nature portfolio

Peer Review File

Missing Interstellar Sulfur in Inventories of Polysulfanes (H_2S_n; n = 2–11) and Molecular Sulfur Crowns (S_8)

Corresponding Author: Professor Ralf Kaiser

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)
I was asked to review the paper entitled "Untangling the Interstellar Sulfur Depletion: Missing Sulfur in Polysulfanes (H2Sn; n = 2–11) and Molecular Sulfur Crowns (S8)". This paper presents the results of new experiments on high energy particle bombardment of H2S ices in order to give constraints on the major products of this process. These experiments are a simulation of the effect of cosmic-rays in dense cores where H2S is presumably easily formed at the surface of the grains. The results are extremely interesting in particular in the context of the sulphur depletion problem. I have a few remarks that could help improve the reading of the paper and understand the conclusions that are drawn.

1) The reason to choose H2S as the irradiated target is not justified well in the paper. From the paper, it seems that the authors chose this molecule because it represents the a common species in comets. However, its abundance is small compared to the abundance of elemental sulphur. I suppose the reason is that chemical models of the ISM predict H2S ices to be the reservoir of sulfur. So to fully understand the strategy behind the experiments, the missing elements in the text are: chemical models predict H2S ices as the main reservoir BUT H2S has not been detected in interstellar ices and maximum abundance is constraining.

2) There has been an experiment by Garozzo et al. (2010). Although they used a mixture of H2S with CO, they also found an efficient formation of H2S2. Jimenez-Escobar & Munoz Caro (2011) studied the irradiation of H2S mixte in water and found the formation of H2S2 and other polymeric sulphur. These experiments should be mentioned in this paper.

3) The experiments presented here are done on pure H2S ices. The effect of ice mixture (especially with H2O and CO) should be discussed even though not measured as ice mixture are more relevant for the ISM.

4) Table 1 should be better introduced in the text as they summarize the detected products with percentage.

5) In the conclusion of the paper, the authors state that "Although the conversion rate of hydrogen sulfide to molecular sulfur of about 4 % as derived in our experiments might appear low, this number can be placed in astronomical context. ». What is molecular sulphur in this context? S8?

6) Since the paper ends with this sentence « … thus eventually resolving the interstellar sulfur puzzle. », I think more discussion is needed on the astrophysical implications (even if it is in the complementary notes). The experiments show that only 33% of H2S is converted. Is the 67% remaining consistent with the non detection of H2S in interstellar ices? Could the identified products be detected in the gas-phase or in the ices considering their observability and their amount? Is the remaining H2S % compatible with the amount observed in comets?

Reviewer #2

(Remarks to the Author)
The authors present laboratory results of H2S ice at 5K processes by electron beams at various energies. The analysis demonstrates the formation of a wide array of sulfanes and of S8. The authors suggest that this process can account for the observational dearth of sulfur species in cold molecular clouds.

1.In my opinion the authors overstate the significance of the 'interstellar sulfur depletion problem'. We can see sulfur emission in hotter regions, HII, photdissociation regions, other star forming regions. We know the sulfur is there in the cold clouds, it's just hard to detect. And, italicizing 'interstellar sulfur depletion problem' is rather annoying.

2. Another sulfur depletion problem has been identified for planetary nebulae. This should be discussed here, although the cause is quite different. See, e.g., Tan ApJL 2024 961 L47.

3. The experimental technique and results are excellent and I recommend publication for that reason.

4. Thioacids - aren't they RCOSH rather than HSCR?
thioamides - aren't they RCSNR' rather than RCSR'?

5. lines 250-251 and maybe elsewhere - S8 is the thermodynamically favored form of elemental sulfur. A reference to this should be given , e.g., Lyons J Sulf Chem 2008 or some of the references therein.

6. line 105 - please give or restate reference for S8 in Ryugu.

7. lines 223-224 - please give supporting calculations for expected abundances of 32S733S and 32S634S2 and compare to reported percentages.

8. The results given in Table 1 seem like they would make a nice figure plotted as abundance vs S chain length.

9. Can you comment on the astronomical detectibility of the sulfane chains, H2Sn

10. Thank you for including your ab initio details.

8.

Reviewer #3

(Remarks to the Author)
Dear Editor,

I have completed my review of the manuscript “Untangling the Interstellar Sulfur Depletion: Missing Sulfur in Polysulfanes (H2Sn; n = 2-11) and Molecular Sulfur Crowns (S8)” by Herath et al. submitted for publication in Nature Communications.

Overall, I found the study to be very robust, making excellent use of combined experimental and theoretical techniques. The results are well supported by the evidence presented, and significant additional information is presented in the supplementary text. However, although this manuscript is certainly worthy of publication, I do not feel that it is suitable for Nature Communications and I recommend that the authors should pursue publication in another established journal (such as The Astrophysical Journal or Astronomy and Astrophysics) instead.

My main objection to publication in Nature Communications is that the manuscript in its current state does not meet a specific condition required for publication in Nature journals: that “for a selective journal like Nature Communications, we would typically expect the paper to provide novel insights to the specific field” (quoted directly from the “For Reviewers” page on the Nature Communications website). The current manuscript does not meet this criterion on at least two counts.

Firstly, the radiolytic synthesis of polysulfanes as a result of irradiating H2S astrophysical ice analogues at low temperatures is not a new result. Previous studies, including studies that have combined experimental and theoretical work, have repeatedly demonstrated this (see works by, for example, Jiménez-Escobar et al., 2012, ApJL 751, L40; Cazaux et al., 2022, A&A 657, A100; Carrascosa et al., 2024, MNRAS 533, 967; Li et al., 2025, PCCP 27, 5961). As far as I can tell, the only difference between those studies and the present work is the utilisation of the extremely sensitive and advanced technique of PI-ReToF-MS to detect polysulfane homologs up to H2S11; whereas previous studies were only able to detect homologs up to and including H2S9. The extension of the identified homolog series from H2S9 to H2S11, though certainly academically interesting, is not so novel as to merit publication in Nature Communications. Moreover, the only sulfur allotrope identified by the present study was the most stable S8 crown structure. In this regard, this study is actually more limited than previous experimental and theoretical works, which have demonstrated the synthesis of several sulfur allotropes Sn as a result of the irradiation of H2S ices (see works by, for example, Mahjoub et al., 2017, ApJ 846, 148; Startsev, 2016, Kinetics & Catalysis 57, 511; Shingledecker et al., 2020, ApJ 888 52; Cazaux et al., 2022, A&A 657, A100).

Secondly, I feel that some of the statements made by the authors as to the impact of the work are over-exaggerated. Specifically, in lines 85-89, the authors claim that they “…afford a compelling solution to the interstellar sulfur depletion problem…”; while in lines 102-105 they state that their “…study affords persuasive evidence … of the source of elemental sulfur … in the carbonaceous asteroid (162173) Ryugu, thus, documenting for the first time the link between interstellar matter and planetary bodies in solar systems including our own.” Finally, in line 301 it is claimed that these results could “… thus eventually resolve the interstellar sulfur puzzle”.

To state that the results of this study solve the interstellar sulfur depletion problem is, in my opinion, somewhat of an exaggeration. Firstly, the implications of this study are only valid if H2S is indeed present in interstellar ices and, to date, no observations of ices in dense molecular clouds or proto-stellar regions have found any evidence of the presence of H_2S (see, for example, McClure et al., 2023, Nature Astronomy 7, 431; Rocha et al., 2024, A&A 683, A124; Rocha et al., 2025, A&A 693, A288). Of course, it is entirely possible that these non-detections are due to the inherently weak infrared absorption features of H_2S. However, even if one were to assume that H_2S is present in these ices, then it would almost certainly be a minor component of an ice dominated by non-sulfur-bearing molecules, such as H_2O, CO, CO_2, NH_3, CH_4, etc. The presence of these other molecules will surely alter the chemical reactions induced within the ice by galactic cosmic rays and, indeed, previous experimental studies on the radiation chemistry of H_2S mixed with other icy species have shown that significant quantities of sulfur can be sequestered into volatile organic or inorganic molecules that should be observable in either the ice phase, or else in the gas phase after desorption or sublimation (see, for example, Moore et al., 2007, Icarus 189, 409; Garozzo et al., 2010, A&A 509, A67; Jiménez-Escobar et al., 2014, MNRAS 443, 343; Chen et al., 2015, ApJ 798, 80; Mahjoub et al., 2017, ApJ 846, 148). Hence, the yield of large sulfur molecules is likely reduced in these more realistic ices.

Moreover, and perhaps critically, the authors' suggestion that the radiation-driven conversion of H_2S to elemental sulfur (which is not active in the mid-infrared region; Trofimov et al., 2009, Journal of Sulfur Chemistry 30, 518) is responsible for the apparent sulfur depletion problem is not in line with contemporary geo/cosmochemical data on the sulfur composition of proto-planetary disks. Specifically, it is known that 80-95% of the sulfur in these disks must be significantly more refractory than H_2O, favoring its incorporation into sulfide minerals rather than allotropic chains or rings (see Kama et al., 2019, ApJ 885, 114 for further details). Hence, it is more likely that sulfide minerals that are difficult to observe in the infrared constitute the majority of the depleted sulfur in dense molecular clouds, and it is likely these minerals that are largely incorporated into carbonaceous asteroids and other rocky solar system bodies.

The authors' claim that their results "…afford a compelling solution to the interstellar sulfur depletion problem" is therefore not convincing. At best, these results provide better insight into one possible mechanism of sulfur depletion; however, the sequestration of sulfur into allotropes cannot account for all the missing sulfur for the reasons described above. In light of this, I would strongly urge the authors to tone down the implications of their results.

The authors may also consider the following (comparatively) minor points:

1. In the methods section, you state that your ices have thicknesses ranging between 1.0-1.6 μm, but that the average penetration depth of your electrons is only about 350 nm, and that 90% of the energy is deposited within the top 420 nm or so. This means that the vast majority of the ice remains unprocessed. What are the astrophysical and astrochemical implications (especially with regards to sulfur chemistry) of having a heavily processed upper layer of the ice and a comparatively pristine lower layer?

2. In the manuscript, you mention that the conversion yield of H_2S to S_8 was 6±1% (line 252), but then later in the manuscript (line 295) you use a conversion yield of 4% to calculate the amount of sulfur that could be produced in ices in the TMC. Is this a typo or did I miss something?

3. I think you have a typo on line 211; an extra 'l' after the comma and before "boat".

I understand that my report will likely be disappointing to the authors of this manuscript; however, I do not wish for my opinions and criticisms to be misconstrued as being a negative opinion of this particular study. Rather, I think that the study is very interesting and scientifically very robust (although I would encourage the authors to address my comments above), but that it would likely be more appropriate to publish in a different non-Nature-type journal.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed all my concerns and the paper can be accepted as it is.

Reviewer #2

(Remarks to the Author)
I've addressed most of the essential points I wished to raise in my first review. The authors have made a sincere effort to address those points. I therefore recommend the paper for publication.

Again, I think the measurements are first rate and worthy of publication in Nat Comm.

Finally, just for a moment, let's consider all of those 4th - 7th row elements also suffering from a depletion problem in the ISM. ;)

Reviewer #3

(Remarks to the Author)
I thank the authors for taking the time to respond to my comments in a thorough a professional manner. The manuscript is now much improved. In particular, the novelty of the study is now much more apparent and the implications of their results with regards to our understanding of the interstellar sulfur depletion problem have been significantly toned down to more appropriate levels. I believe this manuscript is now publishable, following two (very minor) corrections:

1) Lines 332-336 of revised manuscript: I believe there is a small mistake here. In these lines, the authors state that "...if the energetics of the steps are favourable, the photochemical reactions would proceed..." It is important not to mix up photochemical and radiation-chemical reactions, as there are many key differences between these types of chemistry (e.g., the former is limited to selection rules, the latter is not). Here, I believe the authors are referring to chemistry induced by the incident keV electrons, which is radiation-chemical in nature and not photochemical. A minor edit would suffice to correct this mistake.

2) Lines 377-379 of revised manuscript: I would strongly urge the authors to avoid using the word "solution" when referring to the implication of their results to the sulfur depletion problem. These results, although certainly informative and useful, do not "solve" the sulfur depletion problem, but provide better insight and understanding to the problem. I would therefore strongly urge the authors to rephrase the sentence "...in circumstellar discs, eventually reaching solutions to the interstellar sulfur puzzle." to something more like "...in circumstellar discs, providing useful insights to and clearer perspectives on the interstellar sulfur puzzle."

Reviewer#1

I was asked to review the paper entitled "Untangling the Interstellar Sulfur Depletion: Missing Sulfur in Polysulfanes (H2Sn; n = 2–11) and Molecular Sulfur Crowns (S8)". This paper presents the results of new experiments on high energy particle bombardment of H2S ices in order to give constraints on the major products of this process. These experiments are a simulation of the effect of cosmic-rays in dense cores where H2S is presumably easily formed at the surface of the grains. The results are extremely interesting in particular in the context of the sulphur depletion problem. I have a few remarks that could help improve the reading of the paper and understand the conclusions that are drawn.

Thank you for your valuable comments.

1) The reason to choose H2S as the irradiated target is not justified well in the paper. From the paper, it seems that the authors chose this molecule because it represents the a common species in comets. However, its abundance is small compared to the abundance of elemental sulphur. I suppose the reason is that chemical models of the ISM predict H2S ices to be the reservoir of sulfur. So to fully understand the strategy behind the experiments, the missing elements in the text are: chemical models predict H2S ices as the main reservoir BUT H2S has not been detected in interstellar ices and maximum abundance is constraining.

Thank you, the following is included in the introduction to justify the use of hydrogen sulfide in these analog ices. (Lines 45-49)

"Although the simplest sulfur containing molecule: hydrogen sulfide (H_2S) has not been observed yet in interstellar ices via infrared observation,[13–15] chemical models predict that hydrogen sulfide is present in these ices.[16] Since infrared interstellar ice analyses displayed evidence for compounds more volatile than hydrogen sulfide (such as methane) still remaining on the ices,[13] non-detection of hydrogen sulfide is likely due to the weak infrared features."

Additionally, lines 53-58 identifies the detection of H_2S in comets.

"…the interstellar sulfur reservoir has been linked to observations of comets where sulfur-containing molecules such as hydrogen sulfide (H_2S), sulfur monoxide (SO), sulfur dioxide (SO_2), carbonyl sulfide (OCS), and carbon disulfide (CS_2) have been detected.[20–23] Hydrogen sulfide is the most common sulfur species with an abundance of 1.5% with respect to water identified in the comet C/1995 O1 (Hale-Bopp)[20] and at a level of 0.5% in comet C/2014 Q2 (Lovejoy).[23] Hydrogen sulfide (H_2S) was identified in the nitrogen-rich asteroid (101955) Bennu as well.[24]"

Moreover, lines 71-75 discuss the previous experiments which also used hydrogen sulfide ices as the simplest candidate molecules containing sulfur.

"Laboratory simulation experiments exploiting radiation processing of hydrogen sulfide (H_2S) ices provide a key to substantiate these astronomical observations and astrochemical modelling effort through the detection of S-H stretching feature in the infrared spectra of the processed model ices.[32,33] In addition to pure H_2S ices, mixed ice experiments have been reported incorporating the major species detected in the interstellar ices."

2) There has been an experiment by Garozzo et al. (2010). Although they used a mixture of H2S with CO, they also found an efficient formation of H2S2. Jimenez-Escobar & Munoz Caro (2011) studied the irradiation of H2S mixte in water and found the formation of H2S2 and other polymeric sulphur. These experiments should be mentioned in this paper.

Thank you for the suggestion. Please refer to the inclusions below: (line 75 to line 81)

Included text reads "Analog ices of H_2S or H_2S/H_2O via UV irradiation,[32–34] X-ray processing,[35] energetic electron irradiation,[36] protons,[37] or hydrogen atom interactions[38] conducted so far have identified disulfane (H_2S_2). Processing of H_2S/CO ices also found to form H_2S_2.[19,39,40] In these processed H_2S and mixed ices, sulfanes up to H_2S_7 were identified via their subliming mass fragments.[33,41,42] A recent study by Carrascosa, H. *et al.*, displayed the sulfanes (H_2S_4 and H_2S_5) leading to molecular sulfur fragments (S_3^+ and S_4^+).[33] Laboratory experimental studies of pristine H_2S or mixed ices also observed allotropes of sulfur (S_n: S_2, S_3 and S_4).[31,41,43,44]".

3) The experiments presented here are done on pure H2S ices. The effect of ice mixture (especially with H2O and CO) should be discussed even though not measured as ice mixture are more relevant for the ISM.

Please refer to the inclusions to the discussion section below. (lines 332-336)

"…. The presence of other components in these interstellar model ices such as water can affect the reactions forwarded via parallel competing reactions. If the energetics of the steps are favorable, the photochemical reactions would proceed in these ices, regardless of the size or complexity of product molecules.[29,64] In pure hydrogen sulfide ices, in the abundance of hydrogen atoms, sulfanes seem the most favorable product in comparison to molecular sulfurs (S_n), except for octasulfur."

4) Table 1 should be better introduced in the text as they summarize the detected products with percentage.

Thank you, this is addressed in lines 246-254.

Previously "The yields for sulfanes from H_2S_2 to H_2S_8 and S_8 molecules (Table 1) were quantified with the help of the photoionization cross sections at both 10.82 eV and 10.49 eV" now reads as "The yields for sulfanes from H_2S_2 to H_2S_8 and S_8 molecules were quantified with the help of the photoionization cross sections at both 10.82 eV and 10.49 eV. In the 10.82 eV photoionization experiment, a yield of $(3.5 \pm 0.2) \times 10^{-3}$ molecules eV^{-1} was observed for the simplest product: H_2S_2. A yield of $(1.2 \pm 0.2) \times 10^{-3}$ molecules eV^{-1} of H_2S_8 and a $(7.0 \pm 1.0) \times 10^{-4}$ molecules eV^{-1} of S_8 were observed. Consistently, calculations using the 10.49 eV photoionization data, yields $(4.6 \pm 0.2) \times 10^{-3}$ molecules eV^{-1} H_2S_2, $(1.1 \pm 0.5) \times 10^{-3}$ molecules eV^{-1} H_2S_8, and $(6.8 \pm 0.3) \times 10^{-4}$ molecules eV^{-1} of S_8. Table 1 summarizes the calculated photoionization cross sections, yields and the product percentages obtained from photoionization energies 10.82 eV and 10.49 eV."

5) In the conclusion of the paper, the authors state that "Although the conversion rate of hydrogen sulfide to molecular sulfur of about 4 % as derived in our experiments might appear low, this number can be placed in astronomical context. ». What is molecular sulphur in this context? S8?

S_8, yes. To be clearer and streamlined, molecular sulfur is reworded to be octasulfur. (lines 371-372)

The statement "Although the conversion rate of hydrogen sulfide to molecular sulfur of about 4 % as derived in our experiments might appear low, this number can be placed in astronomical context." now reads as "Although the conversion rate of hydrogen sulfide to octasulfur of about 4 % as derived in our experiments might appear low, this number can be placed in astronomical context."

6) Since the paper ends with this sentence « … thus eventually resolving the interstellar sulfur puzzle. », I think more discussion is needed on the astrophysical implications (even if it is in the complementary notes).

We have expanded the argumentation in favor of the claim. The changes are presented below.

Astrophysical implications are discussed in lines 355-358.

"…the sublimation temperatures of higher order sulfanes and octasulfur identified in these hydrogen sulfide ices span up to 330 K. Simulations, or models can utilize these novel volatiles and possible reaction pathways to update the inventories, eventually reaching to realistic predictions about these regions of ISM."

Also, the detectability of the products is discussed in lines 362-364.

"The identified products: sulfanes and octasulfur, should be observable subliming to the gas phase of warmer regions of the ISM above their respective sublimation temperatures, via radio or far infrared (400 – 200 cm^{-1}) measurements.[70]"

> The experiments show that only 33% of H2S is converted. Is the 67% remaining consistent with the non detection of H2S in interstellar ices? Is the remaining H2S % compatible with the amount observed in comets?

Please refer to the inclusion on lines 337-347 discussing the implications of hydrogen sulfide in ices and comets from the current study.

"Pristine hydrogen sulfide sublimes at a relatively low temperature of 90 K, but in the presence of less volatile irradiation products or other components such as water entrapping hydrogen sulfide in the matrix, hydrogen sulfide can co-sublime at warmer temperatures. In these laboratory simulation experiments, an ice thicker than the penetration depth of energetic electrons is utilized to avoid any reactions at the interface of the ice with the substrate (silver wafer). Thus, FTIR measure of 33% of reactants converted to products cannot be compared with the interstellar ice composition of hydrogen sulfide. However, if we consider the conversion rate of ice processed by impinging electrons, 80% of the destructed hydrogen sulfide were identified converted to sulfanes and octasulfur. Nevertheless, efficient conversion of hydrogen sulfide upon ionizing radiation does not imply an absence of hydrogen sulfide in interstellar ices. The observation of about 1% hydrogen sulfide (with respect to water) in several comets[21,65] cannot be quantified with the present study either."

> Could the identified products be detected in the gas-phase or in the ices considering their observability and their amount?

Yes, considering the yields, they should be observable. Please refer to the lines 362-364

"…The identified products: sulfanes and octasulfur, should be observable subliming to the gas phase of warmer regions of the ISM above their respective sublimation temperatures, via radio or far infrared (400 – 200 cm^{-1}) measurements.[70]"

Reviewer #2

The authors present laboratory results of H2S ice at 5K processes by electron beams at various energies. The analysis demonstrates the formation of a wide array of sulfanes and of S8. The authors suggest that this process can account for the observational dearth of sulfur species in cold molecular clouds.

1) In my opinion the authors overstate the significance of the 'interstellar sulfur depletion problem'. We can see sulfur emission in hotter regions, HII, photdissociation regions, other star forming regions. We know the sulfur is there in the cold clouds, it's just hard to detect. And, italicizing 'interstellar sulfur depletion problem' is rather annoying.

Thank you for the comment. The paper aimed to discuss the chemical changes undergoing in the ices of hydrogen sulfide and to reflect and tie the key findings to currently undetected sulfur species in the cold molecular clouds. Please note that italicizing is removed.

Introduction to Sulfur in cold molecular clouds that's not been detected yet is improved in lines 32-35.

"Astronomers and astrochemists theorize that this missing gas-phase sulfur is likely deposited onto interstellar nanoparticles, also referred to as carbonaceous and silicate dust particles (or simply "interstellar grains"),[8,10] but both observational information and experimental evidence are lacking."

2) Another sulfur depletion problem has been identified for planetary nebulae. This should be discussed here, although the cause is quite different. See, e.g., Tan ApJL 2024 961 L47.

Please refer to the inclusion below. (lines 348-352)

"...Even though the analog ices studied here can be utilized to model the transition of ices coated on dust from denser clouds to star forming regions, a sulfur anomaly is reported towards planetary nebulae (PN) as well.[66] Circumstellar sulfur deficits in oxygen rich objects are predicted to be in small molecules of SO, SO_2, H_2S, or CS, and in carbon rich objects, via magnesium or iron sulfides, but underestimation of ionized sulfur species in the gas phase is seen in many current model studies.[67,68] …"

3) The experimental technique and results are excellent and I recommend publication for that reason.

Thank you.

4) Thioacids - aren't they RCOSH rather than HSCR?
thioamides - aren't they RCSNR' rather than RCSR'?

Thioacids RCSH is changed to HSOCR and thioamides RCSR' changed to RCSNR'. (line 39-40)

5) lines 250-251 and maybe elsewhere - S8 is the thermodynamically favored form of elemental sulfur. A reference to this should be given , e.g., Lyons J Sulf Chem 2008 or some of the references therein.

A reference was added for this.

6) line 105 - please give or restate reference for S8 in Ryugu.

Reference restated, thank you.

7) lines 223-224 - please give supporting calculations for expected abundances of 32S733S and 32S634S2 and compare to reported percentages.

These calculations are performed using combinatorial statistical distribution and natural isotopic abundances. Please refer to the changes in lines 221-226 for clarity.

The section "To investigate the presence of H_2S_8 in *m/z* = 258, which is shared with $^{32}S_7{}^{34}S$, the natural isotopic distribution expected in mass channels from *m/z* = 256 to *m/z* = 262 for S_8 were considered. The signal at *m/z* = 257 belongs to $^{32}S_7{}^{33}S$, a 4.25% distribution of S_8 signal, whereas at *m/z* = 260, $^{32}S_6{}^{34}S_2$ should be present at an abundance of 3.78%. The signal observed at *m/z* = 260 may contain signal for both $H_2{}^{32}S_7{}^{34}S$ and $^{32}S_6{}^{34}S_2$." now reads "To investigate the presence of H_2S_8 in *m/z* = 258, which is shared with $^{32}S_7{}^{34}S$, the natural isotopic distribution for S_8 signal was considered. Natural isotopic distribution of sulfur is well known in literature.[51] For S_8, the signal distribution expected in mass channels *m/z* = 256 to *m/z* = 262 can be calculated utilizing the natural isotope probabilities and the combinations of isotopes combinedly resulting each mass. (Supplementary Information) For *m/z* = 257, only contributor is $^{32}S_7{}^{33}S$, a 4.25% distribution of S_8 signal. Whereas *m/z* = 260, isotopologous channel of S_8, $^{32}S_6{}^{34}S_2$ is only a minor contributor with only 3.7%."

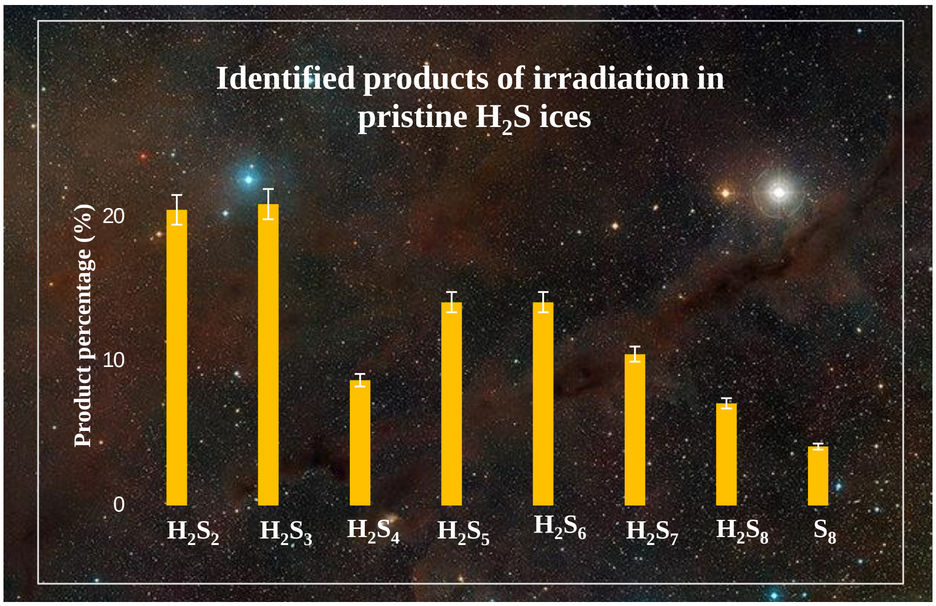
The permutational equation is included in supplementary notes (lines 17-27)

"In calculations to find out the isotopic mass distribution of S_8 in mass channels *m/z* = 256 to *m/z* = 260, the natural isotopic distribution of sulfur[1] and permutational equations were utilized. For each mass channel, the contribution from each combination (A) calculated via: $A = \frac{n!}{a!b!c!} {P_1}^a {P_2}^b {P_3}^c$, where n is the total number of atoms in the molecule, a,b,c are the isotopes in the considered permutation, and P_1, P_2, P_3 are the abundances of each isotope. As an example, for *m/z* = 256, only eight of ^{32}S can contribute to *m/z* = 256, thus a 66.4% (0.950^8) of S_8 signal. Similarly, for *m/z* = 257, only possible contributor is $^{32}S_7{}^{33}S$. Contribution of S_8 into the *m/z* =257 via $^{32}S_7{}^{33}S$ can be calculated as $\frac{8!}{7!1!}\times(0.950)^7\times(0.0076)$: 4.25%.

But for m/z = 258, two possible contributors of S_8 existing, ${}^{32}S_6{}^{33}S_2$ and ${}^{32}S_7{}^{34}S$. Likewise, the contribution of ${}^{32}S_6{}^{33}S_2$ to m/z = 258 would be $\frac{8!}{6!2!}\times(0.950)^6\times(0.0076)^2$: 0.01% and contribution of ${}^{32}S_7{}^{34}S$ to m/z = 258 would be $\frac{8!}{7!1!}\times(0.950)^7\times(0.0422)$: 24.8%. For signal at m/z = 260 from S_8, via ${}^{32}S_6{}^{34}S_2$ is only a minor contributor with only $\frac{8!}{6!2!}\times(0.950)^6\times(0.0422)^2$: 3.7%."

8) The results given in Table 1 seem like they would make a nice figure plotted as abundance vs S chain length.

Thank you for your suggestion. A new figure is included as supplementary figure 7 summarizing the products.



Supplementary Figure 7: Irradiation products of the hydrogen sulfide ice identified via PI-ReToF-MS.

9) Can you comment on the astronomical detectibility of the sulfane chains, H2Sn

Please refer to the inclusions on lines, 362-364. Thank you!

"…The identified products: sulfanes and octasulfur, should be observable subliming to the gas phase in warmer regions of the ISM above their respective sublimation temperatures, via radio or far infrared (400 – 200 cm^{-1}) measurements.[70]"

10) Thank you for including your ab initio details.

Thank you for your valuable comments.

Reviewer #3

My main objection to publication in Nature Communications is that the manuscript in its current state does not meet a specific condition required for publication in Nature journals: that "for a selective journal like Nature Communications, we would typically expect the paper to provide novel insights to the specific field" (quoted directly from the "For Reviewers" page on the Nature Communications website). The current manuscript does not meet this criterion on at least two counts. Firstly, the radiolytic synthesis of polysulfanes as a result of irradiating H2S astrophysical ice analogues at low temperatures is not a new result. Previous studies, including studies that have combined experimental and theoretical work, have repeatedly demonstrated this (see works by, for example, Jiménez-Escobar et al., 2012, ApJL 751, L40; Cazaux et al., 2022, A&A 657, A100; Carrascosa et al., 2024, MNRAS 533, 967; Li et al., 2025, PCCP 27, 5961).

As far as I can tell, the only difference between those studies and the present work is the utilisation of the extremely sensitive and advanced technique of PI-ReToF-MS to detect polysulfane homologs up to H2S11; whereas previous studies were only able to detect homologs up to and including H2S9. The extension of the identified homolog series from H2S9 to H2S11, though certainly academically interesting, is not so novel as to merit publication in Nature Communications.

Moreover, the only sulfur allotrope identified by the present study was the most stable S8 crown structure. In this regard, this study is actually more limited than previous experimental and theoretical works, which have demonstrated the synthesis of several sulfur allotropes Sn as a result of the irradiation of H2S ices (see works by, for example, Mahjoub et al., 2017, ApJ 846, 148; Startsev, 2016, Kinetics & Catalysis 57, 511; Shingledecker et al., 2020, ApJ 888 52; Cazaux et al., 2022, A&A 657, A100).

Thank you for your comment. We respectfully disagree with this referee. Even though H2S ices were studied before, the previous studies were either incomplete, incorrect, or both.

On the other hand, the current study aimed at a comprehensive, scientifically correct understanding of the irradiation products of the pure hydrogen sulfide ices. Novel identifications of the current study can be listed as follows:

(lines 292-294)

"Isomer specific identifications of HSSH (*m/z* = 66), HSSSH (*m/z* = 98) were possible for H_2S_2 and H_2S_3 by fine tuning the photoionization energy at the TPD phase."

(lines 295-296)

"No previous study experimentally observed octasulfur in the processed ices, even if octasulfur was assumed to form on these model ices that identified molecular sulfurs (S_n).[31,41–44]"

(lines 296-298)

"…These sulfanes and octasulfur (S_8) may hold the key to the missing sulfur of the dense clouds; polysulfanes undergo fractionated sublimation from 150 K to 297 K; octasulfur sublimed at 310 K in the warm-up phase…"

Also, in lines 103-105

"Our study further affords persuasive evidence on the molecular level of the source of cyclic octasulfur (S_8) detected recently in the carbonaceous asteroid (162173) Ryugu…"

Yes, in these pure ices of hydrogen sulfide, no other molecular sulfur (S_n) other than octasulfur (S_8) were observed, but fragments in the respective mass channels of S_n. Please refer to inclusions on lines 290-292.

"…Signals observed at mass channels corresponding to molecular sulfur (S_n) observed to be fragments of the higher order sulfane (H_2S_{n+1}), extending the observations by Carrascosa, H. *et al.* to all sulfanes observed.[33]"

And in lines 332-336:

" The presence of other components in these interstellar model ices such as water can affect the reactions forwarded via parallel competing reactions. If the energetics of the steps are favorable, the photochemical reactions would proceed in these ices, regardless of the size or complexity of product molecules.[29,64] In pure hydrogen sulfide ices, in the abundance of hydrogen atoms, sulfanes seem the most favorable product in comparison to molecular sulfurs (S_n), except for octasulfur. "

Further experiments utilizing ionization energies of each conformer of S_n species should be able to explain this further but unfortunately it falls out of the scope of the current study.

Please note that previous work are updated in lines 74-81:

"In addition to pure H_2S ices, mixed ice experiments have been reported incorporating the major species detected in the interstellar ices. Analog ices of H_2S or H_2S/H_2O via UV irradiation,[32–34] X-ray processing,[35] energetic electron irradiation,[36] protons,[37] or hydrogen atom interactions[38] conducted so far have identified disulfane (H_2S_2). Processing of H_2S/CO ices also found to form H_2S_2.[19,39,40] In these processed H_2S and mixed ices, sulfanes up to H_2S_7 were identified via their subliming mass fragments.[33,41,42] A recent study by Carrascosa, H. *et al.*, displayed the sulfanes (H_2S_4 and H_2S_5) leading to molecular sulfur fragments (S_3^+ and

S_4^+).[33] Laboratory experimental studies of pristine H_2S or mixed ices also observed allotropes of sulfur (S_n: S_2, S_3 and S_4).[31,41,43,44]"

Secondly, I feel that some of the statements made by the authors as to the impact of the work are over-exaggerated. Specifically, in lines 85-89, the authors claim that they "…afford a compelling solution to the interstellar sulfur depletion problem…"; while in lines 102-105 they state that their "…study affords persuasive evidence … of the source of elemental sulfur … in the carbonaceous asteroid (162173) Ryugu, thus, documenting for the first time the link between interstellar matter and planetary bodies in solar systems including our own." Finally, in line 301 it is claimed that these results could "…thus eventually resolve the interstellar sulfur puzzle".

Thank you for your comment. These statements are re-worded as follows: lines 87-89

The statement "…by exploiting tunable photoionization reflectron time-of-flight mass spectroscopy (PI-ReToF-MS), we afford a compelling solution of the *interstellar sulfur depletion problem* by revealing the very first complete inventory of sulfur-bearing molecules synthesized in astrophysically-relevant model ices of hydrogen sulfide exposed to proxies of Galactic Cosmic Rays…" now reads "…by exploiting tunable photoionization reflectron time-of-flight mass spectroscopy (PI-ReToF-MS), we reveal the inventory of sulfur and hydrogen bearing molecules synthesized in astrophysically-relevant model ices of hydrogen sulfide exposed to proxies of Galactic Cosmic Rays…"

In lines 103-106, the statement "Our study further affords persuasive evidence on the molecular level of the source of elementary sulfur (S_8) detected recently in the carbonaceous asteroid (162173) Ryugu, thus, documenting for the first time the link between interstellar matter and planetary bodies in solar systems including our own." now reads "Our study further affords persuasive evidence on the molecular level of the source of cyclic octasulfur (S_8) detected recently in the carbonaceous asteroid (162173) Ryugu, thus, documenting for the first time the link between interstellar matter and planetary bodies in solar systems including our own"

Lines 375-379

The statement "…Therefore, only a minor fraction of elemental sulfur synthesized in the molecular cloud from which our Solar System originated had to be eventually delivered to proto Earth to rationalize the contemporary abundance of present-day sulfur on Earth, thus eventually resolving the interstellar sulfur puzzle." now reads "Trapped amongst refractory or less volatile matrices, only a minor fraction of elemental sulfur synthesized in the molecular cloud from which our Solar System originated had to be eventually delivered to proto-Earth and other scattered objects, thus rationalizing the contemporary geochemical ties between the interstellar clouds and objects in circumstellar discs, eventually reaching solutions to the interstellar sulfur puzzle."

To state that the results of this study solve the interstellar sulfur depletion problem is, in my opinion, somewhat of an exaggeration. Firstly, the implications of this study are only valid if H2S is indeed present in interstellar ices and, to date, no observations of ices in dense molecular clouds or proto-stellar regions have found any evidence of the presence of H2S (see, for example, McClure et al., 2023, Nature Astronomy 7, 431; Rocha et al., 2024, A&A 683, A124; Rocha et al., 2025, A&A 693, A288).

Of course, it is entirely possible that these non-detections are due to the inherently weak infrared absorption features of H2S.

Please note that the claims are updated and we have improved the discussion to justify. Thank you.

Even though hydrogen sulfide is not observed on interstellar ices, H_2S is observed in comets, meteorites and modelling studies predict the presence as well. The limitations in observation techniques should be the cause of non-detection of H_2S in interstellar ices.

Following are included in the introduction to justify the use of hydrogen sulfide in these analog ices. (Lines 45-49)

"Although the simplest sulfur containing molecule: hydrogen sulfide (H_2S) has not been observed yet in interstellar ices via infrared observation,[13–15] chemical models predict that hydrogen sulfide is present in these ices.[16] Since infrared interstellar ice analyses displayed evidence for compounds more volatile than hydrogen sulfide (such as methane) still remaining on the ices,[13] non-detection of hydrogen sulfide is likely due to the weak infrared features."

Additionally, lines 53-58 identifies the detection of H_2S in comets.

"…the interstellar sulfur reservoir has been linked to observations of comets where sulfur-containing molecules such as hydrogen sulfide (H_2S), sulfur monoxide (SO), sulfur dioxide (SO_2), carbonyl sulfide (OCS), and carbon disulfide (CS_2) have been detected.[20–23] Hydrogen sulfide is the most common sulfur species with an abundance of 1.5% with respect to water identified in the comet C/1995 O1 (Hale-Bopp)[20] and at a level of 0.5% in comet C/2014 Q2 (Lovejoy).[23] Hydrogen sulfide (H_2S) was identified in the nitrogen-rich asteroid (101955) Bennu as well.[24]"

Also included is an discussion on the limitations of FTIR, lines 358-362.

"Visible residues left on the substrates at 330 K did not show any characteristic features in the mid-IR region, thus reiterating the functional limitations of FTIR in interstellar characterizations. Therefore, it should be noted that interstellar observations relying on a single technique, such as infrared heavily undermines the present-day knowledge of realistic ice compositions."

However, even if one were to assume that H2S is present in these ices, then it would almost certainly be a minor component of an ice dominated by non-sulfur-bearing molecules, such as H2O, CO, CO2, NH3, CH4, etc. The presence of these other molecules will surely alter the chemical reactions induced within the ice by galactic cosmic rays and, indeed, previous experimental studies on the radiation chemistry of H2S mixed with other icy species have shown that significant quantities of sulfur can be sequestered into volatile organic or inorganic molecules that should be observable in either the ice phase, or else in the gas phase after desorption or sublimation (see, for example, Moore et al., 2007, Icarus 189, 409; Garozzo et al., 2010, A&A 509, A67; Jiménez-Escobar et al., 2014, MNRAS 443, 343; Chen et al., 2015, ApJ 798, 80; Mahjoub et al., 2017, ApJ 846, 148). Hence, the yield of large sulfur molecules is likely reduced in these more realistic ices.

Thank you for your comment. In lines 332-336 discusses the alterations that would cause in the reactions in mixed ices compared to pure H_2S ices:

"The presence of other components in these interstellar model ices such as water can affect the reactions forwarded via parallel competing reactions. If the energetics of the steps are favorable, the photochemical reactions would proceed in these ices, regardless of the size or complexity of product molecules.[29,64] In pure hydrogen sulfide ices, in the abundance of hydrogen atoms, sulfanes seem the most favorable product in comparison to molecular sulfurs (S_n), except for octasulfur."

Effects of other constituents in the ice mixtures towards these identified products and the changes of yield will be studied in future studies.

Moreover, and perhaps critically, the authors' suggestion that the radiation-driven conversion of H2S to elemental sulfur (which is not active in the mid-infrared region; Trofimov et al., 2009, Journal of Sulfur Chemistry 30, 518) is responsible for the apparent sulfur depletion problem is not in line with contemporary geo/cosmochemical data on the sulfur composition of proto-planetary disks. Specifically, it is known that 80-95% of the sulfur in these disks must be significantly more refractory than H2O, favoring its incorporation into sulfide minerals rather than allotropic chains or rings (see Kama et al., 2019, ApJ 885, 114 for further details). Hence, it is more likely that sulfide minerals that are difficult to observe in the infrared constitute the majority of the depleted sulfur in dense molecular clouds, and it is likely these minerals that are largely incorporated into carbonaceous asteroids and other rocky solar system bodies.

Thank you for your comment. It is agreed that the majority of all these identified products are expected to be in the gas phase in temperatures above 340 K. Octasulfur in the study is reflected as a possible sink of sulfur temperatures up to 340 K in the solid state. (lines 352-358)

"…Current models on protoplanetary disks favor interpreting the sulfur composition of interstellar dust available to incorporate in planet formation predominantly of FeS and other sulfide minerals at higher temperatures relying on the sublimation temperatures of water or smaller sulfur chains (S_n) subliming below 200 K,[69] the sublimation temperatures of higher order sulfanes and octasulfur identified in these hydrogen sulfide ices span up to 330 K. Simulations, or models can utilize these novel volatiles and possible reaction pathways to update the inventories, eventually reaching to realistic predictions about these regions of ISM."

Also, about the detectability of these formed molecules in lines 362-364:

"The identified products: sulfanes and octasulfur, should be observable subliming to the gas phase in warmer regions of the ISM above their respective sublimation temperatures, via radio or far infrared (400 – 200 cm^{-1}) measurements.[70]"

The study further extends the probability of only a small amount of thus created products can be trapped in refractory matrices and transferring to planet and star forming regions. (lines 375-379)

"Trapped amongst refractory or less volatile matrices, only a minor fraction of elemental sulfur synthesized in the molecular cloud from which our Solar System originated had to be eventually delivered to proto-Earth and other scattered objects, thus rationalizing the contemporary geochemical ties between the interstellar clouds and objects in circumstellar discs…"

The authors' claim that their results "…afford a compelling solution to the interstellar sulfur depletion problem" is therefore not convincing. At best, these results provide better insight into one possible mechanism of sulfur depletion; however, the sequestration of sulfur into allotropes cannot account for all the missing sulfur for the reasons described above. In light of this, I would strongly urge the authors to tone down the implications of their results.

Please note the improvements to the claim below. (lines 87-90)

Previous "Here, by exploiting tunable photoionization reflectron time-of-flight mass spectroscopy (PI-ReToF-MS), we afford a compelling solution of the *interstellar sulfur depletion problem* by revealing the very first complete inventory of sulfur-bearing molecules synthesized in astrophysically-relevant model ices of hydrogen sulfide exposed to proxies of Galactic Cosmic Rays (GCRs)[34] over typical lifetimes of cold molecular clouds from 10^6 to a few 10^7 years at temperatures of 5 K." now reads "Here, by exploiting tunable photoionization reflectron time-of-flight mass spectroscopy (PI-ReToF-MS), we reveal the inventory of sulfur and hydrogen bearing molecules synthesized in astrophysically-relevant model ices of hydrogen sulfide exposed to proxies of Galactic Cosmic Rays (GCRs)[41] over typical lifetimes of cold molecular clouds from 10^6 to a few 10^7 years at temperatures of 5 K."

An implication of the study is also in lines: 97-99.

"These studies provide an experimental testimony on two key sinks of sulfur carrying molecules: polysulfanes with up to eleven sulfur atoms (H_2S_n; n = 2-11) and octasulfur (S_8) exclusively in the *crown* conformation…"

The authors may also consider the following (comparatively) minor points:

1) In the methods section, you state that your ices have thicknesses ranging between 1.0-1.6 μm, but that the average penetration depth of your electrons is only about 350 nm, and that 90% of the energy is deposited within the top 420 nm or so. This means that the vast majority of the ice remains unprocessed.
   Yes, the ices are deposited thicker than the calculated penetration depth in order to make sure no reaction would undergo at the interface of ice and the substrate (silver wafer in this case). Please refer to the new inclusions. (lines 339-341)

"In these laboratory simulation experiments, an ice thicker than the penetration depth of energetic electrons is utilized to avoid any reactions at the interface of the ice with the substrate (silver wafer)."

In lines 300-308, a discussion about the photochemical reactions undergoing in the ices is included.

"Proxies for the effect of GCRs on the icy grains over a typical lifespan of cold molecular clouds, are replicated in these experiments at astrophysically relevant temperatures and pressures. The secondary electron cascades formed in the ices are replicated with energetic electron irradiation. These electrons deposit the energy that drives photochemical reactions on the reagents in the ice. Having identified the products formed on processed hydrogen sulfide ices resulting from energetic electron radiation, potential formation mechanisms are investigated to link the reactants to the identified products. During the irradiation of the deposited ices to a typical depth of 350 nm, depositing a dose of 7 eV molecule^{-1}, the energetic electrons can easily break the S-H bonding of hydrogen sulfide (H_2S) generating suprathermal sulfur and hydrogen atoms.[59,60]"

   What are the astrophysical and astrochemical implications (especially with regards to sulfur chemistry) of having a heavily processed upper layer of the ice and a comparatively pristine lower layer?

Included in lines 337-347 is a discussion on the implications of irradiation products in these hydrogen sulfide ices on interstellar ices or comets.

"Pristine hydrogen sulfide sublimes at a relatively low temperature of 90 K, but in the presence of less volatile irradiation products or other components such as water entrapping hydrogen sulfide in the matrix, hydrogen sulfide can co-sublime at warmer temperatures. In these laboratory simulation experiments, an ice thicker than the penetration depth of energetic electrons is utilized to avoid any reactions at the interface of the ice with the substrate (silver wafer). Thus, FTIR measure of 33% of reactants converted to products cannot be compared with the interstellar ice composition of hydrogen sulfide. However, if we consider the conversion rate of ice processed by impinging electrons, 80% of the destructed hydrogen sulfide were identified converted to sulfanes and octasulfur. Nevertheless, efficient conversion of hydrogen sulfide upon ionizing radiation does not imply an absence of hydrogen sulfide in interstellar ices. The observation of about 1% hydrogen sulfide (with respect to water) in several comets[21,65] cannot be quantified with the present study either."

2) In the manuscript, you mention that the conversion yield of H2S to S8 was 6±1% (line 252), but then later in the manuscript (line 295) you use a conversion yield of 4% to calculate the amount of sulfur that could be produced in ices in the TMC. Is this a typo or did I miss something?

It is a typo. Thank you, this is fixed

3) I think you have a typo on line 211; an extra 'l' after the comma and before "boat".

Thank you, this is fixed.

Reviewer#1

The authors have addressed all my concerns and the paper can be accepted as it is.

Thank you!

Reviewer#2

I've addressed most of the essential points I wished to raise in my first review. The authors have made a sincere effort to address those points. I therefore recommend the paper for publication.

Again, I think the measurements are first rate and worthy of publication in Nat Comm.

Thank you!

Finally, just for a moment, let's consider all of those 4th - 7th row elements also suffering from a depletion problem in the ISM. ;)

Thank you for your suggestion.

Reviewer#3

I thank the authors for taking the time to respond to my comments in a thorough a professional manner. The manuscript is now much improved. In particular, the novelty of the study is now much more apparent and the implications of their results with regards to our understanding of the interstellar sulfur depletion problem have been significantly toned down to more appropriate levels. I believe this manuscript is now publishable, following two (very minor) corrections:

1) Lines 332-336 of revised manuscript: I believe there is a small mistake here. In these lines, the authors state that "...if the energetics of the steps are favourable, the photochemical reactions would proceed..." It is important not to mix up photochemical and radiation-chemical reactions, as there are many key differences between these types of chemistry (e.g., the former is limited to selection rules, the latter is not). Here, I believe the authors are referring to chemistry induced by the incident keV electrons, which is radiation-chemical in nature and not photochemical. A minor edit would suffice to correct this mistake.

Thank you! Yes, it is corrected. Please note the lines 333-336 "If the energetics of the steps are favorable, the photochemical reactions would proceed in these ices,…" now reads "If the energetics of the steps are favorable, these radiation initiated reactions would proceed in these ices,…".

2) Lines 377-379 of revised manuscript: I would strongly urge the authors to avoid using the

word "solution" when referring to the implication of their results to the sulfur depletion problem. These results, although certainly informative and useful, do not "solve" the sulfur depletion problem, but provide better insight and understanding to the problem. I would therefore strongly urge the authors to rephrase the sentence "...in circumstellar discs, eventually reaching solutions to the interstellar sulfur puzzle." to something more like "...in circumstellar discs, providing useful insights to and clearer perspectives on the interstellar sulfur puzzle."

Thank you for your comment. This is addressed as below in lines 375-379, "in circumstellar discs, eventually reaching solutions to the interstellar sulfur puzzle." now reads "…in circumstellar discs, providing insights to the interstellar sulfur puzzle."