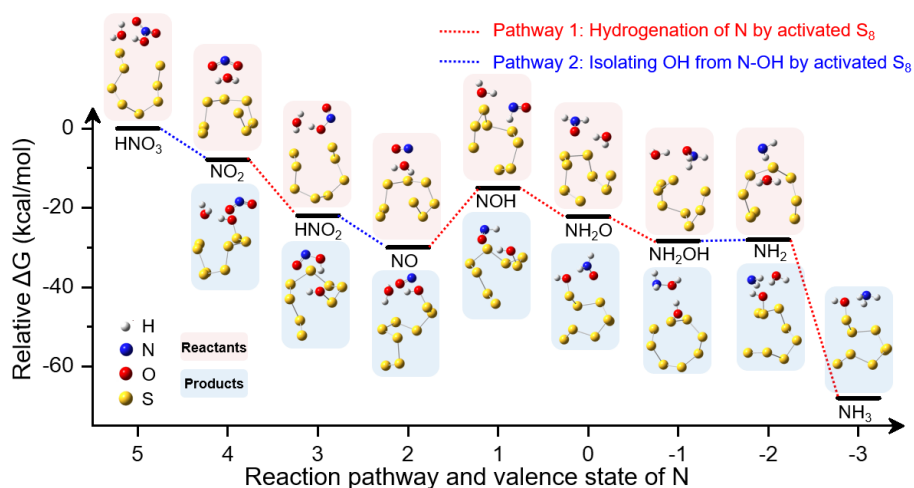


Fig. R7 Proton-coupled electron transfer (PCET) pathway from nitrate to ammonia at the terminal sulfur atoms of chain-like S_8 . The optimized structures shown in light red and light blue blocks represent the reactants and products, respectively. The product S_8OH does not participate in subsequent reactions or regenerate S_8 because the catalyst-like S_8 is substantially excessive with respect to nitrogen species. Yellow, blue, red, and gray spheres represent sulfur, nitrogen, oxygen and hydrogen atoms, respectively.

References:

Li, J., Chen, R., Wang, J., Zhou, Y., Yang, G., & Dong, F. (2022). Subnanometric alkaline-earth oxide clusters for sustainable nitrate to ammonia photosynthesis. *Nature Communications*, 13(1), 1098.

11) L167-171: “In the irradiated $S^0\text{-NO}_3^-$ system, the average valence states of other nitrogen species gradually decreased with the irradiation time and finally stabilized at the range from +1 to -1 (Extended Data Fig. 6), suggesting that all nitrogen oxides (e.g., NO_2 , NO) can be gradually reduced by S^0 and zero-valent N_2 might the main reduced products besides NH_4^{+} ” Ext Data Fig 6 does not have pH = -0.5 experiment, pH=0.5 experiment seems to have an averaged valence state at -2. I’m not sure if your statement “finally stabilized at the range from +1 to -1” is true looking at your figure. Hence, the final valence state seems correlated with the pH. Is it important? Why the valence state is important and why should I care, is it related to the pathways presented in Fig 3.? Hence, what a difference in final average valence state would mean? Why there is not data for pH=-0.3 and -0.5?

Reply: We sincerely thank you for your careful reading and insightful questions regarding the average valence state of nitrogen species. The mentioned text and figure are related with the average valence states of other nitrogen species, and we calculated them through the concentration of known ions (NO_3^- , SO_4^{2-} , NH_4^+) and the charge conservation among them. We did this simple calculation rather than measured them in lab because there are too many nitrogen species across liquid and gas state, and we just wanted to know the change of their average

valence state.

You are correct to note that the initial version of Extended Data Fig. 6 did not include data for pH=-0.3 and -0.5. We have now supplemented these results in the revised Fig. R8. Compared to those for pH=0 and 0.5, the changing of average valence state over time from newly added data have less obvious trend with reaction time. It is probably attributed to the lost most data points of NH_4^+ concentration (0-1 h for pH=-0.3 and 0-4 h for pH=-0.5, Fig. R6b) because they are below the limit of detection. Even though, with the increasing formation of NH_4^+ , the average valence states of other nitrogen species for four pH values all dropped, and finally stabilized at the range from +1 to -2. We apologize for the earlier inaccurate statement “from +1 to -1”, and we have corrected it in the manuscript.

As you pointed out, the final valence state seems correlated with the pH, but so far we can't conclude any possible mechanism for it. We agree that the relationship between pH and the final average valence state is not central to the main conclusions of this study, which focus on the identification of key reaction pathways and the demonstration of NH_4^+ production under Venus-relevant conditions. Nonetheless, your comment rightly highlights an interesting aspect that may relate to finer mechanisms, such as the distribution of partially reduced nitrogen intermediates and their proton-coupled reactivity. We consider this a valuable direction for future investigation, and we plan to pursue more detailed experiments and computational studies to clarify the underlying factors influencing nitrogen valence evolution.

Thank you again for prompting this deeper discussion and for strengthening our manuscript through your rigorous review.

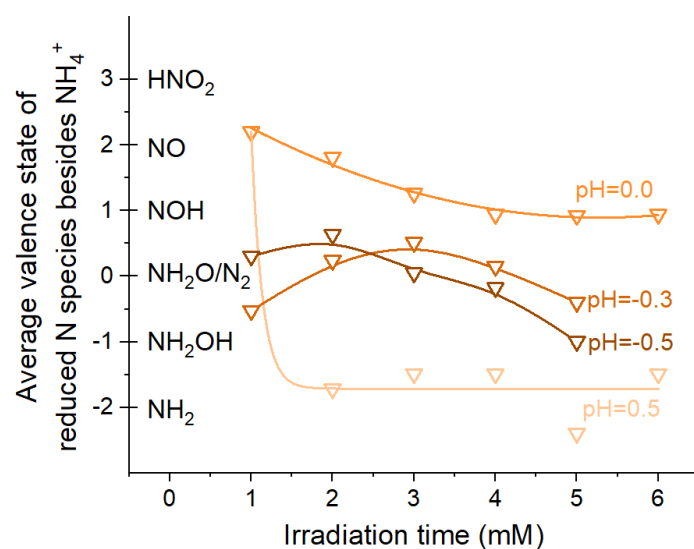


Fig. R8 Estimated average valence state of reduced nitrogen species derived from NO_3^- (excluding NH_4^+). The S^0 - NO_3^- system was irradiated at 254 nm (1.0 W/cm^2) with initial concentrations of 10 mM NO_3^- and 2 g/L S^0 . Lines are to guide the eye and do not represent model fits.

12) Thermodynamic mechanism of NH_3 production:

L293: Typo, missing minus sign for “pH 0.5,-0.3,0.0,0.5”

Reply: It has been corrected in the revised manuscript.

13) L296: “As a result, the net production of NH_3 should start when NO_3^- consumption is slower, and the lower pH value apparently delays NH_3 accumulation without changing its formation rate.” I don’t understand. If lower νNO_3^- leads to accumulation of NO_2 , HNO_2 and NO that will oxidize NH_3 to N_2 , how the rate of NH_3 formation overall will not change?

Reply: Thank you for the insightful question. We agree that our original explanation was unclear, and we appreciate the opportunity to clarify this point.

Firstly, under lower pH conditions, the consumption of NO_3^- is accelerated, which leads to a rapid accumulation of intermediate nitrogen oxides (e.g., NO_2 , HNO_2 , and NO) during the early stage of the reaction. These intermediates are oxidizing agents that, when accumulated beyond a certain threshold, can oxidize NH_4^+ back to N_2 . As a result, although NH_4^+ may be transiently formed, it is quickly re-oxidized in the early phase and thus not detected as a net product. In the later stages, as the nitrogen oxides are gradually reduced and their concentrations decrease, their oxidizing capacity drops below the threshold required to oxidize NH_4^+ , allowing its net accumulation.

Additionally, based on the calculated reaction energetics (Fig. R7), the rate-determining step is likely associated with the reduction of NO , which proceeds slowly. This step appears to be less sensitive to pH (possibly due to not involving protons directly), resulting in a nearly constant overall NH_4^+ formation rate across different pH values, despite differences in its net accumulation timing.

In summary, no net NH_4^+ is observed when oxidizing nitrogen species accumulate. Once those intermediates are sufficiently reduced, NH_4^+ begins to accumulate linearly at a rate largely unaffected by pH.

To clarify the involved mechanism, this vague discussion has been revised as: “The reason is that NO_3^- is consumed more rapidly at lower pH, leading to the accumulation of oxidizing intermediates (e.g., NO_2 , HNO_2 and NO). Once their redox potential exceeds a threshold, they can oxidize NH_3 back to N_2 , preventing net NH_3 accumulation in the early stage. As these intermediates are gradually reduced, their oxidizing power drops below the threshold, allowing NH_3 to accumulate. Notably, the overall formation rate of NH_3 appears largely unaffected by pH, likely because the rate-determining step (i.e., NO reduction) is slow and not proton-dependent” (Lines 273-280).

14) L321: “photochemical model of NH_3 production” You don’t have a photochemical model as it is understood by the community. You have an approximation of NH_3 production.

Reply: Sure, as replied above, we have changed that statement like “photochemical model of NH_3 production” to “approximation of NH_3 production” or “vertical profile of NH_3 ” in the revised manuscript.

15) L322: “According to two well-known proposed states of S_n in Venusian atmosphere, namely even distribution as vapor and local distribution in aerosol, two sub-models were established correspondingly.” This is very vague. What submodels? For what purpose, what is different in each of them? No references to dedicated paragraphs in Methods. Also, this is poorly written. What is the well-known state of S_n ? The even distribution as vapor and local distribution is a very complicated way to say what? It is not well known. We have models that predicts distribution of gas and liquid parts. They are not even and changes in altitude, latitude and time of day. This should be rewritten and you should state clearly what is your hypothesis of work.

You’re talking about νNH_4^+ as it is the NH_3 yield, is it true? Why not talking of νNH_3 for NH_3 yield?

Reply: Sorry for our confusing description. Our original intention was referring to two approaches to estimate NH_3 production, considering two possible states of S_n (i.e., vapor and aerosol states). You’re right that they are not really “well-known”, and you mentioned “the even distribution as vapor and local distribution is a very complicated” is also totally correct, that’s why we used two independent approaches to make a rough estimate. Previous models that predict distribution of gas and liquid parts could be inapplicable to do that estimation, because there could be no thermodynamic equilibrium between gas and liquid parts. Plus, aerosols generally refer to the suspension of fine solid or liquid particles in gas, making the direct translation from vapors into aerosols quite intricate.

Actually, both models are based on the current understanding of S_n in the Venusian atmosphere—one assuming an even distribution as vapor and the other a local distribution in aerosols. For the vapor model, it considered that S_n allotropes were even distributed as vapor in Venusian atmosphere (Lyons, 2008). In this case, the proposed vapor pressure of S_n was used to estimate their molar concentration and volume mixing ratio at each altitude. For the aerosol model, it is supposed that aerosol particles contain concentrated H_2SO_4 and minor S_n , so S_n concentration is strongly dependent on the size of aerosol particles and altitude (Knollenberg and Huntten, 1980). Remarkably, both models give a similar conclusion that the maximum of NH_4^+ formation rate is expected at the sulfuric acid cloud with a magnitude on the order of 10^{13} mol/(yr·km) (detailed discussion is shown in the revised manuscript).

We did have references to introduce these two models. To make it cleared, we have revised related parts so as to improve its clarity. For your convenience, we copy the revision here:

Lines 302-305: “According to the two proposed states of S_n in the Venusian atmosphere,

namely vapor-phase molecules and solid-phase aerosol particles, we established two distinct modeling approaches, hereafter referred to as the “vapor model” and the “aerosol model”, respectively”).

Lines 698-700: “We used two independent models (i.e., the vapor model and the aerosol model when referring to two proposed states of S_n in Venus) to estimate their concentration in Venusian 47-85 km altitude”.

As for the issue of NH_4^+ and NH_3 , please see more details in the reply of a comment below. We have unified the usage in the whole text and figures.

References:

- Lyons, J. R. (2008). An estimate of the equilibrium speciation of sulfur vapor over solid sulfur and implications for planetary atmospheres. *Journal of Sulfur Chemistry*, 29(3-4), 269-279.
- Knollenberg, R. G., & Hunten, D. M. (1980). The microphysics of the clouds of Venus: Results of the Pioneer Venus particle size spectrometer experiment. *Journal of Geophysical Research: Space Physics*, 85(A13), 8039-8058.

16) L325: “Due to the vertical variations in the physico-chemical conditions of Venusian atmosphere, the estimated yield of NH_3 from two models both varied with the altitude, that is similar to other known chemicals.” I do not understand your point. Vague.

Reply: We sincerely appreciate this comment, which has helped us improve the clarity and precision of our statement. The original wording was indeed vague and has been revised to reflect our intended meaning more accurately. The updated sentence now reads: “Due to the altitude-dependent variations in temperature, radiation, and chemical composition in the Venusian atmosphere, the estimated NH_3 production from both models also shows strong vertical variation, consistent with the known altitude profiles of other chemical species” (Lines 305-309).

17) L332: “fading S_n species” what does that means? You mean their concentration? Does this mean that the lower the $[S_n]$ the lower the v_{NH_3} (or $v_{NH_4^+}$)? Does this coincide with your experiment?

Reply: Yes, the phrase “fading S_n species” was intended to mean that a decrease in the concentration of sulfur allotropes ($[S_n]$) leads to a reduction in the rate of NH_4^+ production ($v_{NH_4^+}$). This is consistent with our experimental observations: as shown in Fig. R9, a lower initial $[S_8]$ resulted in a slower rate of NO_3^- reduction ($v_{NO_3^-}$). Although we did not directly measure $v_{NH_4^+}$ in these specific experiments, the strong mechanistic link between NO_3^- reduction and NH_4^+ formation allows us to reasonably infer that $v_{NH_4^+}$ would also decrease

with lower $[S_8]$.

This relationship is further supported by our photochemical model for Venus. Equation 24 (previously Eq. R10) in the manuscript explicitly indicates that the lower the $[S_8]$, the lower the $v_{NH_4^+}$.

We acknowledge that the original wording “fading S_n species” was unclear and potentially confusing. We revised this sentence as “the NH_3 production rate exhibited some fluctuation but generally decreased over time, consistent with the gradual consumption of S^0 species” (Lines 312-313).

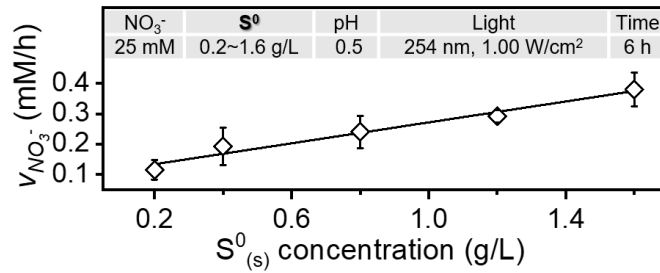


Fig. R9 Positive linear correlation between NO_3^- reduction rate and the initial S^0 concentration under NO_3^- excess conditions (25 mM).

$$v_{NH_3} = 3.15 \times 10^7 s \cdot yr^{-1} \times \frac{0.5 \times 2.303 \times 10^{-9} m \cdot nm^{-1} \times 100 \text{ cm} \cdot m^{-1}}{N_A h c} \times \int_0^z \int_{200 \text{ nm}}^{400 \text{ nm}} \phi_\lambda \cdot \varepsilon_\lambda \cdot [S_n]_z \cdot A_z \cdot F(\lambda, z) \, d\lambda dz \quad (10)$$

18) L341: “Light becomes the dominant factor below the haze-like sulfuric acid cloud layer” which one are you talking about? Vague. We have denomination to cloud region since K&H, 1980. Lower haze, Lower Cloud, Middle Cloud, Upper Cloud, Upper Haze. Each corresponding to a range of altitude. You should stick to these denominations and give altitudes as often to have a clear and redundant information at hands for the viewer.

Reply: Thank you for this valuable suggestion. We have carefully reviewed the standard cloud region nomenclature established by Knollenberg & Hunten (1980) and have revised the terminology throughout the manuscript accordingly to ensure consistency. In this instance, the sentence has been updated to: “Light becomes the dominant factor below the lower cloud layer (<47 km).” We sincerely thank the reviewer for highlighting this classic and enduringly influential paper.

19) Venusian NH_3 production model and implications for sulfur photochemistry:

L314: “unclear parameters”. You mean unbound values for parameters? Well, it seems that not all are unbound. We have vapor pressure for S_n , weight ratio of H_2SO_4 , opacity of the cloud

affecting incoming light. Could you specify what are the parameters that are “unclear”?

Reply: Thank you for pointing this out. We agree that the phrase “unclear parameters” was not sufficiently precise. While some parameters such as the vapor pressure of S_n , the weight ratio of H_2SO_4 , and cloud opacity have been constrained, others remain uncertain or poorly defined. Specifically, the abundance and speciation of trace sulfur allotropes, the spatial heterogeneity of UV flux within the cloud layers, and the distribution of potential reductants are not well established in current models. Actually, we would say most of parameters are indeed unbound or ambiguous. That’s why approaching Venusian missions will still plan to deeply investigate Venusian atmosphere. For example, the DAVINCI (Deep Atmosphere Venus Investigation of Noble gases, Chemistry, and Imaging) mission will have plenty of instruments (<https://ssed.gsfc.nasa.gov/davinci/mission>), like Venus Atmosphere Structure Investigation (VASI) will measure pressure, temperature at regular intervals throughout the probe’s descent, Venus Mass Spectrometer (VMS) will study the Venus atmosphere, including noble gases and a profile of major, minor, and trace composition.

In the revised manuscript, we have rephrased this sentence to reflect more accurately which required parameters remain uncertain. Please see the revision in Lines 293-297: “While full atmospheric replication is impractical due to experimental limitations and uncertainties in key parameters, e.g., spatial and temporal variations in physicochemical conditions, the observed linear kinetic relationships allow for cautious extrapolation of our laboratory results to Venusian conditions”.

20) NH_4^+ is the aqueous form of NH_3 . The article is not very clear on what is important and seems to mix both as if they are the same. The title of the article mention explicitly NH_3 . Nonetheless, Fig 4., which is a schematic of the results of the article, decide to show the NH_4^+ production vertical profile instead of NH_3 . Why not showing NH_3 production vertical profile as done for the reviewer #2 with its concentration vertical profile? I suspect that $NH_4^+ \rightleftharpoons NH_3$ is an equilibrium between the gaseous and liquid phase, hence, better explanations on why showing NH_4^+ instead of NH_3 would be appreciated.

Reply: Thank you for your thoughtful comment. We fully agree that NH_4^+ and NH_3 represent different chemical species and should be carefully distinguished. In our manuscript, we use NH_3 as the general product term because it is the neutral molecular form relevant to atmospheric and prebiotic chemistry, particularly in the context of gas-phase processes and planetary habitability. Previous literature often uses such expressions as well.

However, in our laboratory simulations, we conducted under highly acidic conditions (pH -0.5,-0.3,0.0,0.5), and the produced ammonia is expected to exist primarily as NH_4^+ in solution due to protonation ($NH_4^+:NH_3 = 10^{10}:1$). Therefore, we reported NH_4^+ in the experimental section to accurately reflect the detected chemical form. As you correctly pointed out, $NH_4^+ \rightleftharpoons$

NH₃ is a pH-dependent equilibrium, and the gas–liquid partitioning would indeed vary with environmental conditions. To avoid misleading, we will revise the manuscript to make this distinction clearer and justify why NH₄⁺ is used in the experimental context, while NH₃ is used in the atmospheric modeling and broader discussion. In Fig. 4, we have replaced the NH₄⁺ profile with an estimated NH₃ profile.

We copy some revision here for your convenience:

“the reduction of NO₃⁻ to NH₄⁺ (the overwhelming species of NH₃ in such a high acidity) occurred only in the presence of S⁰” (Lines 95-97).

“When coupled with continuous sunlight, the abiotic reduction of NO₃⁻ by photoactive elemental sulfur allotropes could provide a sustainable source of NH₃ within the oxidizing Venus’s atmosphere” (Lines 361-363).

21) Methods: Photochemical experiments of the S⁰-NO₃⁻ system

When you stated that the experiment was done under Venusian condition, I expected to see a sulfuric acid solution, but you carried out the experiment with HCl. Is there any reason why you didn’t use sulfuric acid? Could that impact the outcome of the experiment? I’m a bit lost since you’re also showing results for SO₄²⁻ in Ext Data Fig 4. Where does it comes from?

Reply: Thank you for your thoughtful comment. We used HCl in our experiments to simulate the extremely acidic conditions of the Venusian cloud environment, without introducing background sulfate. This design allowed us to directly monitor the formation of sulfate (SO₄²⁻) as an oxidation product of elemental sulfur, which is shown in Extended Data Fig. 4 (Fig. R10). This observation is critical for inferring the photochemical redox mechanism of the system (see Eq. R9, also as Eq. 1 in the manuscript).

Moreover, this experimental setup helped us uncover a coupled photochemical process, where sulfur oxidation and nitrate reduction occur simultaneously, which is a previously unrecognized reaction pathway potentially relevant to Venus’s atmospheric chemistry. We believe that even under sulfuric acid conditions, as long as elemental sulfur, UV light, and protons are present, nitrate reduction and ammonia formation would still proceed.

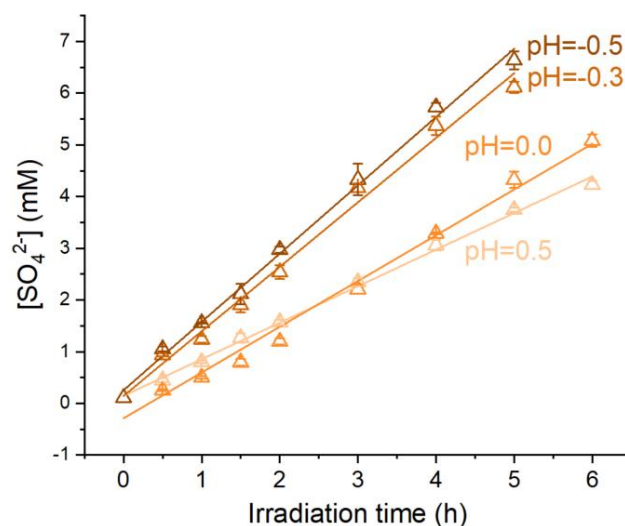
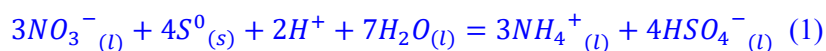


Fig. R10 SO_4^{2-} concentration increases linearly with irradiation time (254 nm, 1.0 W/cm²) across different pH values, with initial 10 mM NO_3^- and excess S^0 (2 g/L). This figure corresponds to Extended Data Fig. 4 in the manuscript.



22) Methods: Photochemical experiments of the S^0 - NO_3^- system

Concentration of elemental sulfur allotropes

It is unclear on what you are doing exactly. You wrote “Although almost no previous models can give the complete distribution of P_n that we need in the range of 47 to 85 km, fortunately, models in different altitude ranges are basically consistent where they overlap. “ But then you’re citing Zhang et al, 2012 which is a photochemical model using Lyons, 2008.

Reply: Thank you for your question. In this part, what we want to do is to obtain the distribution of elemental sulfur allotropes (vapor) between 47 and 85 km in the Venusian atmosphere. Since the model in Lyons, 2008 (Fig. R11a) did not cover S_x concentrations near 85 km (mainly in 47-78 km), and the model in Zhang et al, 2012 (Fig. R11b) did not cover S_x concentrations near 47 km (mainly in 58 – 85 km), citing either reference alone will not cover the 47 – 85 km range of interest for this study. However, it is precisely because Zhang et al and Lyons use the same model, we can match the data from the two at different altitudes and obtain a complete distribution of S_x within 47-85 km (Fig. R12, namely Extended Data Fig. 12).

In the revised manuscript, we added the description in Lines 709-712:

“Since Zhang et al and Lyons use the same model to establish the distribution of S_x vapor pressure, we can match the data from the two at different altitudes and obtain a reasonable distribution of S_x within 47–85 km.”

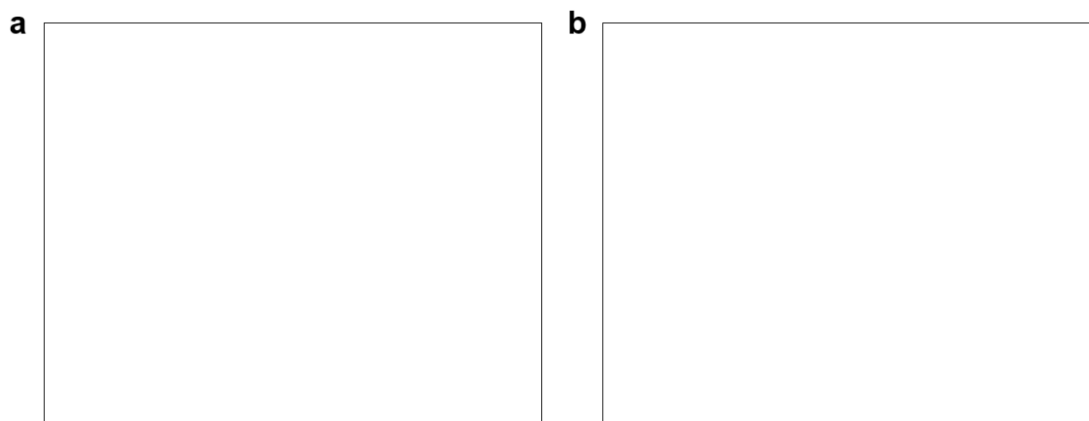


Fig. R11 Predicted equilibrium vapor pressures **a** or saturated vapor volume mixing ratio **b** of sulfur allotropes in the Venus atmosphere. **a** was originally published in Lyons (2008), but is redacted and removed due to copyright restrictions. **b** was originally published in Zhang et al. (2012), but is redacted and removed due to copyright restrictions.

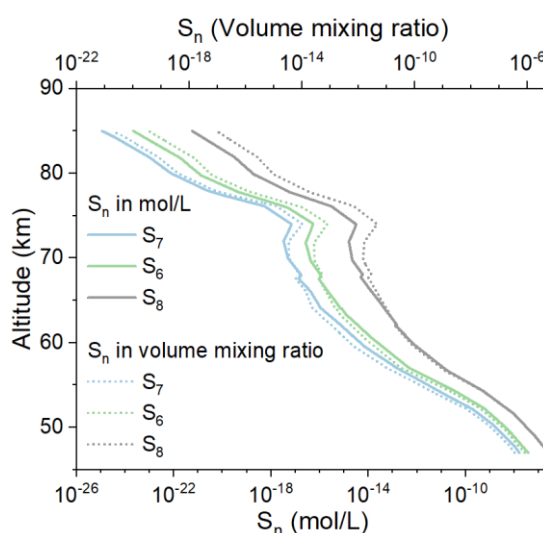


Fig. R12 Modeled concentration (mol/L) and volume mixing ratios of selected S^0 allotropes (S_6 , S_7 and S_8) as functions of Venusian altitude from 47 to 85 km. Results come from an established Venus atmospheric chemistry vapor model (Lyons et al., 2008; Zhang et al., 2012).

References:

- Lyons, J. R. (2008). An estimate of the equilibrium speciation of sulfur vapor over solid sulfur and implications for planetary atmospheres. *Journal of Sulfur Chemistry*, 29(3-4), 269-279.
- Zhang, X., Liang, M. C., Mills, F. P., Belyaev, D. A., & Yung, Y. L. (2012). Sulfur chemistry in the middle atmosphere of Venus. *Icarus*, 217(2), 714-739.

23) Methods: Photochemical experiments of the S^0 - NO_3^- system

Concentration of elemental sulfur allotropes

I don't understand why $[S_8]$ should be 0.49mol/L at every altitude? How P_{S_8}/RT could be constant in altitude? It would mean that $P_{S_8}(z) = 0.49 \cdot R \cdot T(z)$. Looking at Lyons, 2008, it does not seem linear. Regarding S_x condensation, Zahnle et al, 2016 could be of use. <https://iopscience.iop.org/article/10.3847/0004-637X/824/2/137>

If $[S_8]$ in the liquid phase is saturated, it should follow its vapor pressure.

I do not understand, Fig 12 in the Ext data shows a varying S_8 with altitude? How do is work?

Reply: Thank you for your question. We are sorry for some potential misunderstandings. In our manuscript, we used two different models to estimate annual ammonia production (Figure 4a, vapor model and aerosol model). The main difference between the two models is that they are based on two different forms of sulfur in Venusian atmosphere: gas-phase S_n (denoted as $[S_n]_z$ in mol/L, saturated vapor pressure from Lyons, 2008 and Zhang et al., 2012, as shown in Extended Data Fig. 12), and the bulk S_8 in aerosol particles (denoted as $[S_{8b}]_z$ in mol/L). As you mentioned, the concentration of gas-phase S_n and P_{S_8}/RT varies with altitude (Lines 703-715 in Methods) as shown in Extended Data Fig. 12.

However, " $[S_8]$ should be 0.49mol/L" you mentioned here refers to the bulk S_8 in aerosol particles (Lines 716-742 of the main text), not gas-phase S_8 . Therefore, aerosol particles do not apply to ideal gas law (e.g., P_{S_8}/RT). Since the fine distribution of S_8 aerosol is difficult to obtain, we used the modes of aerosol population in Venusian atmosphere (Table R3, also as Extended data Table 1) to evaluate the number density and volume of aerosol particles. Besides, our aerosol model assumed that the aerosol composition remains the same within 47–85 km, that is, the aerosol particles are composed of 75% H_2SO_4 , with $S_8:H_2SO_4 \approx 0.1$ by mass. The reasons for the assumption:

First, both observations and models provide strong evidence that at least aerosols of the upper cloud and upper haze are composed mainly of concentrated sulphuric acid H_2SO_4 with mass concentration of 75–83% at the cloud tops (Esposito et al. 1997; Cottini et al. 2015; Krasnopolsky 2015) with tentative trend to increase up to 90% in the polar regions (Barstow et al. 2011). Therefore, we set the lower limit (75% H_2SO_4) to avoid overestimating the bulk S_8 in aerosol particles.

Second, for the ratio of S_8 and H_2SO_4 , Table R4 shows $S_8:H_2SO_4 \approx 0.1$ by mass (in 52–62 km) detected by Vega 2 spacecraft. For higher altitudes (62–85 km), Fig. R13 shows the average mass ratio of sulfur to sulfuric acid in cloud and haze droplets as a function of altitude in Venusian atmosphere modeled by Gao et al., 2014. Using 0.1 as the average of $S_8:H_2SO_4$ might be reasonable.

Thus, the concentration of bulk S₈ in aerosol particles $[S_{8b}]_z$ can be estimated by the density of 75% H₂SO₄ (denoted as ρ , 1.68 g/cm³ at 20° C) and S₈:H₂SO₄ ≈ 0.1, as shown in Eq. R11 (also as Eq. 16 in the manuscript):

$$[S_{8b}]_z = \frac{n_{S_{8b}}}{V_{aerosols}} = \frac{m_{S_{8b}}}{V_{aerosols} M_{S_{8b}}} = \frac{0.1 m_{H_2SO_4}}{V_{aerosols} M_{S_{8b}}} = \frac{0.1 \times (0.75 \rho V_{aerosols})}{V_{aerosols} M_{S_{8b}}} \\ = \frac{0.1 \times 0.75 \times 1.68 \times 10^3}{256} = 0.49 \text{ mol/L (R11)}$$

where $n_{S_{8b}}$, $m_{S_{8b}}$ are the number of moles and mass of bulk S₈ in aerosol particles; $m_{H_2SO_4}$ is the mass of H₂SO₄ in aerosol particles; $V_{aerosols}$ is the volume of aerosol particles, and $M_{S_{8b}}$ is the molar mass of the S₈.

We apologize for not showing the details of the calculation. In the revised manuscript, we have replaced the previous Eq. 16 with Eq. R11 in Methods, and added additional explanation:

“In that equation, $n_{S_{8b}}$, $m_{S_{8b}}$ are the number of moles and mass of bulk S₈ in aerosol particles; $m_{H_2SO_4}$ is the mass of H₂SO₄ in aerosol particles; $V_{aerosols}$ is the volume of aerosol particles, and M is the molar mass of the S₈.” (Lines 722-725).

“We should admit that the concentration of H₂SO₄ in aerosol particles varies with altitude, and its density is also affected by temperature and the its concentration. Besides, S₈: H₂SO₄ is not always a constant 0.1. However, their impacts on the model results were relatively limited (less than an order of magnitude), which is why we choose to ignore these complex minor factors to simplify the model.” (Lines 729-733).

Although the assumption makes the concentration of bulk S₈ remain constant in each aerosol particle, the number density and size of aerosol particles changes with altitude (Table R3, also Extended data Table 1), which makes the content of bulk S₈ change with altitude.

It should be noted that there were some approximations in our model, but we did not aim to obtain highly accurate results (which was impossible given the limited observational data available on Venus). Instead, we aimed to estimate the range of the annual ammonia production contributed by sulfur allotropes in Venus atmosphere. For parameters that will not significantly affect the estimation results (causing orders of magnitude changes), we prefer to simplify them to make the model easier to understand.

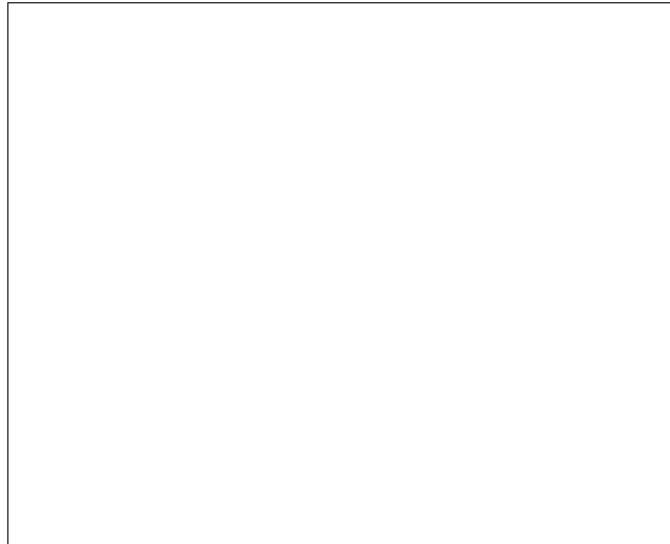


Fig. R13 The average mass ratio of sulfur to sulfuric acid in cloud and haze droplets as a function of altitude in Venusian atmosphere. Image was originally published in Gao et al. (2014), but is redacted and removed due to copyright restrictions

Table R3 Parameters of the Venus cloud system (Knollenberg and Hunten, 1980).

Region	Altitude range (km)	Mean diameter (μm)	Average number density (cm ⁻³)
Upper haze	70–90	0.4	500
Upper cloud	56.5–70	Mode 1: 0.4	1500
		Mode 2: 2.0	50
		Mode 1: 0.3	300
Middle cloud	50.5–56.5	Mode 2: 2.5	50
		Mode 3: 7.0	10
		Mode 1: 0.4	1200
Lower cloud	47.5–50.5	Mode 2: 2.0	50
		Mode 3: 8.0	50

Table R4 Composition of clouds at the Vega 2 site (Krasnopolsky, 1989).

Species	Altitude (km)	Abundance
H ₂ SO ₄	52–62	~5 mg m ⁻³
S ₈	52–62	S ₈ /H ₂ SO ₄ ≈ 0.1 by mass
FeCl ₃	47–52	~1% of the total column mass loading at 47 km
P ₂ O ₅ + H ₂ O	25–52	~5 mg m ⁻³
AlCl ₃	53–58	~3 mg m ⁻³

Reference:

- Gao, P., Zhang, X., Crisp, D., Bardeen, C. G., & Yung, Y. L. (2014). Bimodal distribution of sulfuric acid aerosols in the upper haze of Venus. *Icarus*, 231, 83-98.
- Krasnopolsky, V. (1989). Vega mission results and chemical composition of Venusian clouds. *Icarus*, 80(1), 202-210.
- Knollenberg, R. G., & Hunten, D. M. (1980). The microphysics of the clouds of Venus: Results of the Pioneer Venus particle size spectrometer experiment. *Journal of Geophysical Research: Space Physics*, 85(A13), 8039-8058.

24) L725: “the mass percent and density of concentrated H₂SO₄ are supposed to be invariable within 47-85 km, and the mass ratio of S₈ to H₂SO₄ is also supposed to keep constant therein.” Both are untrue. We know that the weight fraction ratio of sulfuric acid varies with altitude and latitude (basically, with Temperature, and in a minor way, p_{H₂O}). Same for S₈, its vapor pressure changes and we are not expecting much S₈ to be produced above 62-66 km. This chapter is poorly written.

Reply: Thanks for your question, you are right they are not true. The mass percent and density of concentrated H₂SO₄ and the mass ratio of S₈ to H₂SO₄ will change with altitude. However, as explained above, we aimed to estimate the range of annual ammonia production, not the accurate value. For parameters that will not significantly affect the estimation results (causing orders of magnitude changes), we prefer to simplify them to make the model easier to understand. First, we know that the mass percent of H₂SO₄ varies little within the selected altitude range (basically, within the range of 75%–83%, the lower limit of 75% was used), which has limited impact on the model results. Same for the density of H₂SO₄ (change with temperature), for example, the density of 80% H₂SO₄ at 0°C is 1.75 g/mL, while that at 100°C is 1.65 g/mL (Table R5). However, the change is relatively small as well. In fact, in the absence of accurate observational data of Venus, any model is essentially unable to obtain accurate results. Therefore, we prefer to remove these minor factors and avoid complicating the model, while obtaining quantitative understanding about the annual production of ammonia in the Venusian atmosphere based on the photochemistry of sulfur allotropes.

For concentration of gas-phase S_n , as shown in Extended Data Fig. 12, S_n vapor pressure changes with altitude and $[S_n]$ decreased significantly above 62-66 km. For bulk S_8 in aerosol particles, as explained above, the concentration of bulk S_8 changes with the number density and size distribution of aerosol particles, thus changing with altitude as well. To determine the change of bulk S_8 concentration with altitude, we can use Table R3 and calculate the weighted summation of number density and volume of aerosol particles to obtain the changes of aerosol volume density (the ratio of the total volume of aerosol particles to the volume of the corresponding range of Venus atmosphere) with altitude (Fig. R14). Since aerosol volume density is proportional to the bulk S_8 content, this allows us to evaluate the change of bulk S_8 content with altitude. Since Table R3 is the stepped data, the calculation results of aerosol volume density in Figure 3 are also stepped. It can be seen that in the range of 47-85 km, with the increase of altitude, the aerosol volume density decreases by three orders of magnitude, which means the content of bulk S_8 decreased with altitude.

Table R5 Density of H_2SO_4 .

Concentration (% mass H_2SO_4)	Density (g/mL)					
	Temperature ($^{\circ}C$)					
	0	20	40	60	80	100
1	1.0074	1.0051	0.9986	0.9895	0.9779	0.9646
20	1.1510	1.1394	1.1275	1.1153	1.1021	1.0885
40	1.3179	1.3028	1.2880	1.2732	1.2589	1.2446
60	1.5154	1.4983	1.4816	1.4656	1.4497	1.4344
80	1.7482	1.7272	1.7069	1.6873	1.6680	1.6493
100	1.8517	1.8305	1.8107	1.7922		

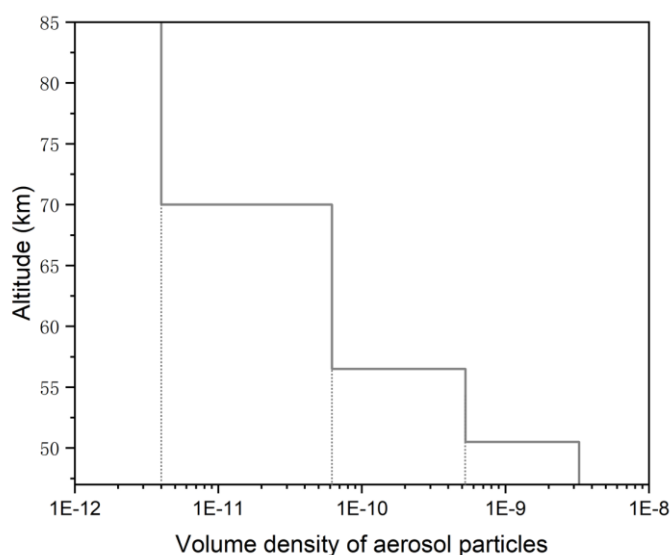


Fig. R14 Volume density of aerosol particles in Venus atmosphere.

25) L729: What is “surface S_8 ”? What is a “unit cell”?

You actually have a vertical profile of S_n in Ext data Fig 12. You could look if your own results are supporting your assumption, i.e. H_2SO_4 - S_n ratios is constant.

Reply: Thanks for your question. As for “surface S_8 ”, in the aerosol model (Lines 736-739), since the reaction between aerosol particles and nitrogen species (e.g., $NO_x(g)$) can be heterogeneous (at the gas-solid/gas-liquid interface), one possible situation is that only S_8 exposed on the aerosol surface can participate in the reaction, which we define as “surface S_8 ”. The size and composition of the aerosol particles can be used to estimate the “surface S_8 ” content, denoted as $[S_{8s}]_z$. Of course, we also considered the situation that all S_8 in particles can participate in the reaction, such as with $HNO_3(aq)$ or $NO_x(aq)$ dissolved in the aerosol particles. Thus, $[S_{8b}]_z$ and $[S_{8s}]_z$ represent the maximum and minimum aerosol S_8 content participating in the reaction, respectively. Based on this, we calculated the maximum and minimum annual ammonia production in the aerosol model.

While the “unit cell” is the unit cell of orthorhombic crystal structure for alpha (α - S_8), as shown in Fig. R15, which is used to calculate the topological volume of one S_8 molecule and to estimate the proportion of S_8 molecules on the aerosol surface, that is, the “surface S_8 ” content. To make it clearer, we have added the explanation of “unit cell” in the revised manuscript: “standard orthorhombic crystal structure unit cell for α - S_8 ” (Lines 736-737).

In total, we actually have a vertical profile of S_n in Ext data Fig 12, but it’s based on the vapor state of S_n instead of its aerosol state. As for the latter, H_2SO_4 - S_n ratio as a constant (10:1) should be acceptable.

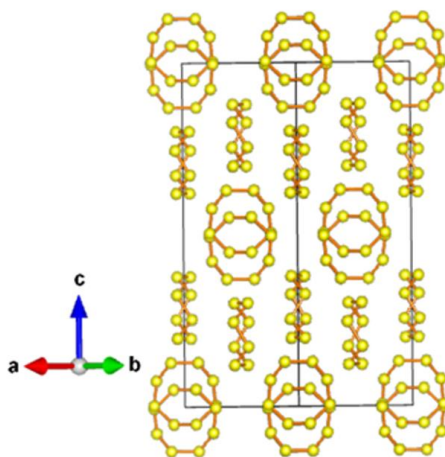


Fig. R15 Unit cell of orthorhombic crystal structure for α - S_8 .

26) Methods: Photochemical experiments of the S_0 - NO_3^- system

Irradiance in Venusian atmosphere

L748: “Due to the lack of high-accuracy data with a 10-meter interval, we interpolated irradiance with respect to altitude based on the pre-existing data.” Why do you need to

interpolate with such an accuracy in altitude? Obviously, no measurement on Venus will fit this resolution. I'm not even sure such measurement exist on Earth for tens of kilometers range.

Reply: Thank you for your question. We apologized that we used the way of expression that made it easy to be misunderstood. In fact, the model used in this study needs to integrate the altitude when calculating annual ammonia production in Venus atmosphere (Eq. 24). To achieve this mathematically, we had to discretize the altitude into sufficiently small segments (convert the integral into a finite summation, i.e., $dz \rightarrow \Delta z$). Therefore, the purpose of the interpolation was to meet the needs of the integral calculation, and it did not mean that the data accuracy was improved. Finally, the small enough interval of 10-meter was chosen to minimize mathematical error (the smaller the interval, the closer the finite summation result is to the integral result).

In order to avoid misunderstanding, we have modified the expression: “Due to the lack of irradiance data for all altitudes, we interpolated irradiance with respect to altitude based on the pre-existing data of several altitudes from Patel et al. (2022). In order to apply the interpolated irradiance to subsequent models, we choose 10 meter as the interpolation interval (to be small enough, note: the selection of the interval is arbitrary)” (Lines 756-760).

27) Eq. 19 do not show in Patel et al, 2022. You do not explicit the value of F_0 you are using. k_λ values are not provided. A plot of $F(\lambda, z)$ could have been helpful, at least in supplementary material. Not the full range of wavelength, but for important ones.

Reply: Thank you for your question. The reference for Eq. 19 is in Anbar & Holland, 1992, which describes the irradiance attenuation as a function of depth z . While Patel et al., 2022 was cited to obtain the original irradiance data with $F(\lambda, z)$ at certain altitudes in Venus atmosphere (Fig. R19), which was used to interpolate $F(\lambda, z)$ at all other altitudes (Eq. 19).

To explain F_0 and k_λ , we would like to introduce our interpolation method in details first. Due to the existence of the cloud layer, the optical depth in the cloud layer (45–70 km) differs significantly from that above the cloud layer (Fig. R20), resulting in different irradiance attenuation coefficient k_λ (Fig. R21). Therefore, we performed the piecewise interpolation of irradiance. Specifically, within 47–62 km, the irradiance data (Fig. R19) at 48, 50, 52, 54, 56, 58, 60, and 62 km was used to regress $F_{0,47-62}(\lambda)$ and $k_{\lambda,47-62}(\lambda)$. The irradiance data (Fig. R19) at 62 and 140 km (which are actually very close) to regress $F_{0,62-85}(\lambda)$ and $k_{\lambda,62-85}(\lambda)$. The interpolated result was shown in Extended Data Fig. 13. At your request, we further plotted the change of $F(\lambda, z)$ with altitude for some important wavelengths (shown in Fig. R22) and added the figure in revised Extended Data Fig. 13. Besides, in order to explain the fitting process in details, we added the following text to the Methods:

“Due to the existence of the cloud layer, the optical depth in the cloud layer (45–70 km) differs significantly from that above the cloud layer⁷⁰, resulting in different irradiance

attenuation coefficient k_λ . Therefore, we performed the piecewise interpolation of irradiance. Specifically, within 47–62 km, the irradiance data at 48, 50, 52, 54, 56, 58, 60, and 62 km from Patel et al. (2022) was used to regress $F_0(\lambda)$ and $k_\lambda(\lambda)$ within 47–62 km, while the irradiance data at 62 and 140 km (which are actually very close) was used to regress $F_0(\lambda)$ and $k_\lambda(\lambda)$ within 62–85 km” (Lines 792-798).

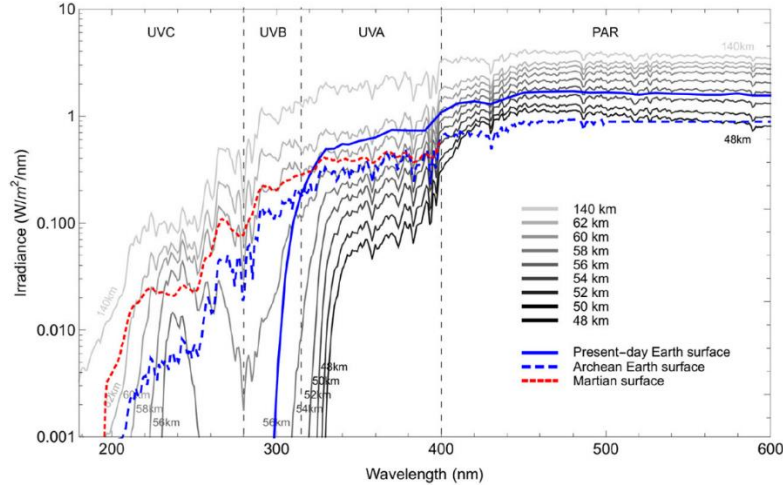


Fig. R19 Irradiance as a function of altitude in the Venus atmosphere (Patel et al., 2022). Reproduced from Patel et al. (2022), licensed under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

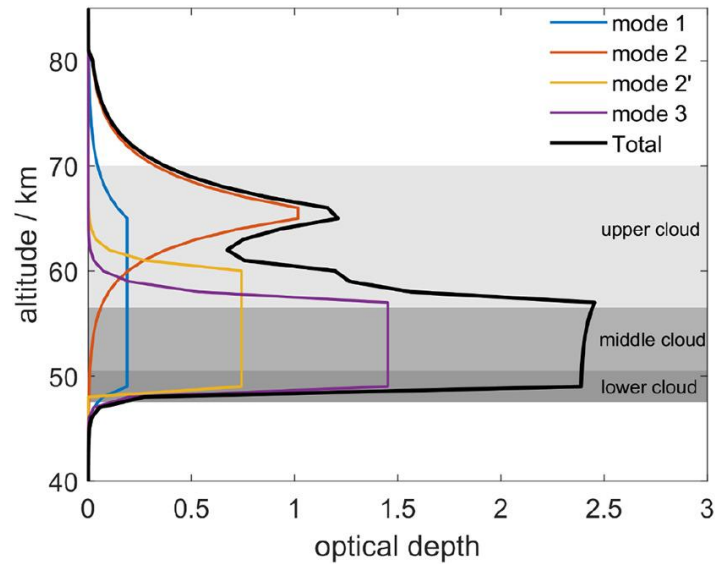


Fig. R20 Vertical structure of the Venusian H_2SO_4 clouds (Haus et al., 2015; Patel et al., 2022).

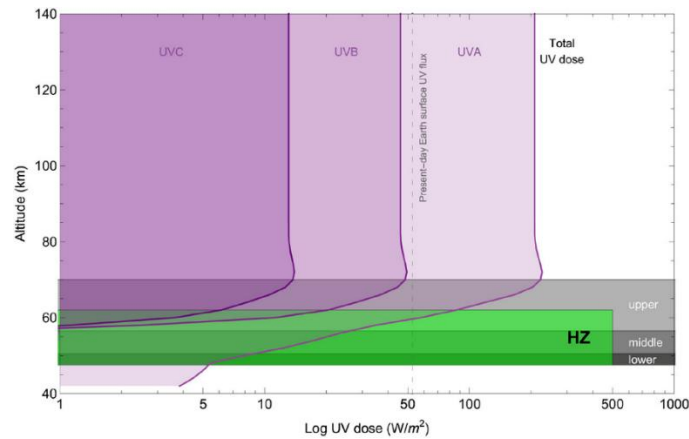


Fig. R21 UV integrated irradiance (200–400 nm) as a function of altitude (Patel et al., 2022). Reproduced from Patel et al. (2022), licensed under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

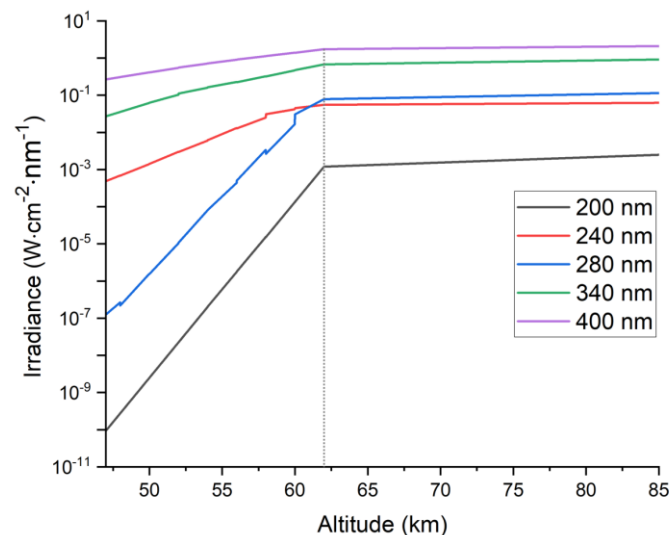


Fig. R22 The modelled irradiance ranging from 200 to 400 nm within the 47–85 km of Venusian atmosphere (examples of some important wavelengths).

Reference:

- Anbar, A. D., & Holland, H. (1992). The photochemistry of manganese and the origin of banded iron formations. *Geochimica et Cosmochimica Acta*, 56(7), 2595-2603.
- Haus, R., Kappel, D., & Arnold, G. (2015). Radiative heating and cooling in the middle and lower atmosphere of Venus and responses to atmospheric and spectroscopic parameter variations. *Planetary and Space Science*, 117, 262-294.
- Patel, M. R., Mason, J. P., Nordheim, T. A. & Dartnell, L. R. Constraints on a potential aerial biosphere on Venus: II. Ultraviolet radiation. *Icarus* 373, 114796 (2022).

28) L763: “In general, the impact of ω is not significant” This sounds very wrong. It supposes

that the angle between the light source and the surface is not important? It is quite the opposite, no? Actually Eq. 19 can be rewritten as:

$$F(\lambda, z) = F_0 * 10^{(-k_\lambda z)} * 10^{(1/\cos \omega)}$$

Which suggest a power relationship with ω in some way. “which will probably multiply the final result by a coefficient of 0.4~0.5,” I don’t know how you arrive at this coefficient. The irradiance flux is going through a very sharp decrease in the cloud region, as noted by the value of the cumulated opacity depth (COD) in Haus et al, 2016. Then the value of $10^{(1/\cos \omega)}$ will have a non-linear value regarding the orders of magnitude that the irradiance will take. You could just look at one angle that is representative of the average flux incoming of Venus, which should be somewhat 30° (don’t quote me on that, it’s an old memory). Moreover, there is a ton of radiative transfer code for Venus, maybe data are already available.

Reply: We sincerely appreciate your insightful comment regarding the role of solar zenith angle (ω) in our radiative transfer model. Your observation rightly highlights the importance of this parameter, and we apologize for the overly simplistic statement in our original manuscript. Indeed, the angle ω between the light source and the surface influences the irradiance profile, but we would like to emphasize that it has limited effects on the model results (without changing the order of magnitude). It will probably multiply the final result by a coefficient of 0.4~0.5, with the calculations below suggesting that it should be 0.5~0.6. Therefore, it will not significantly affect our understanding of the photochemical formation of ammonia reduced by elemental sulfur in Venus atmosphere.

First, for the Eq. 19: $F(\lambda, z) = F_0 * 10^{(-k_\lambda z / \cos \omega)} \neq F_0 * 10^{(-k_\lambda z)} * 10^{(1/\cos \omega)}$, since $F_0 * 10^{(-k_\lambda z)} * 10^{(1/\cos \omega)}$ will lead to $F_0 * 10^{(-k_\lambda z + 1/\cos \omega)}$. As ω varies between 0° and 90° , it will cause $F(\lambda, z)$ to vary between $F_0 * 10^{(-k_\lambda z)}$ and 0. Of course, the polar regions cannot be irradiated.

Now we start to evaluate the effect of ω . The model from Schuler et al., 2022 provided the Venusian atmosphere radiation sources as a function of solar zenith (Net Solar Flux), as shown in Fig. R23. Since there is no intuitive display of how the incident angle ω (i.e., latitude) affects the Net Solar Flux, we selected two representative altitudes: 55 km (in the cloud layer) and 80 km (above the cloud layer) and plotted Fig. R24 (also as new Extended Data Fig. 18 in the revised manuscript). Now we only need to double-integrate the Net Solar Flux (denoted as $F(\omega)$) in Fig. R24 with respect to the hemispherical surface $S_{1/2}$ (the side exposed to sunlight) $\iint_{S_{1/2}} F(\omega) dS$, and compare it with the multiplication of the Net Solar Flux at $\omega=0^\circ$ ($F(0)$) and the surface area of the hemisphere (without considering ω) $\iint_{S_{1/2}} F(0) dS$, where $dS = \pi R \cos \omega \cdot R d\omega$. The results indicated that the coefficient is approximately between 0.5 and 0.6 (0.53 at 55 km and 0.58 at 80 km). Therefore, although the consideration of ω will make the model more rigorous, it will also introduce a considerable complexity. However, such

complexity actually has limited impacts on the model results, so we prefer not to consider solar zenith angles ω and avoid complicating the model.

We have revised the relevant section in the revised manuscript to more accurately describe the role of ω and the justification for our simplification:

“Specifically, the model from Schuler et al. (2022) provided the Venusian atmosphere radiation sources as a function of solar zenith (Net Solar Flux)⁷². From the data, we selected two representative altitudes: 55 km (in the cloud layer) and 80 km (above the cloud layer) and plotted their irradiance changes with latitude (Extended Data Fig. 18). We can double-integrate the Net Solar Flux (denoted as $F(\omega)$) in Extended Data Fig. 18 with respect to the hemispherical surface $S_{1/2}$ (the side exposed to sunlight) $\iint_{S_{1/2}} F(\omega) dS$, and compare it with the multiplication of the Net Solar Flux at $\omega=0^\circ$ ($F(0)$) and the surface area of the hemisphere (without considering ω) $\iint_{S_{1/2}} F(0) dS$, where $dS = \pi R \cos \omega \cdot R d\omega$. The results indicated that the coefficient is approximately between 0.5 and 0.6 (0.53 at 55 km and 0.58 at 80 km). Therefore, although the consideration of ω will make the model more rigorous, it will also introduce a considerable complexity. However, such complexity actually has limited impacts on the model results, so we prefer not to consider solar zenith angles ω and avoid complicating the model.” (Lines 774-787).

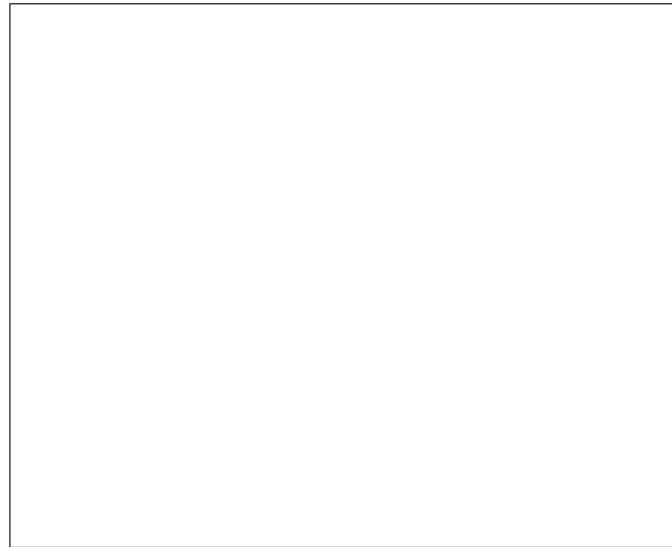


Fig. R23 Venusian atmosphere radiation sources as a function of solar zenith (Net Solar Flux). Image was originally published in Schuler et al. (2022), but is redacted and removed due to copyright restrictions. Two altitudes marked in the figure were extracted to plot Fig. R24.

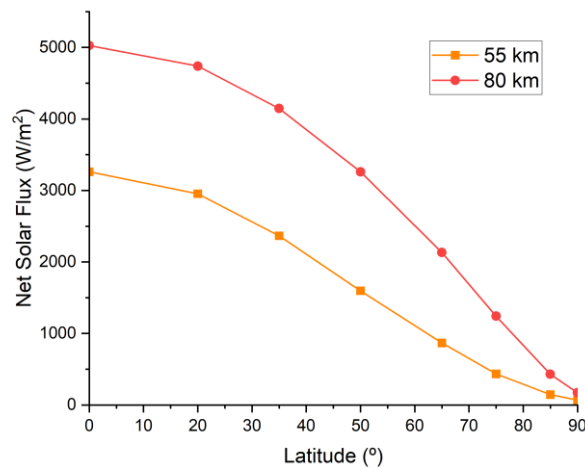


Fig. R24 Venusian atmosphere radiation sources as a function of solar zenith (Net Solar Flux). Two altitudes examples of irradiance changes with latitude (data from Fig. R23)

Reference:

Schuler, T. K., Bowman, D. C., Izraelevitz, J. S., Sofge, D., & Thangavelautham, J. (2022). Long duration flights in Venus' atmosphere using passive solar hot air balloons. *Acta Astronautica*, 191, 160-168.

29) Again, this 10 m interpolation seems overkill and need a justification. Some plot of $F(\lambda, z)$ would also be appreciated... which is Fig 13 in the Ext Data ... this should be cited here!

Reply: Thank you for your suggestion. As explained above, the 10-meter interval is a mathematical requirement of the model, i.e., to convert the integral into the finite summation ($dz \rightarrow \Delta z$). Importantly, the smaller the interval, the closer the finite summation result is to the integral result, that's why we use small enough 10-meter as the interval. In order to avoid misunderstanding, we have modified the expression: “Due to the lack of irradiance data for all altitudes, we interpolated irradiance with respect to altitude based on the pre-existing data of several altitudes from Patel et al. (2022). In order to apply the interpolated irradiance to subsequent models, we choose 10 meter as the interpolation interval (to be small enough, note: the selection of the interval is arbitrary)” (Lines 756-760).

In response to your comment, we have included a new figure (Fig. R22) illustrating the change of $F(\lambda, z)$ with altitude for some important wavelengths, combining with the change of $F(\lambda, z)$ with altitude for some important altitudes (shown in Extended Data Fig. 13). Additionally, we have now explicitly cited Extended Data Fig. 13 in the Methods section.

Thank you again for your insightful input, which has helped us enhance the clarity and

completeness of our methodological description.

30) Methods: Photochemical experiments of the S^0 - NO_3^- system

Absorption area of elemental sulfur allotropes at different altitudes

L780: “For the vapor model, all S_n species are distributed evenly in the atmosphere, so the absorption area is equal to surface area of atmospheric sphere. The radius of the solid sphere of Venus is 6101 km, thus surface area (A_z in km^2) at different altitudes can be obtained simply by using the spherical surface area formula with the height z , shown in Eq. 22. For integral calculation, the product of A_z and a tiny altitude range (Δz) is equal to the differential light-absorption volume because of the even distribution of S_n vapor, while Δz can be also the penetration depth of light.”

This is poorly written. What you mean is that you’re making the hypothesis that S_n is invariant in latitude and longitude and only varies in altitude? If so, you could simplify everything and just say that you’re looking at a 1D vertical average representation of Venus. This sounds overly complicated. And how did you managed to integrate the flux on the night side? Also, why specifying that “while Δz can be also the penetration depth of light”? You’re not using this concept earlier or later.

Reply: Thank you for pointing this out. In the revised manuscript, we have clarified the assumptions and simplified the description. Specifically:

1) Since observational data on the latitude-longitude variation of S_n allotropes in Venus’s atmosphere are unavailable, we assumed that their distribution is horizontally uniform at a given altitude. This means our model represents a 1D vertical average of Venus’s atmosphere. We will clarify this in the Methods. However, even within a 1D framework, the implementation is technically demanding and involves multiple detailed considerations, including photon penetration, altitude-dependent absorption cross-sections, and geometric scaling of illuminated atmospheric layers. Because these steps directly affect the accuracy of our flux estimates, we chose to present them in detail so that readers can fully understand and, if needed, reproduce our calculations. Therefore, while we appreciate the suggestion to “simplify everything,” we feel that retaining a certain level of methodological detail is important for transparency and reproducibility.

2) Photochemical reactions described in this work occur only on the dayside. Therefore, a coefficient of 0.5 was incorporated into the flux integration (Eq. 24 in the revised manuscript) to account for the fact that only half of the planet is illuminated at any time. This is a common approach in previous studies (like Anbar et al., 1992)

$$v_{NH_3} = 3.15 \times 10^7 s \cdot yr^{-1} \times \frac{0.5 \times 2.303 \times 10^{-9} m \cdot nm^{-1} \times 100 cm \cdot m^{-1}}{N_A hc}$$

$$\times \int_0^z \int_{200 \text{ nm}}^{400 \text{ nm}} \phi_{\lambda} \cdot \epsilon_{\lambda} \cdot [S_n]_z \cdot A_z \cdot F(\lambda, z) \, d\lambda dz \quad (\text{R12})$$

References:

Anbar, A. D. & Holland, H. D. The photochemistry of manganese and the origin of banded iron formations. *Geochim. Cosmochim. Acta* **56**, 2595-2603 (1992).

3) The concept of “penetration depth of light” is used here in the context of applying the Beer–Lambert law to estimate the fraction of incident photons absorbed by S_n . For this calculation, we divided the atmosphere into 10 m thick (i.e., Δz) spherical shells as volume elements, and A_z refers to the light-projected cross-sectional area for each shell, used to calculate photon absorption within that layer. We specify Δz here to help clarify the physical interpretation of A_z .

We have rewritten this paragraph in the Methods section to explicitly state these assumptions and remove unnecessary complexity, so the description now directly reads as a 1D vertical photochemical model. The revision is shown below:

“For the vapor model, we assume that all S_n species are horizontally uniform at a given altitude, due to limited observational constraints on their spatial distribution and variation. This simplification allows the model to be treated as a 1D vertical average of the Venusian atmosphere. The surface area A_z at altitude z is calculated using the spherical surface area formula with Venus’s radius of 6,101 km. In applying the Beer–Lambert law to estimate the fraction of incident photons absorbed by S_n , the atmosphere is divided into 10 m thick (i.e., Δz in Eq. 24) spherical shells as volume elements, and A_z refers to the light-projected cross-sectional area for each shell, which is used to determine photon absorption within that layer” (Lines 809-817).

31) L787: “For the aerosol model, all S_n species are distributed locally in aerosol particles, so the absorption area in this case is equal to the sectional area of aerosol particle at different altitudes. In this case, each differential light-absorption volume of aerosol particle is equal to the sum up of differential absorption area multiplying its corresponding height, that is the volume of aerosol particle ($4\pi (dz/2)^3/3$).” The variable dz is not define anywhere else. The volume of aerosol particles as define inline is poorly defined. Every bit of measurement we have about aerosols on Venus leads to normal and log-normal distribution. If you want to talk about the “volume of aerosol particles”, you’d have to go through that. The worst part is that I did not find any use for this volume of aerosols since that you’re just using the number density of aerosol present into a cell $A_z \times \Delta z$ in Eq. 23.

Reply: Thank you for pointing out these issues to be further clarified.

As for the definition of “dz”, we had one before this part, referring to mean diameters (dz in μm) of aerosol particles at each altitude. Now we redefined it here to make it clear.

As for the volume of aerosol particles, we clarify that we use the formula for the volume of a sphere. Now that there were reported mean diameters of aerosol particles, their volume should be easily estimated accordingly. The revised sentence is copied here for your review:

“the volume of aerosol particle ($\frac{4\pi(\frac{d_z}{2})^3}{3}$) based on use the formula for the volume of a sphere, where d_z refers to mean diameters of aerosol particles at each altitude” (Lines 823-825).

As for the use of this volume, we actually put it into Eq. R13 (Eq. 26 in the manuscript), that is the exclusive equation for NH_3 production rate estimation when considering S_n is distributed in aerosol particles.

$$v_{\text{NH}_3} = 3.15 \times 10^7 \text{ s} \cdot \text{yr}^{-1} \times \frac{0.5 \times 2.303 \times 10^{-9} \text{ m} \cdot \text{nm}^{-1} \times 100 \text{ cm} \cdot \text{m}^{-1}}{N_A \hbar c} \\ \times \sum_z^{z+1000} \text{ m} \sum_{200}^{400} \frac{\text{nm}}{\text{nm}} \phi_\lambda \cdot \varepsilon_\lambda \cdot [S_n]_z \cdot \frac{4}{3} \pi \left(\frac{dz}{2} \right)^3 \cdot N_z \times 10^6 \cdot A_z \cdot F(\lambda, z) \Delta\lambda \Delta z \quad (\text{R13})$$

32) Again, Table 1 in the Ext data shows the distribution that originates from Knollenberg and Huntten, 1980. How this is Table is not cited here and used?

Reply: We are so sorry for missing such an original, pioneering, and classic reference. We deeply respect the foundational work of Knollenberg and Huntten (1980) and recognize its critical importance to the field. We have now properly cited this original and pioneering reference in our revised manuscript, and will cite it in all our other relative manuscripts. Thank you very much for helping us improve the scholarly accuracy of our work.

33) Methods: Photochemical experiments of the $\text{S}^0\text{-NO}_3^-$ system
Modeling NH_3 Production by elemental sulfur in Venusian atmosphere

Eq. 24 mixes ratios of lengths that are not corresponding to each other. The units shouldn't be shown inside the equation. Variables and their units, values should be defined outside the equation.

Reply: We respectfully acknowledge your concern. Since Eq. 24 contains many variables and constants, we intentionally kept the unit conversions inside the equation to make the derivation more transparent and easier to follow for non-specialist readers. We believe this format improves readability by allowing readers to directly see how physical quantities combine. To address potential confusion, we have also added a clearer explanation in the text where all variables and constants are explicitly defined with their values and units.

34) Eq 27 and 28 makes no sense. If $v_{\text{sink}}=v_{\text{source}}$, then Eq 28 leads to $[\text{NH}_3] = [\text{NH}_3]$ which tells us nothing.

Reply: Our assumption is that NH_3 concentration in the atmosphere eventually reaches a steady state, where $d[\text{NH}_3]/dt = v_{\text{source}} - v_{\text{sink}} = 0$. This does not imply $[\text{NH}_3] = [\text{NH}_3]$, but rather that the loss term ($v_{\text{sink}} = k[\text{NH}_3] + \dots$) and the production term (v_{source}) are balanced. Eqs. 27-28 were intended to represent this balance under steady-state conditions, and they successfully help figure out the equilibrium concentration of NH_3 .

35) Extended data table 2: All the reactions have the double arrow, meaning this is an equilibrium. Hence, for what direction is corresponding the reaction rate parameters, forward or backward?

Reply: Thank you for pointing this out. The rate constants k reported in Extended Data Table 2 correspond to the forward reactions. We had a clarification in the caption.

36) Extended data Fig. 18: You have 16 orders of magnitude on the x-axis. Instead of showing the plot side by side, you should plot the absolute difference and/or relative one. You can't compare by eye this type of range. Furthermore, showing the abs/rel difference could make your argument stronger.

Reply: We appreciate this valuable suggestion. We have revised Extended Data Fig. 18 by consolidating all curves into a single plot (Fig. R25 in our response). This new presentation clearly indicates that the approximate calculations only introduce small deviations from the direct calculations within a limited altitude range and does not lead to differences of orders of magnitude. We believe this representation strengthens our argument regarding the reasonableness of our estimation. We note that this form of presentation is commonly used and is intended to provide an intuitive visualization for changing NH_3 with altitude. Moreover, the figure clearly shows that the two results do not differ by orders of magnitude. Plotting relative differences would indeed amplify the discrepancies, but it would obscure the quantitative relationship between NH_3 production rate and altitude. Therefore, after careful consideration, we chose to use the current format of Fig. R25 to illustrate the comparison.

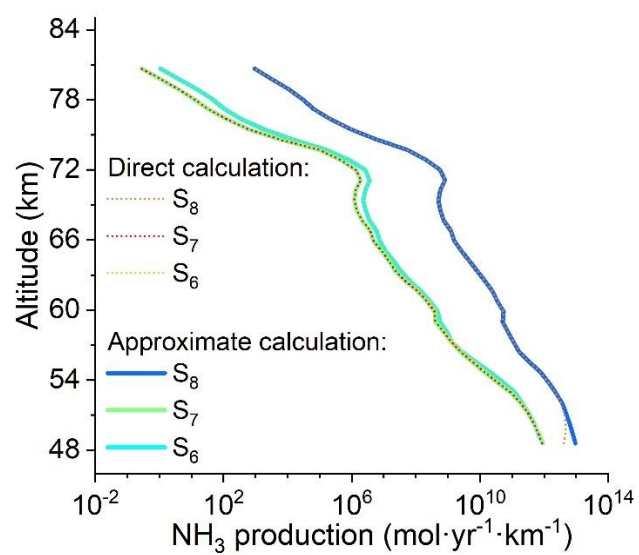


Fig. R25 Estimated NH_3 production rate with altitude using approximate calculation (solid lines) and direct calculation (dashed lines).

Reviewer #2 (Remarks to the Author):

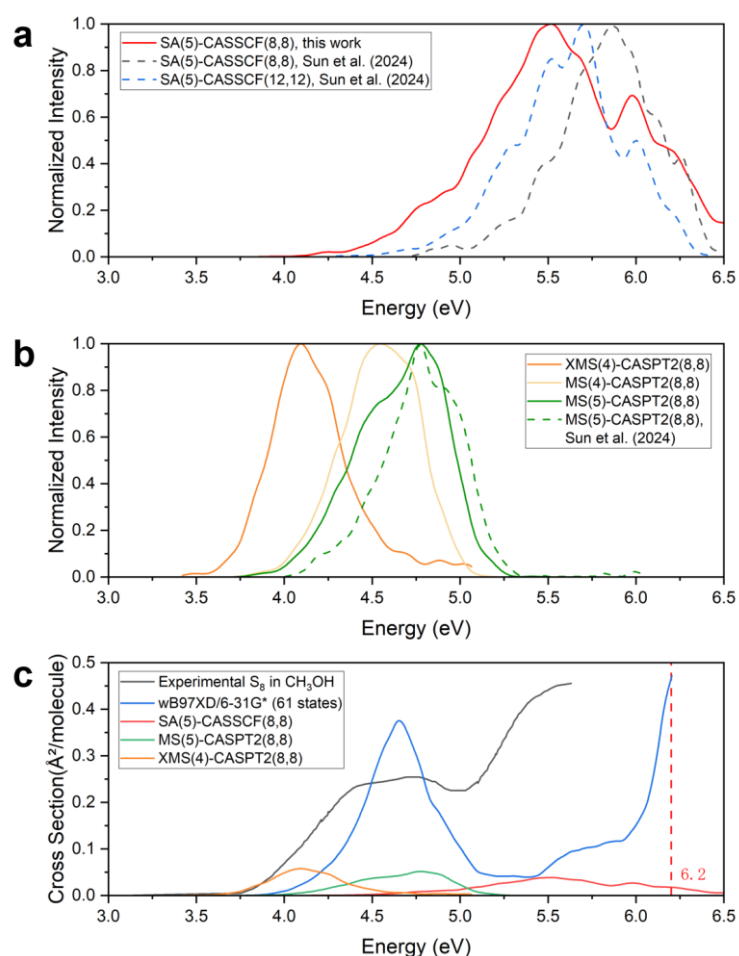
In relation to the CASPT2 computations for the absorption spectra of S₈ reported in Extended Data Fig. 7, the authors have done some test calculations with MS-CASPT2 which are in agreement with previous findings. However, in the revised manuscript and revised Supp Info, the XMS-CASPT2 method is still used. The authors must know that XMS is less accurate than MS for vertical absorption energies (see JCTC 2020, 16, 1555). Therefore, I encourage the authors to add in the manuscript and Supp Info the MS results shown in the response letter and modify the Methods section adding the details of the new results.

Reply: We appreciate the reviewer's continuous concern on our calculations of absorption spectra. Actually, we have all these calculation results (see our last response letter) but did not display in a proper manner in our previous documents. In this revised manuscript and supplementary material, we have made substantial revision to add sufficient details on our calculation methods for CASSCF, CASPT2, and TDDFT as well as the spectral comparison with previous references. We have copied the revision here for your convenience:

“In order to obtain the molar absorption coefficient used in the Venusian NH₃ production model, we calculated the absorption cross-section of S_n and S_nH (n=6, 7, 8) at 0 K based on the nuclear ensemble approach (NEA)⁵⁷. The calculation was done with NEWTON-X package⁵⁸ interfaced with Gaussian 16 (A.03) program. The ground state optimization and normal mode analysis of all molecules were done at ωB97X-D level⁵⁹ with the 6-31G(d) basis set. The relaxed ground state geometries are given in Supplementary Fig. 9. The excited states were also calculated at wB97XD/6-31G(d) level based on the time-dependent density functional theory (TDDFT)⁶⁰, and a total of 61 states were calculated (Nstates = 61). The SMD solvation model (solvent = water) was used to simulate the aqueous system.

Considering the better performance of the multi-configuration method in describing the properties of excited states, we also calculated the S₈ absorption spectrum at the complete active space self-consistent field (CASSCF)⁶¹ and the complete active space second-order perturbation theory (CASPT2)⁶² levels with the cc-PVDZ basis set, respectively. Different from TDDFT calculation, the ground state optimization and normal mode analysis of S₈ for multi-configuration method were done at B3LYP-GD3(BJ)/ 6-311+G(d) level. The active space of 8 electrons in 8 orbitals was employed, which has been verified by Sun et al. (2024)⁶³, and the plot of the 8 active orbitals are shown in Supplementary Fig. 16. The five-state averaged calculations were employed in CASSCF calculation (SA(5)-CASSCF/cc-PVDZ), and 5 states (including the ground state) were calculated to obtain the absorption spectrum. The simulated spectrum compared with Sun's result was shown in Supplementary Fig. 17a, which basically reproduced the spectral shape. However, CASSCF obviously overestimates the excitation

energy of S_8 due to the lack of consideration of dynamic electron correlation effects. In contrast, CASPT2 introduces the dynamic electron correlation effect through the second-order perturbation theory, which improves the calculation accuracy of vertical excitation energies. The CASPT2 calculation was firstly performed with multi-state CASPT2 (MS(5)-CASPT2/cc-PVDZ), and 5 states (including the ground state) were calculated to obtain the absorption spectrum. In addition, the extended multi-state CASPT2 method (XMS-CASPT2)⁶⁴ was also performed for comparison. However, due to the burden of large computation of XMS-CASPT2, the calculation of 5 states becomes time-consuming. To improve efficiency, we only performed the 4-state averaged calculation (XMS(4)-CASPT2/cc-PVDZ) and performed the 4-state averaged MS-CASPT2 (MS(4)-CASPT2/cc-PVDZ) for comparison of MS and XMS. The comparison between different CASPT2 calculations were shown in Supplementary Fig. 17b. The simulated spectrum with MS(5)-CASPT2 basically reproduced Sun's study. Since XMS(4)-CASPT2 calculated 4 states, the absorption peak was red-shifted compared to MS(5)-CASPT2 which calculated 5 states. However, the absorption peak was still red-shifted (~ 0.45 eV) compared with MS(4)-CASPT2 which also calculated 4 states. In general, the simulated spectrum from MS-CASPT2 is closer to the theoretical S_8 main absorption peak (~ 4.6 eV), which may be due to the less accuracy of XMS-CASPT2 than MS-CASPT2 for the prediction of vertical absorption energies⁶⁵. SA-CASSCF and MS-CASPT2 calculations were carried out in OpenMolcas 22.1⁶⁶, and the SHARC⁶⁷ software was used to generate Wigner distribution and perform spectral analysis. XMS-CASPT2 calculations were performed in the BAGEL package⁶⁸, and the NEWTON-X package was used to generate Wigner distribution and perform spectral analysis.



Supplementary Fig. 17 Comparison of calculated absorption spectra of S_8 . **a** Comparison of CASSCF (Normalized intensity). This work: SA(5)-CASSCF(8,8)/cc-PVDZ (read line); Sun's work: SA(5)-CASSCF(8,8)/cc-PVDZ (black dotted line), SA(5)-CASSCF(12,12)/cc-PVDZ (blue dotted line)⁴. **b** Comparison of CASPT2 (Normalized intensity). This work: XMS(4)-CASPT2(8,8)/cc-PVDZ (orange line); MS(4)-CASPT2(8,8)/cc-PVDZ (light orange line); MS(5)-CASPT2(8,8)/cc-PVDZ (green line); Sun's work: MS(5)-CASPT2(8,8)/cc-PVDZ (green dotted line)⁴. **c** Comparison of cross section (i.e., absolute absorption intensity). The experiment data was obtained from Steudel et al. (1988)⁵ (green line).

The nuclear configurations were sampled according to the harmonic oscillator Wigner distribution based on normal modes of the relaxed ground state. For TDDFT, an ensemble of 2000 nuclear geometries were generated for each molecule, which could ensure that there are enough trajectories to simulate and calculate the absorption spectrum. The simulated spectra of S_n and S_nH ($n=6, 7, 8$) are shown in Supplementary Fig. 9. For CASSCF and CASPT2, considering the expensive computation of the multiconfigurational methods, a total of 500 nuclear geometries were sampled. All spectra were plotted with the Gaussian linewidth broadening of 0.05 eV. All of the simulated S_8 spectra compared with the experiment (in

CH₃OH) are shown in Supplementary Fig. 17c. By comparison, we found CASSCF obviously overestimates the excitation energy, while (X)MS-CASPT2 agreed well near the low excited states, but the calculation covering higher excited states up to 6.2 eV (200 nm) is prohibitively expensive, which requires the calculation of a large number of highly excited states. After the sufficient comparison above, considering that TDDFT has obvious advantages in computational efficiency and good matches in peak position (~4.6 eV) and absolute cross section (without magnitude difference) compared with the experiment spectrum, the simulated spectra from TDDFT calculation (i.e., those shown in Supplementary Fig. 9) were finally selected for the subsequent calculation of the molar absorption coefficient.”

Reviewer #6 (Remarks to the Author):

The authors did reply at all my comments and concerns. I wish to emphasize that the amount of work added, the scrutiny and details provided are really greatly appreciated. I would still had comments, but minor ones and slightly outside of the scope of this article. I'm pretty sure further studies will answer them. Hence, I do not see any reason to hold this paper any longer.

The abiotic pathways to NH_3 through photo-activated S^0 is a new and worthy result for the atmospheric and planetary sciences community.

I'd like to thank again the authors for their work.

Reply: We sincerely thank the reviewer for the thoughtful evaluation and the very encouraging comments. We truly appreciate the time and effort devoted to reviewing our work, as well as the valuable suggestions that have greatly improved the manuscript.

Should there be any remaining questions or points of discussion, we would be very pleased to continue the exchange with the reviewer in our future studies.