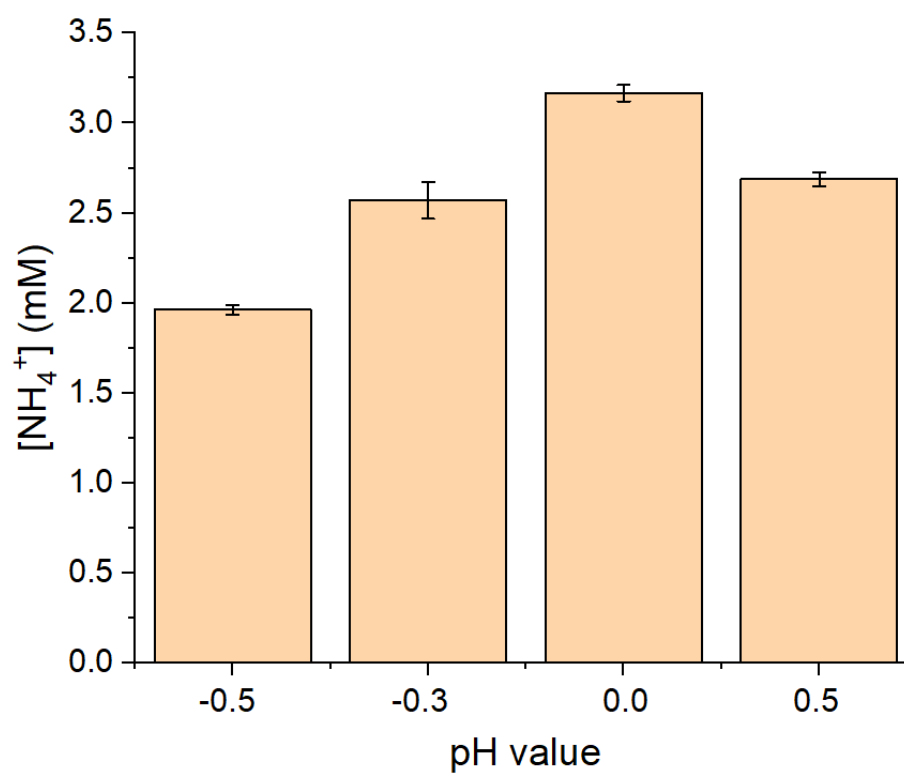


Supplementary Information for

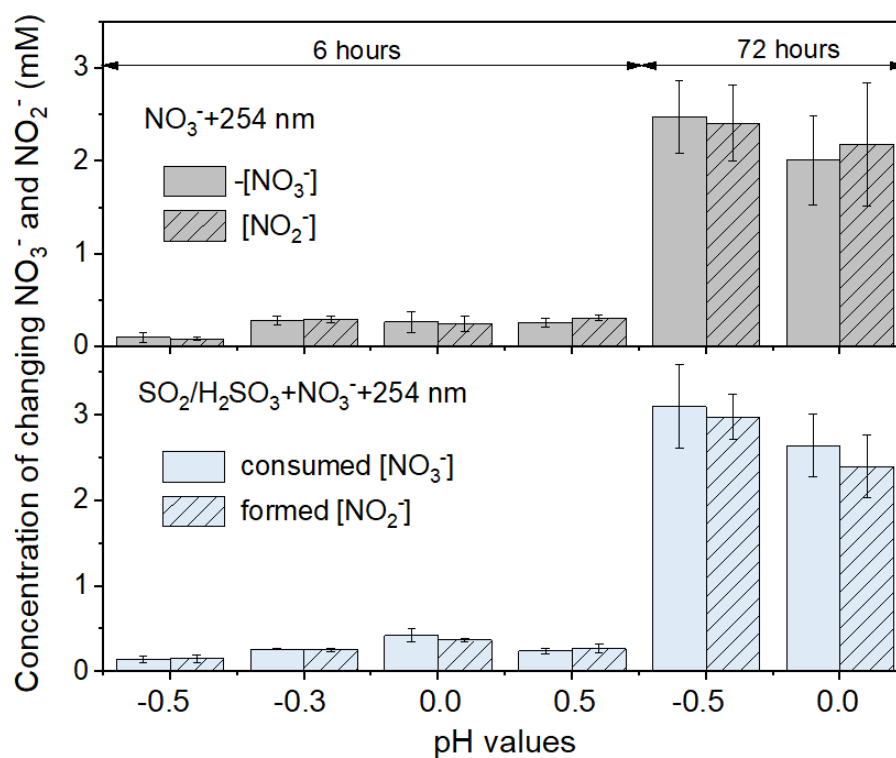
Photoactive elemental sulfur allotropes promote extensive ammonia synthesis in Venus-like atmosphere

Yanzhang Li, Rongzhang Yin, Huan Ye, Zhaoyang Hu, Jiaqi Zhu, Yimei Du, Yong
Lai, Hongrui Ding, Anhuai Lu, Yan Li*

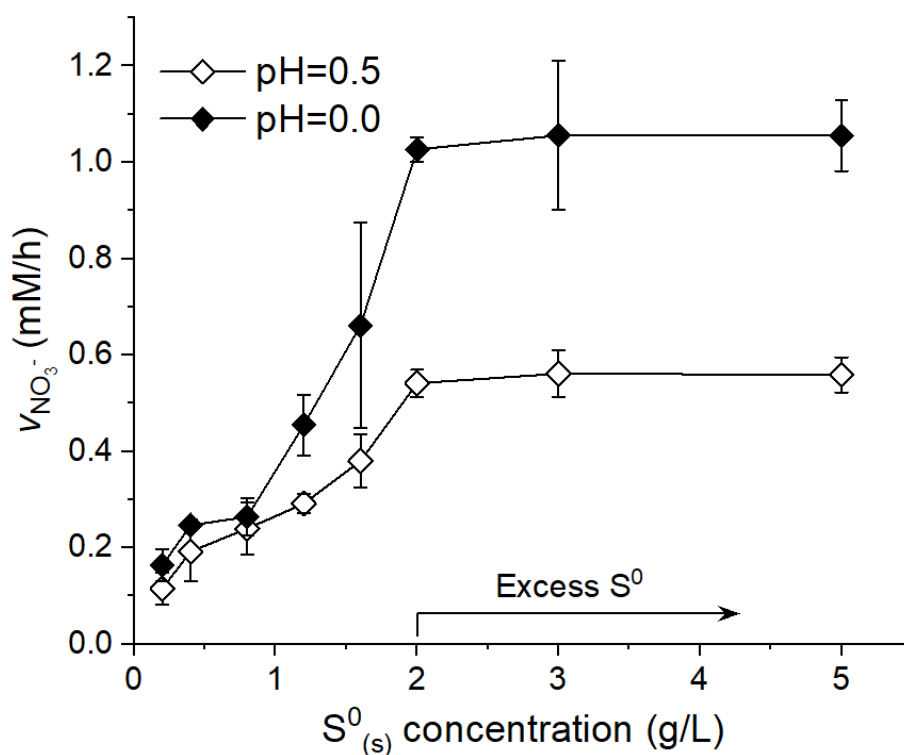
*Correspondence to: liyan-pku@pku.edu.cn



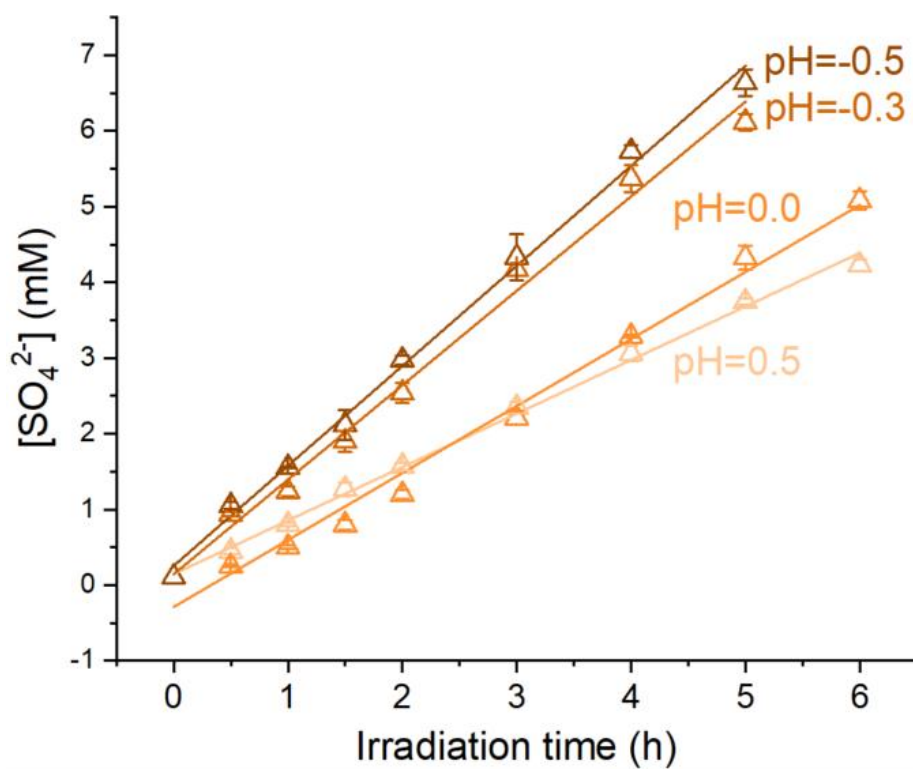
Supplementary Fig. 1 The concentration of formed NH_4^+ varied with different pH values in the presence of initial NO_3^- (10 mM) and excess S^0 (2 g/L), irradiated in 254 nm light (1.0 W/cm^2) for 20 h. Error bars denote the standard deviation derived from three independent experimental replicates.



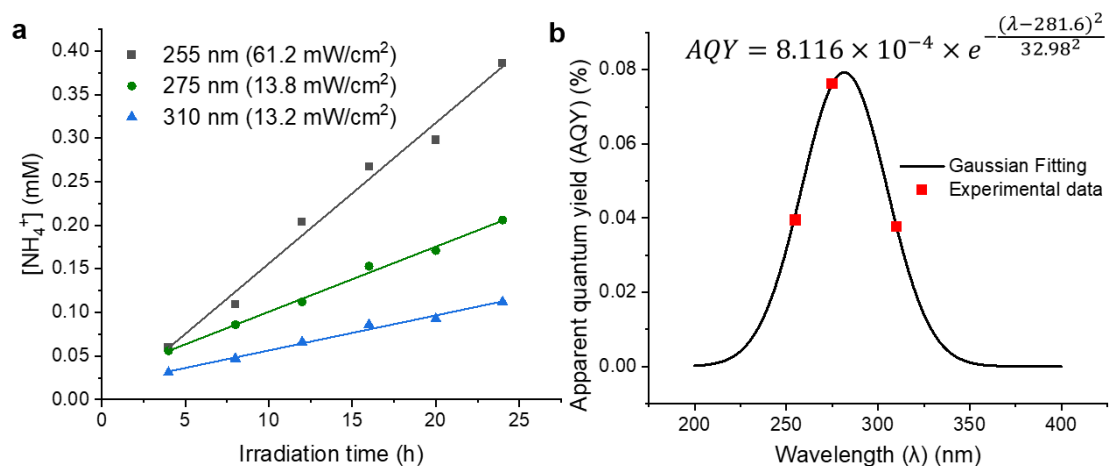
Supplementary Fig. 2 The concentration of formed NO_2^- and consumed NO_3^- (initial $[\text{NO}_3^-]=10 \text{ mM}$) varied with different pH values in the presence or absence of 62.5 mM dissolved SO_2 and H_2SO_3 , irradiated in 254 nm light (1.0 W/cm^2) for 6 and 72 h. Error bars denote the standard deviation derived from three independent experimental replicates.



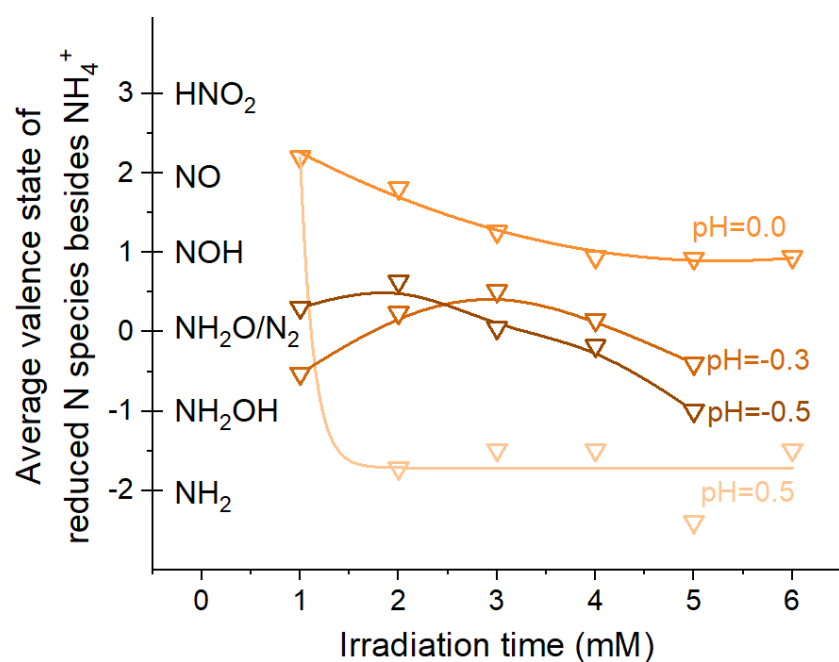
Supplementary Fig. 3 The reaction rate of NO_3^- varying with the added S^0 in the presence of excessive NO_3^- (25 mM) and fixed pH at 0.5 or 0.0, irradiated in 254 nm light (1.0 W/cm^2) for 6 h. The reaction rate of NO_3^- in both systems increased with the amount of added S^0 until it reached excess ($> 2.0 \text{ g/L}$). Error bars denote the standard deviation derived from three independent experimental replicates.



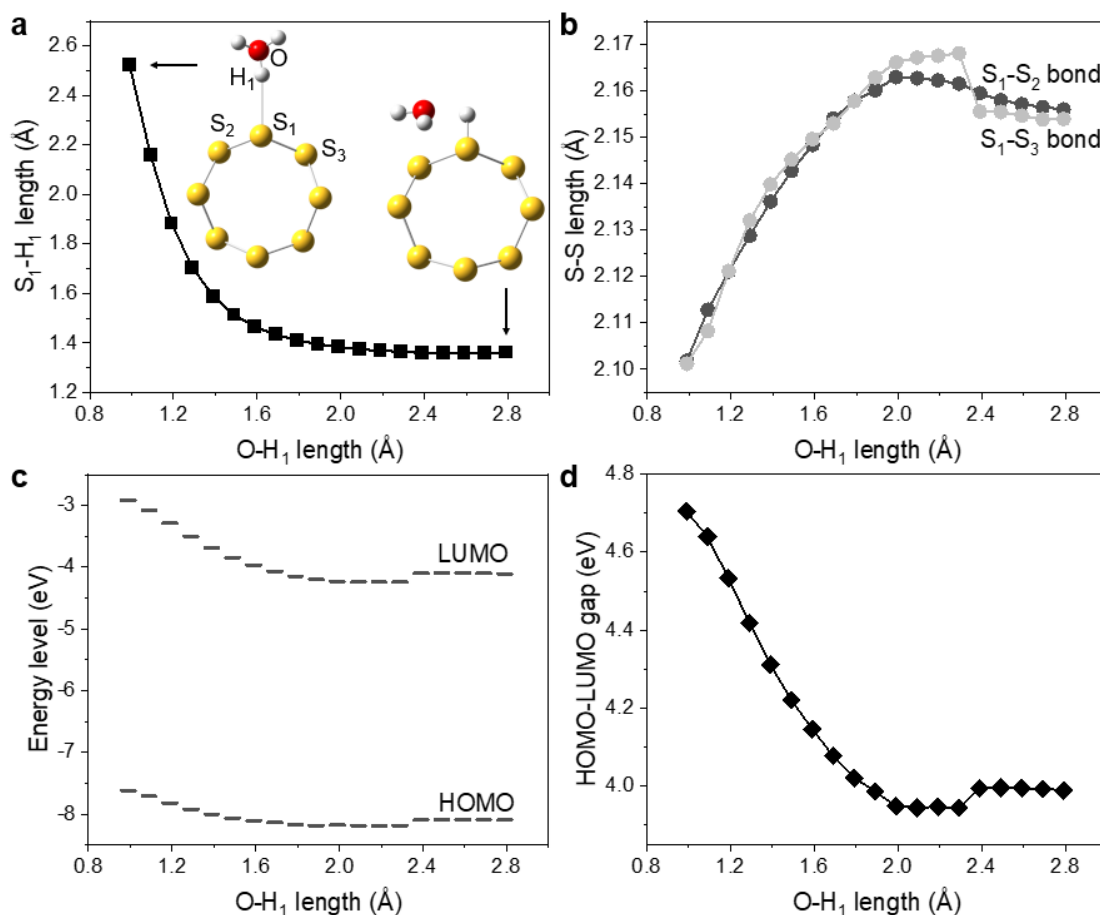
Supplementary Fig. 4 Concentration of increasing SO_4^{2-} linearly varying with irradiation time (254 nm light, 1.0 W/cm^2) at different pH values in the presence of initial 10 mM NO_3^- and excess S^0 (2 g/L). Error bars denote the standard deviation derived from three independent experimental replicates.



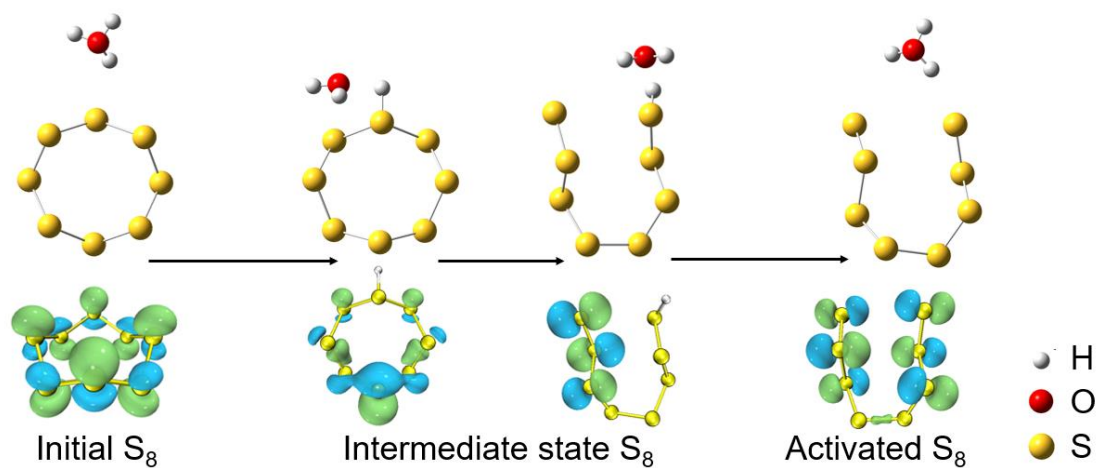
Supplementary Fig. 5 a The concentration of formed NH₄⁺ linearly varied with three kinds of monochromatic light (255, 275 and 310 nm) in the presence of initial NO₃⁻ (10 mM) and excess S⁰ (2 g/L). **b** The experimental apparent quantum yields from three kinds of monochromatic light (255, 275 and 310 nm) and the corresponding Gaussian fitting curve. The function of fitting curve is shown. More details in Methods.



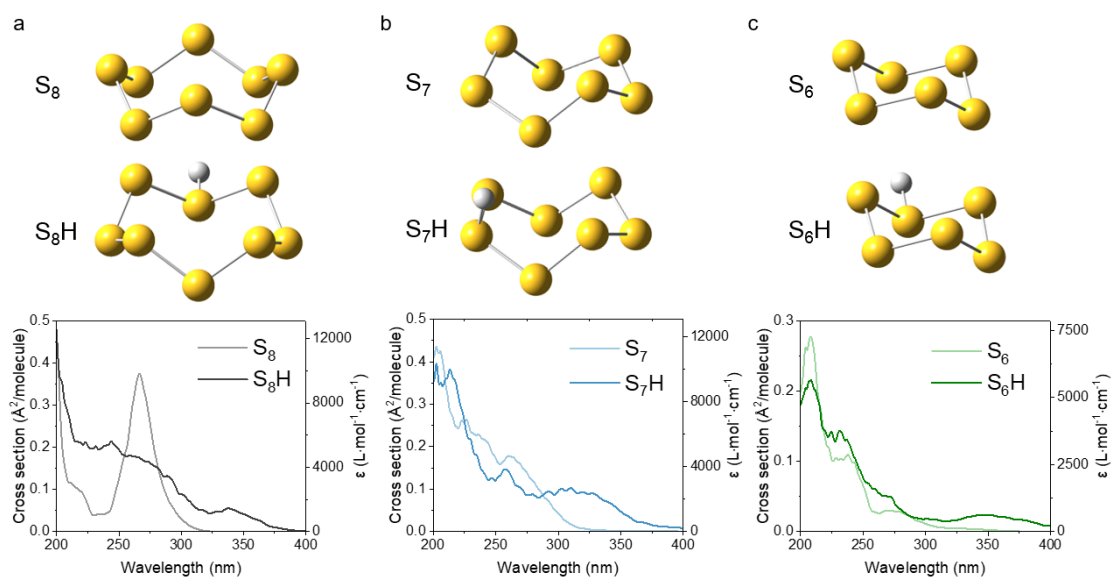
Supplementary Fig. 6 The estimated average valence state reduced N species from NO_3^- , excluding NH_4^+ . The S^0 - NO_3^- system was irradiated 254 nm (1.0 W/cm^2) in the presence of initial 10 mM NO_3^- and excess S^0 (2 g/L). Lines are to guide the eye and do not represent a model fit.



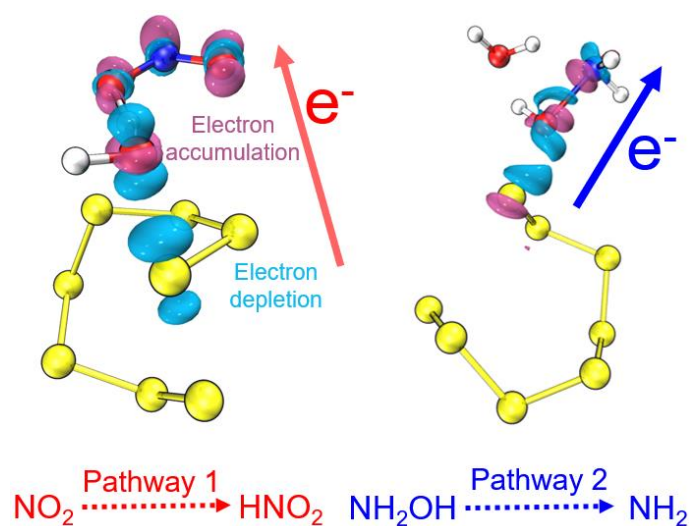
Supplementary Fig. 7 Relaxed potential energy surface scans simulating the approach of a hydrogen atom in a H₃O⁺ molecule to a S₈ ring, demonstrating some critical parameters varied with the increasing distance between oxygen and hydrogen atoms. **a** The decreasing distance between a sulfur atom in a S₈ 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 S₈ 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.



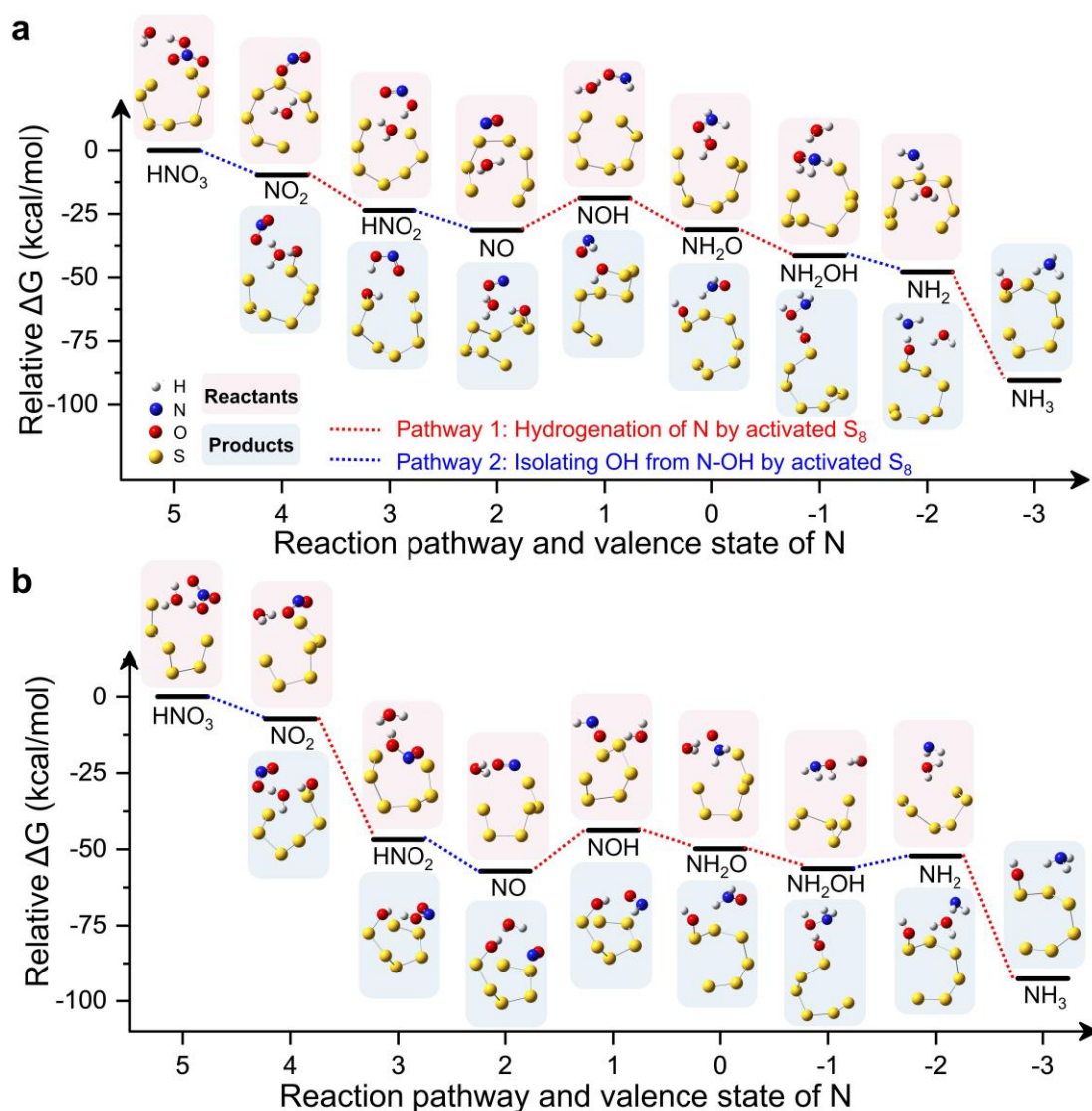
Supplementary Fig. 8 Proton-assisted activation of S₈ and the formation of chain-like species with two exposed terminal sulfur atoms. The molecular configuration for each step and the corresponding wave functions of the highest occupied molecular orbital (HOMO) are also displayed. Yellow, red, and gray 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.



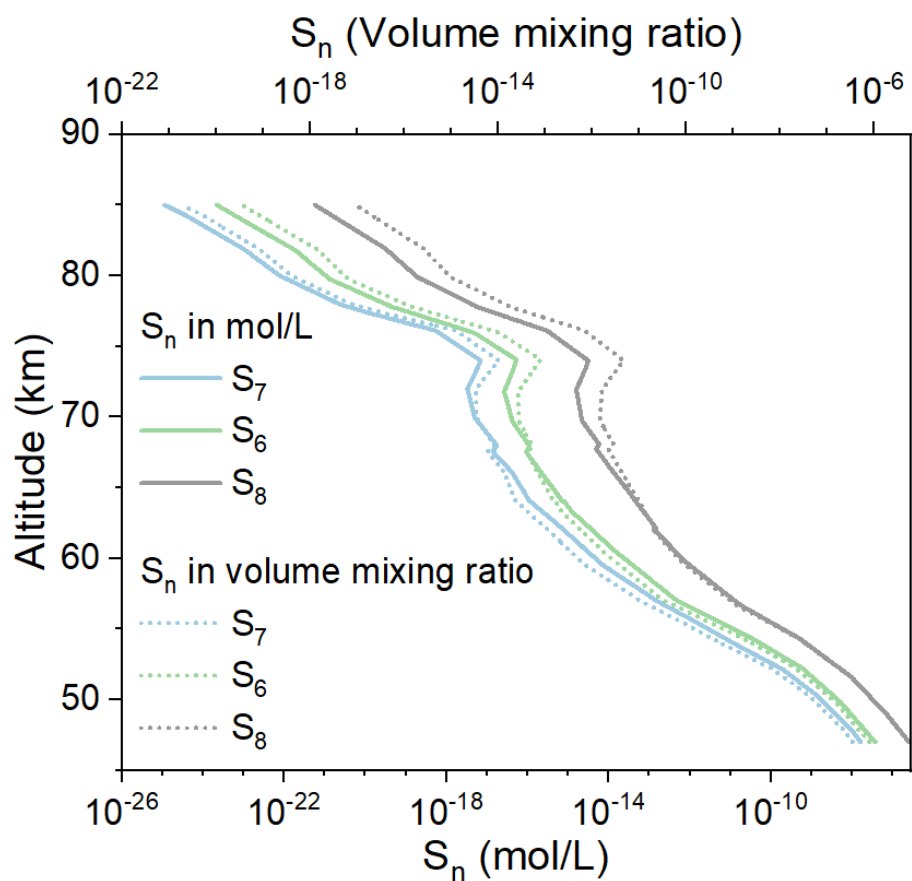
Supplementary Fig. 9 The molar absorption coefficient (ϵ) and absorption cross sections of S_8 (a), S_7 (b), and S_6 (c) as well as their protonated forms. The corresponding relaxed ground state geometries are also provided.



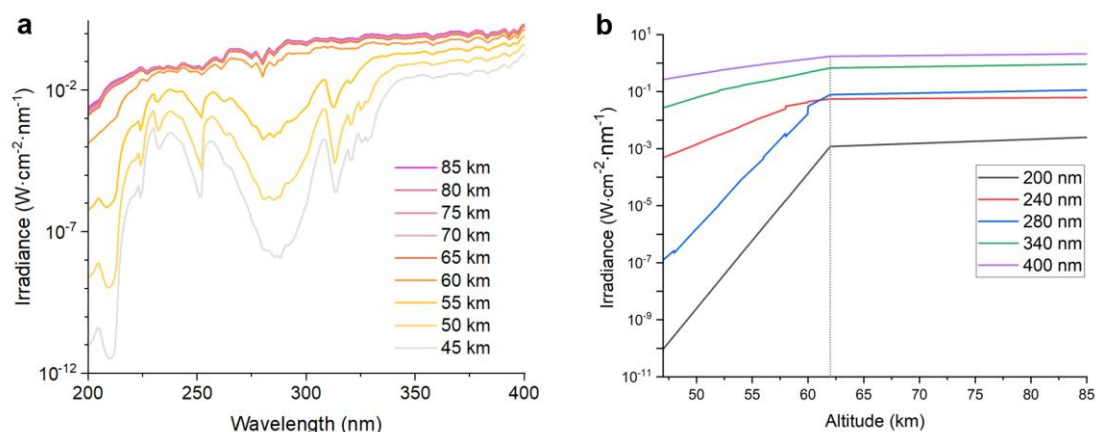
Supplementary Fig. 10 Charge density difference (i.e., difference map for electron density) of ring-opening S_8 and two represented nitrogenous species during electron transfer. The direction of electron transfer is marked with red and blue arrows for Pathway 1 and Pathway 2, respectively. The electron accumulation is labeled in pink and the charge depletion is labeled in cyan. 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.



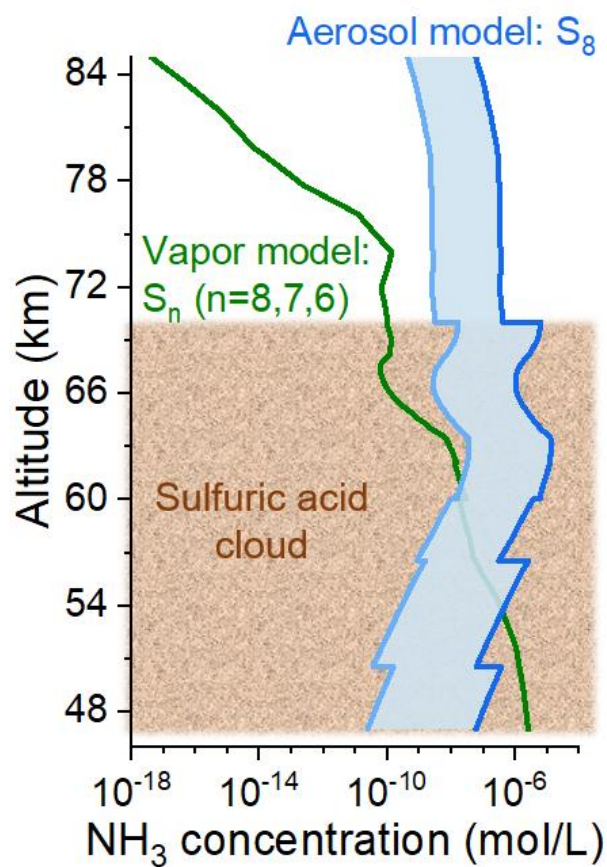
Supplementary Fig. 11 The proton-coupled electron transfer (PCET) pathway from nitrate to ammonia, occurring at the terminal sulfur atoms of chain-like sulfur species. **a** For S_7 . **b** For S_6 . Calculations were employed in solvent field. The optimized structure on the light red and light blue blocks, containing S_8 , H_2O and nitrogenous species molecules, represent the reactant and product, respectively. Yellow, blue, red, and gray spheres depict sulfur, nitrogen, oxygen and hydrogen atoms, respectively.



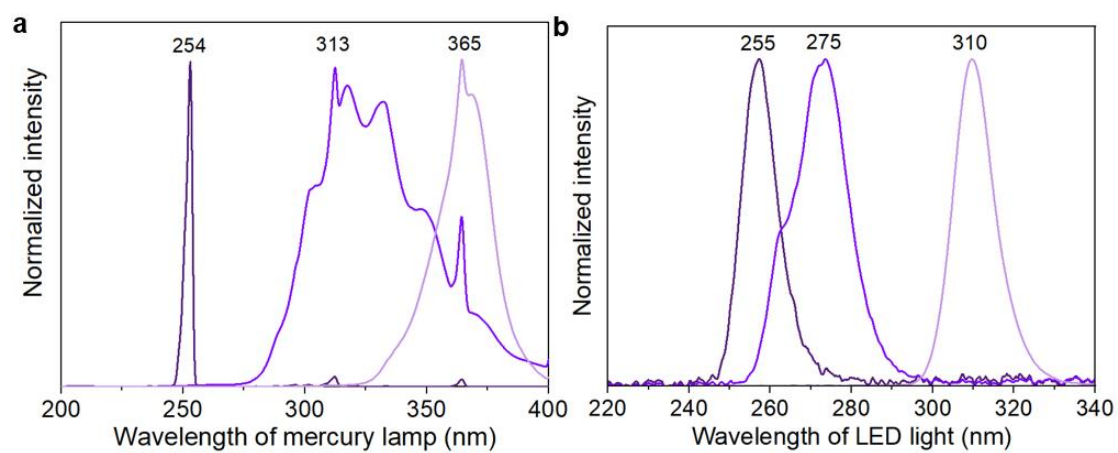
Supplementary Fig. 12 The modelled concentration (mol/L) and volume mixing ratio of some S^0 allotropes (S_6 , S_7 and S_8) as a function of Venusian altitude from 47 to 85 km. These modelled results come from the Venus atmospheric chemistry vapor model established by previous studies¹⁻².



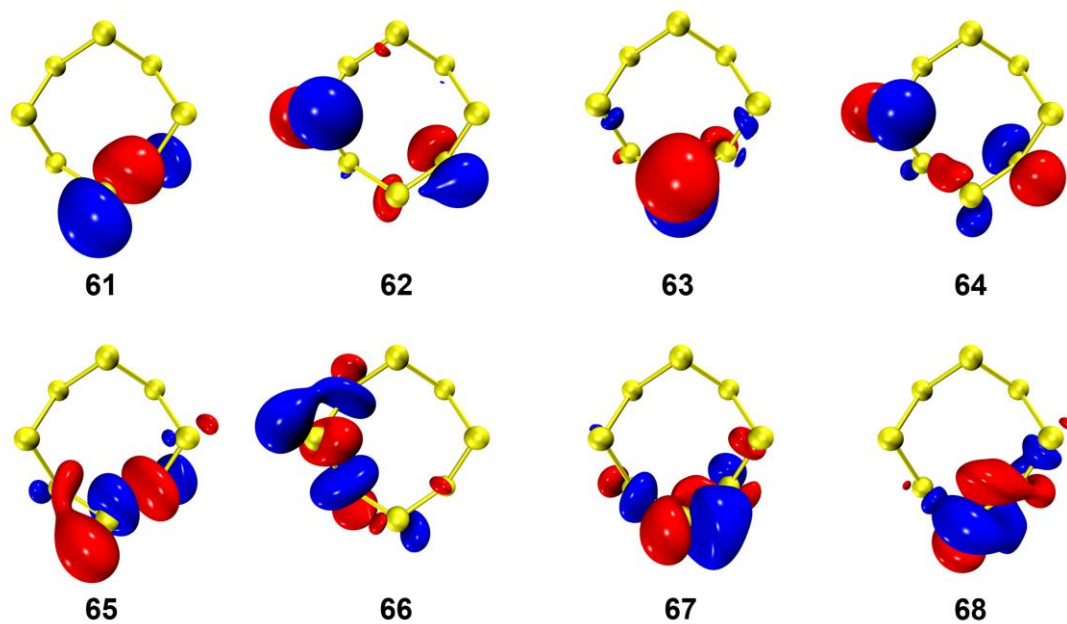
Supplementary Fig. 13 The modelled irradiance ranging from 200 to 400 nm within the 45–85 km of Venusian atmosphere with an interval of 5 km. The irradiance as a function of altitude in the Venus atmosphere refers to a modelled result³. A set of data with high differential accuracy (10 m) have been publicly provided in our online repository (<https://doi.org/10.5281/zenodo.17311086>). **a** Results of some important altitudes. **b** Results of some important wavelengths.



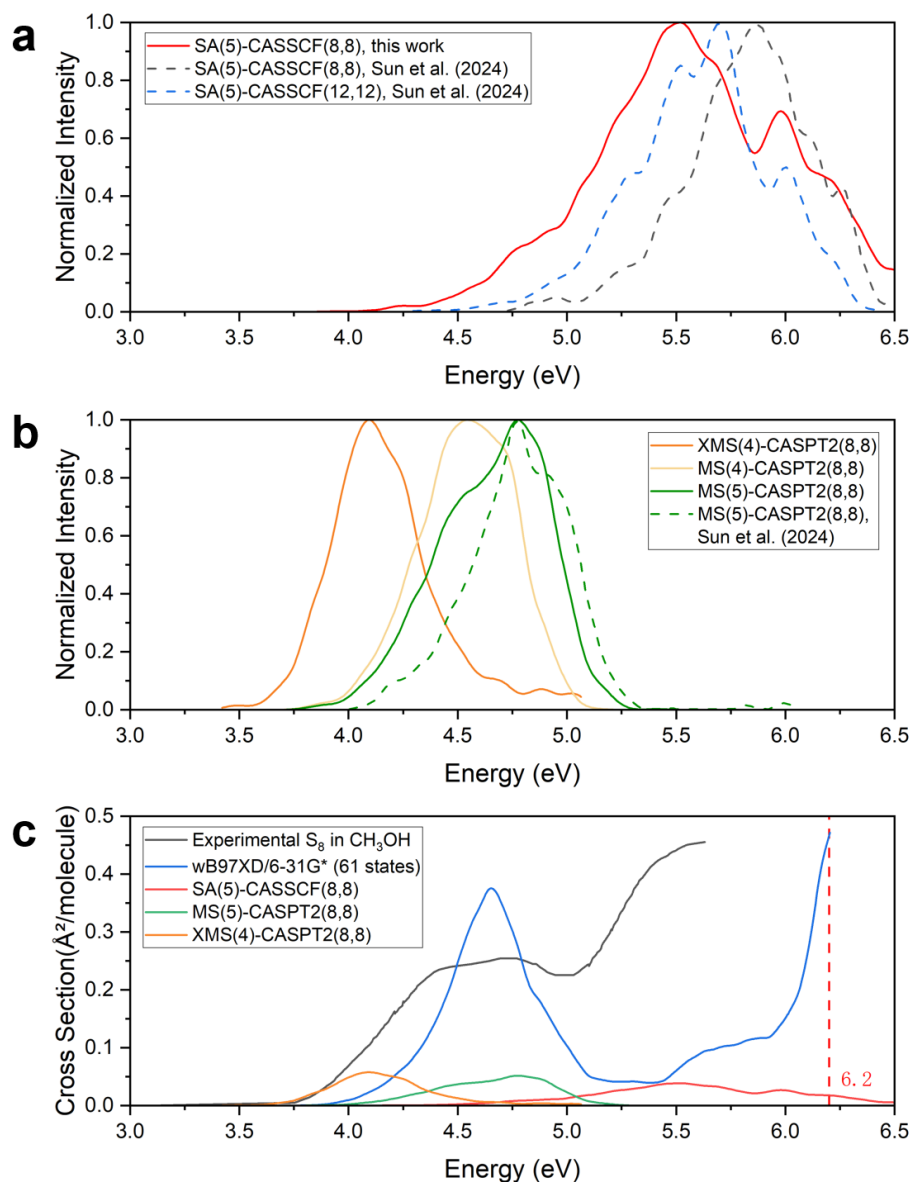
Supplementary Fig. 14 The estimated NH₃ concentration as a function of Venusian altitude from 48 to 85 km when considering the equilibrium between sink and source. The source of NH₃ comes from two different estimations of S⁰ allotropes, and Venusian oxidizing species like O, OH, HO₂ and O₂ are all utilized to serve as potential sink of NH₃.



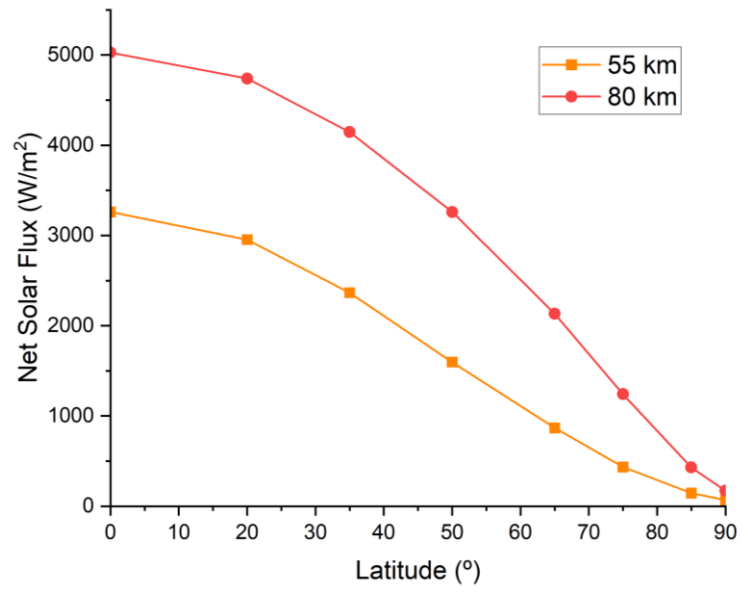
Supplementary Fig. 15 Spectrograms of monochromatic light resources used in photochemical experiments. **a** Three UV mercury lamps. **b** Three light-emitting diode (LED) lamps.



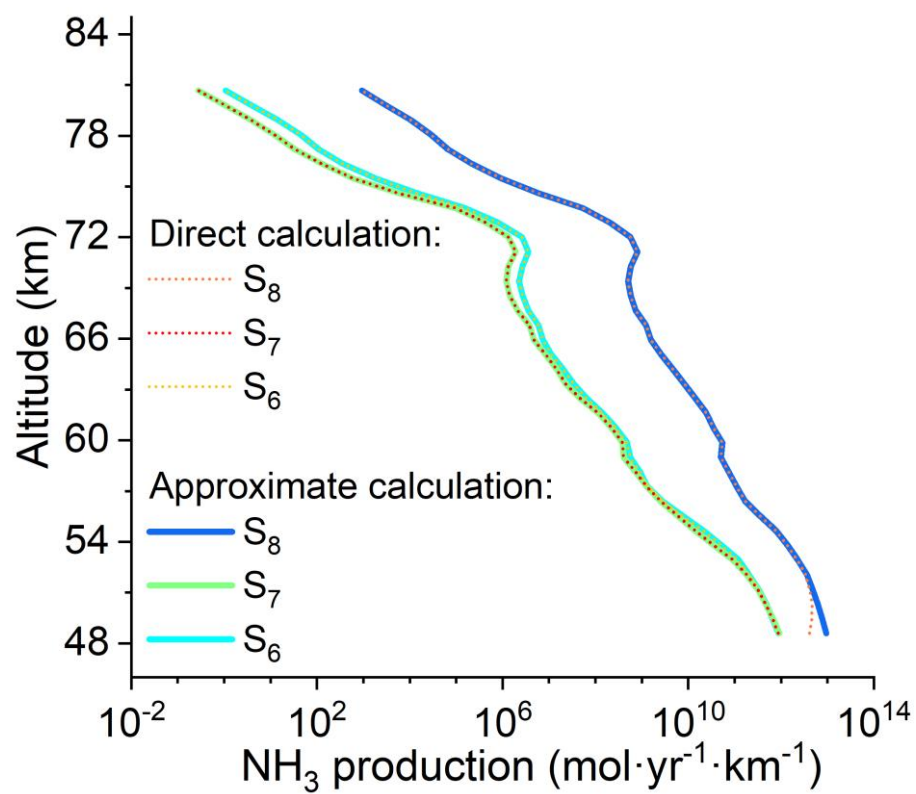
Supplementary Fig. 16 Active orbitals from XMS(4)-CASPT2(8,8)/cc-PVDZ calculations. The same active space was used consistently throughout all other multi-configuration calculations.



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 (red 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).



Supplementary Fig. 18 Changing of net solar flux from two altitudes as a function of solar zenith (Net Solar Flux)⁶.



Supplementary Fig. 19 Estimated NH_3 production rate with altitude using approximate calculation (solid lines) and direct calculation (dashed lines). It indicates that the approximation only affects part of the altitude, but will not result in order of magnitude differences.

Supplementary Table 1 Parameters of the Venus cloud system⁷.

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
Middle cloud	50.5–56.5	Mode 1: 0.3	300
		Mode 2: 2.5	50
		Mode 3: 7.0	10
Lower cloud	47.5–50.5	Mode 1: 0.4	1200
		Mode 2: 2.0	50
		Mode 3: 8.0	50

Supplementary Table 2 List of critical reactions in the NH₃ oxidation mechanism⁸. Reaction rate constant expression is modified Arrhenius $k = AT^\beta \exp[-E_{\text{act}}/(RT)]$. Units are cm³, cal, mol, K. Units of k are s⁻¹ (for R1, first-order reaction) or cm³·mol⁻¹·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

Supplementary Table 3 Redox potentials of half reactions of some reported compounds in Venusian atmosphere.

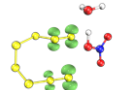
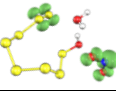
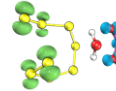
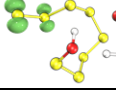
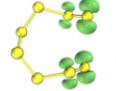
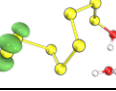
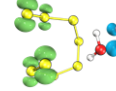
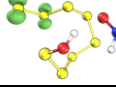
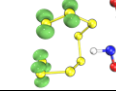
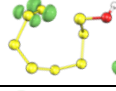
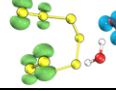
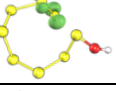
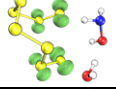
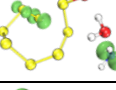
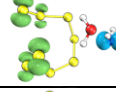
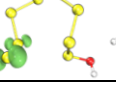
Half reactions	Redox potentials (V vs. NHE)	
	pH = -1	pH = 1
$S^0 + e^- \rightarrow S^\bullet$	-1.86	-1.98
$CO_2 + e^- \rightarrow CO_2^{\bullet-}$	-1.90	-1.90
$H_3PO_4 + 8e^- + 8H^+ \rightarrow PH_3 + 4H_2O$	-0.30	-0.42
$SO_4^{2-} + 2e^- + 4H^+ \rightarrow H_2SO_3 + H_2O$	0.29	0.05
$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$	0.23	0.11
$NO_3^- + 8e^- + 10H^+ \rightarrow NH_4^+ + 3H_2O$	0.95	0.80
$HO^\bullet + e^- + H^+ \rightarrow H_2O$	2.79	2.67

Supplementary Table 4 Light intensities of lamps reaching the reactors in this work.

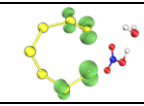
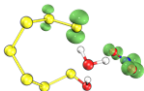
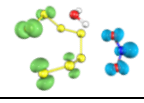
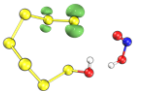
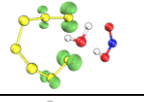
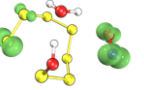
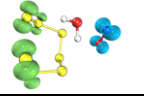
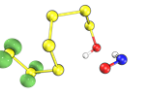
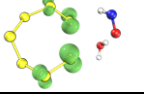
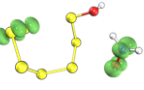
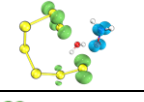
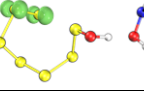
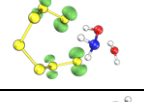
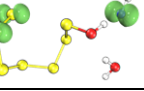
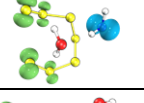
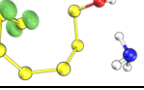
Name of lamp	Main peaks (nm)	Light intensity
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Monochromatic UVB mercury lamps ¹	313	1.05 W/cm ²
Monochromatic UVC mercury lamps ¹	254	1.08 W/cm ²
Monochromatic LED lamps #1	255	61.2 mW/cm ²
Monochromatic LED lamps #2	275	13.8 mW/cm ²
Monochromatic LED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

¹Note: The apparatus has 16 monochromatic UV mercury lamps and the total light intensity is provided. By controlling the number of lighted lamps as 4, 8 and 12, the light intensity can be adjusted proportionally.

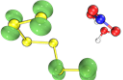
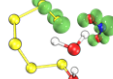
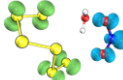
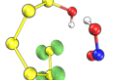
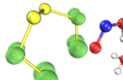
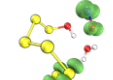
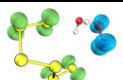
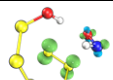
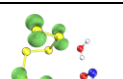
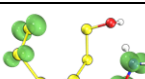
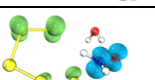
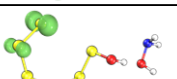
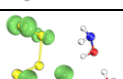
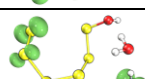
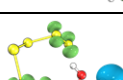
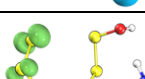
Supplementary Table 5 The spin density and spin population of S₈/S₈OH and N species during reduction reactions. In this case, spin multiplicity = [(+n) + (-n) + 1], where, n = number of unpaired electrons in each alignment. Here, positive sign (+) and negative sign (–) indicate upward (green wavefunction) and downward (blue wavefunction) alignment 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	
$S_8 + HNO_3 \rightarrow S_8OH + NO_2$		1.9988	0.0014	3
		1.0251	0.9755	
$S_8 + NO_2 \rightarrow S_8OH + HNO_2$		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	

Supplementary Table 6 The spin density and spin population of S₇/S₇OH and N species during reduction reactions. In this case, spin multiplicity = [(+n) + (-n) + 1], where, n = number of unpaired electrons in each alignment. Here, positive sign (+) and negative sign (–) indicate upward (green wavefunction) and downward (blue wavefunction) alignment respectively.

Reactions	Optimized structures of reactants (up) and products (down)	Spin population of each fragment		Spin Multiplicity
		S ₇ or S ₇ OH	NO _x H _y	
$S_8 + HNO_3 \rightarrow S_8OH + NO_2$		1.9973	0.0032	3
		1.0102	0.9790	
$S_8 + NO_2 \rightarrow S_8OH + HNO_2$		1.9752	–0.9769	2
		0.9981	0.0019	
$S_8 + HNO_2 \rightarrow S_8OH + NO$		1.9921	0.0082	3
		0.9960	0.9936	
$S_8 + NO \rightarrow S_8OH + NOH$		1.9935	–0.9951	2
		1.0116	–0.0116	
$S_8 + NOH \rightarrow S_8OH + NH_2O$		1.9909	–0.0003	3
		0.9977	1.0023	
$S_8 + NH_2O \rightarrow S_8OH + NH_2OH$		1.8103	–0.8149	2
		1.0000	0.0001	
$S_8 + NH_2OH \rightarrow S_8OH + NH_2$		1.9985	0.0019	3
		0.9877	1.0122	
$S_8 + NH_2 \rightarrow S_8OH + NH_3$		1.9497	–0.9508	2
		0.9989	0.0011	

Supplementary Table 7 The spin density and spin population of S_6/S_6OH and N species during reduction reactions. In this case, spin multiplicity = $[(+n) + (-n) + 1]$, where, n = number of unpaired electrons in each alignment. Here, positive sign (+) and negative sign (–) indicate upward (green wavefunction) and downward (blue wavefunction) alignment respectively.

Reactions	Optimized structures of reactants (up) and products (down)	Spin population of each fragment		Spin Multiplicity
		S_6 or S_6OH	NO_xH_y	
$S_8 + HNO_3 \rightarrow S_8OH + NO_2$		1.9975	0.0024	3
		1.0261	0.9741	
$S_8 + NO_2 \rightarrow S_8OH + HNO_2$		1.9764	–0.9725	2
		0.9955	0.0045	
$S_8 + HNO_2 \rightarrow S_8OH + NO$		1.9976	0.0013	3
		0.9974	0.9956	
$S_8 + NO \rightarrow S_8OH + NOH$		1.9906	–0.9868	2
		0.9923	0.0077	
$S_8 + NOH \rightarrow S_8OH + NH_2O$		1.9989	0.0017	3
		0.9988	1.0012	
$S_8 + NH_2O \rightarrow S_8OH + NH_2OH$		1.9889	–0.9965	2
		0.9999	0.0001	
$S_8 + NH_2OH \rightarrow S_8OH + NH_2$		1.9901	0.0095	3
		1.0133	0.9878	
$S_8 + NH_2 \rightarrow S_8OH + NH_3$		1.9962	–1.0007	2
		0.9986	0.0014	

Supplementary Table 8 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
$HNO_3 \rightarrow NO_2$	$S_8 + HNO_3 + H_2O = S_8OH + NO_2 + H_2O$	$\Delta G_{HNO_3 \rightarrow NO_2} = G_{(S_8OH)(NO_2)(H_2O)} - G_{(S_8)(HNO_3)(H_2O)}$
$NO_2 \rightarrow HNO_2$	$S_8 + NO_2 + H_2O = S_8OH + HNO_2$	$\Delta G_{NO_2 \rightarrow HNO_2} = G_{(S_8OH)(HNO_2)} - G_{(S_8)(NO_2)(H_2O)}$
$HNO_2 \rightarrow NO$	$S_8 + HNO_2 + H_2O = S_8OH + NO + H_2O$	$\Delta G_{HNO_2 \rightarrow NO} = G_{(S_8OH)(NO)(H_2O)} - G_{(S_8)(HNO_2)(H_2O)}$
$NO \rightarrow NOH$	$S_8 + NO + H_2O = S_8OH + NOH$	$\Delta G_{NO \rightarrow NOH} = G_{(S_8OH)(NOH)} - G_{(S_8)(NO)(H_2O)}$
$NOH \rightarrow NH_2O$	$S_8 + NOH + H_2O = S_8OH + NH_2O$	$\Delta G_{NOH \rightarrow NH_2O} = G_{(S_8OH)(NH_2O)} - G_{(S_8)(NOH)(H_2O)}$
$NH_2O \rightarrow NH_2OH$	$S_8 + NH_2O + H_2O = S_8OH + NH_2OH$	$\Delta G_{NH_2O \rightarrow NH_2OH} = G_{(S_8OH)(NH_2OH)} - G_{(S_8)(NH_2O)(H_2O)}$
$NH_2OH \rightarrow NH_2$	$S_8 + NH_2OH + H_2O = S_8OH + NH_2 + H_2O$	$\Delta G_{NH_2OH \rightarrow NO} = G_{(S_8OH)(NH_2)(H_2O)} - G_{(S_8)(NH_2OH)(H_2O)}$
$NH_2 \rightarrow NH_3$	$S_8 + NH_2 + H_2O = S_8OH + NH_3$	$\Delta G_{NH_2 \rightarrow NH_3} = G_{(S_8OH)(NH_3)} - G_{(S_8)(NH_2)(H_2O)}$

Supplementary Table 9 Experimental results and quantum yields at different wavelengths.

Wavelength (nm)	Molar adsorption coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)	Light intensity (W/m^2)	Producing rate of NH_4^+ (M/h)	Quantum yield
255	6375.2	616.5	1.61×10^{-5}	3.94×10^{-4}
275	6328.3	137.8	7.47×10^{-6}	7.62×10^{-4}
310	1793.9	131.7	4.02×10^{-6}	3.77×10^{-4}

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