**Response to Reviewers**

**Referee: 1**

***Comments to the Author***

This study presents a well-executed and compelling investigation into the first experimental formation of thiocarbonic acid in interstellar ice analogs under simulated astrophysical conditions, representing a significant advancement in the field. This work addresses a significant question in astrochemistry regarding the sulfur depletion problem and contributes valuable insights into the formation pathways of sulfur-bearing molecules in the interstellar medium. The selection of a full paper format is appropriate for the scope and depth of the presented work. The title is concise, unambiguous, and accurately reflects the content of the article, incorporating relevant search terms such as “experimental formation”, “thiocarbonic acid”, and “interstellar ice analogs”, thereby maximizing its discoverability. The abstract is well-structured and self-contained, effectively summarizing the key results, methodologies, and implications of the research without requiring reference to the main body of the text. The novelty of the study, namely the first experimental formation of thiocarbonic acid, is clearly stated, alongside the contextual relevance to astrochemistry and the sulfur depletion problem. This article is highly suitable for Physical Chemistry Chemical Physics, given the study’s emphasis on detailed physical chemistry experiments utilizing ice analogs, VUV spectroscopy, and mass spectrometry, complemented by state-of-the-art computational quantum chemistry to elucidate the underlying processes pertinent to astrochemistry. Publication in PCCP is recommended following consideration of the minor points outlined below. Despite these limitations, it is clear that a tremendous amount of work has been done in both the experimental and theoretical sections.

**Reply**: Thank you very much for the careful review of our work and for providing us with suggestions. We replied to your comments or suggestions below. All changes are highlighted in yellow in the revised manuscript.

1. In Reference 22 related to the article “On the formation of carbonic acid (H2CO3) in solar system ices”, the work you cite examines two double-step mechanisms after H2O → OH + H reaction:  
1) H + CO2 → HOCO (ΔG = −11.7 kJ mol-1) and HOCO + OH → H2CO3;  
2) OH + CO2 → HOCOO (ΔG = −26.4 kJ mol-1) and HOCOO + H → H2CO3.  
Furthermore, the initial addition of the hydroxyl radical was found to be more exoergic compared to an atomic hydrogen addition. That same study noted the failure to detect the HOCOO radical. Even considering the oxygen-sulfur analogy, why was the reaction pathway SH + CS2 → HSCSS, HSCSS + H → H2CS3 not considered a priori, while only H + CS2 → HSCS, SH + HSCS → H2CS3 (Scheme 1, Figure 10, equations 2 and 3 in your work) was examined? Specifically, was the radical HSCSS not observed in this case? It would be of interest to see a comparison of the energetic differences between the two channels for sulfur.

**Reply**: Thank you for your comment. The second possible reaction pathway (SH + CS2 → HSCSS, HSCSS + H → H2CS3) was not considered for two reasons: the HSCSS radical was not observed from our FTIR results (Figure 3) and the first addition (SH + CS2 → HSCSS, ΔrG= −22 kJ mol–1) is 43 kJ mol–1 less exoergic, compared to the one of the other reactionpathway (H + CS2 → HSCS, ΔrG = −65 kJ mol-1).

For clarification we have added the sentences in the introduction section (page 4):

“An alternative reaction pathway following H2S homolysis (Equation 1) is shown in Equations (2’) and (3’). However, based on the study from Zheng and Kaiser on the formation of carbonic acid,25 this pathway leading to the formation of thiocarbonic acid was ruled out, as in our case reaction (2’) is 43 kJ mol–1 less exoergic than reaction (2).”

Free enthalpy energies (ΔrG) as well as Equations (2’) (SH + CS2 → HSCSS) and (3’) (HSCSS + H → H2CS3) have been added to the manuscript for clarity.

2. Regarding the oxygen-sulfur analogy, no direct comparisons were made within the article for either experimental or theoretical investigations. S-H and O-H bonds are known to exhibit notable differences in their properties stemming from the difference in electronegativity and atomic size of sulfur and oxygen: sulfur is less electronegative than oxygen, resulting in a less polar bond, S-H bonds are weaker hydrogen bond donors than O-H bonds.

**Reply**: Thank you for your suggestion. Direct comparison between oxygen and sulfur atoms properties has been included in the introduction in order to support our experimental and theoretical investigations. Please refer to the inclusion below (page 4):

“Sulfur counterparts of oxygenated molecules exhibit properties that are noticeably different stemming from the electronegativity difference between sulfur (χ(S) = 2.64)21 and oxygen (χ(O) = 3.61),21 and the fact that sulfur (R = 87 pm)22 is significantly bigger than oxygen (R = 47 pm);22 consequently, S–H bonds are less polarized than O­–H ones, and are weaker hydrogen bond donors.23 Even though properties can be different between those two atoms, their reactivity remains similar as they both belong to the chalcogen family. Indeed, a previous study by Wang *et al.* revealed that replacing CO–H2O precursors with CO–H2S yielded the sulfur counterpart of formic acid.24”

References below have been added:

“21 D. Bergmann and J. Hinze, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 150-163.

22 D. C. Ghosh and R. Biswas, *Int. J. Mol. Sci.*, 2002, **3**, 87-113.

23 K. Wendler, J. Thar, S. Zhan, and B. Kirchner, *J. Phys. Chem. A.*, 2010, **114**, 9529-9536.”

3. The article mentions that energetic barriers may be somewhat changed in a condensed phase compared to gas-phase calculations due to the influence of surrounding molecules. Returning to point 2 regarding the differences in hydrogen bonding between S-H and O-H bonds, what implications might these distinctions have within a condensed phase, particularly in the context of your experimental findings? The incorporation of these oxygen-sulfur comparisons would significantly strengthen the argumentation presented in the article.

**Reply**: These distinctions might imply closer results between condensed phase experiments and gas phase calculations for energy barriers with sulfur-bearing molecules. We have added a sentence in the discussion section as follows (page 11):

“However, sulfur being a weaker hydrogen bond donor compared to oxygen,23 sulfur-containing ices are less organized in the condensed phase and energy values may be consequently closer to gas phase calculations.”

4. In your article there was a statement “IEs were calculated for dimer structures focusing on the three most stable ones” specifying Reference 52 related to the article “Insights into the structure and stability of the carbonic acid dimer”. You had tried to narrow down the range of H2CS3 dimers studied, again based on the analogy with H2CO3 in the paper with Reference 52. However, according to Reference 52 the most stable dimers shown in Figure 2 are (cis-cis)-(cis-cis), (cis-cis)-(cis-trans), and (cis-trans)-(cis-trans) isomers. For some reason, you have considered the (trans-trans)-(trans-trans) isomer (number 39 in Figure 5 of the paper with Reference 52) instead of the (cis-cis)-(cis-trans) isomer (numbers 2 and 4 in Figure 2 of the paper with Reference 52). Could you please explain this discrepancy? It is very unclear how the (trans-trans)-(trans-trans) isomer came to be classified as one of the most stable dimers. Have you calculated the other dimers before supporting this conclusion? This information is not present in the reviewed SI.

Moreover, how reasonable is it to make this oxygen-sulfur analogy and excluding all other dimer configurations, considering, firstly, that the energy refinements for the oxygen dimers in the 2010 paper with Reference 52 were performed with only double-zeta aug-cc-pVDZ basis set? Secondly, given that various combinations of hydrogen bonds play a crucial role in dimer formation, and as mentioned previously that S-H bonds are weaker hydrogen bond donors than O-H bonds.

The incorporation of all possible dimers would provide a more comprehensive and visually clear understanding of hydrogen bonding in sulfur-containing dimers, and would make the similarities to oxygen-containing systems much more apparent.

**Reply**: Indeed, calculation of the 40 possible dimer structures would give a complete overview of the sulfur-containing dimers. However, the aim of this study was not to identify the exact structure of the possible formed dimers but rather to understand their possible formation in order to assign Peak III and confidently conclude on the formation of thiocarbonic acid.

Based on the Reference 56 (previously 52), we did a selection on the dimer structures. We decided to study the three most stable ones (number 1(cc-cc), 2(cc-ct), 3(ct-ct)) and the least stable dimer structure (number 40 (tt-tt)) in order to have an idea on the possible formed and detected dimers with regard to their stability.

However, calculations for dimer number 40 did not converge (we did not reach a minimum), consequently we used calculations on the second least stable dimer structure (number 39 (tt-tt)). Moreover, dimers number 2 and 3 led to same IEs (2 (cc-ct =1b-1a): 7.93 eV, 3(ct-ct=1a-1a): 7.93 eV). That’s why, given that at first we were wondering about the possible conformer selective nature of the reaction, we choose to focus on dimer 3 rather than on dimer 2. To clarify our choices we have revised the sentence in the manuscript in the mass spectrometry section (page 10):

“IEs were calculated for dimer structures focusing on two of the three most stable ones (**1a-1a** and **1b-1b** as dimers **1a-1a** and **1b-1a** have the same IEs (Table S4)) and the least stable dimer structure we found (**1c-1c**), in order to investigate dimer formation and detection with regard to their stability.56”

Table S4 has been added to show the outputs of **1b-1a** dimer quantum calculations. The optimized geometry and harmonic frequencies (for cation and neutral) were incorporated in Table S7 and Table S8 respectively.

5. Despite the stated uncertainty of 0.04 eV in Tables 1 and 2, it would be beneficial for clarity to specify within the Computational Section that this value represents the computational uncertainty associated with the relative energies of isomers and adiabatic ionization energies, citing the appropriate source.

**Reply**: Thank you for your suggestion, the following reference has been added:

“49 J. Zhang and E. F. Valeev, *J. Chem. Theory Comput.,* 2012, **8**, 3175-3186.”

We have added the following sentence in the computational section (page 7):

“The IEs employ error analysis which takes into account the computational uncertainty of ± 0.04 eV49 and a correction of −0.03 eVcaused by the electric-field-induced Stark effect.24”

6. Given that the CCSD(T)-F12/cc-pVTZ-F12 method was employed for geometry optimizations in reactions related to H2CS3 formation, bypassing density functional theory, and considering the significant computational cost already invested, why was the possibility not explored of supplementing these calculations with cc-pVDZ-F12 and cc-pVQZ-F12 basis sets, followed by three-point extrapolation to the complete basis set limit?

**Reply**: The cc-pVTZ-F12 basis set produces the same quality of energies as the canonical cc-pV5Z basis set according to the reference DOI: 10.1063/1.5020436 (Győrffy, Werner, and Hans-Joachim Werner. *The Journal of Chemical Physics* 148.11, 2018), even though the title says the article is about analytic gradients.

7. In the Computational Section, it is stated that dimer optimizations and ZPVE calculations were performed using the ωB97X-D/aug-cc-pVTZ method. However, Table 2 reports ZPVE values as ZPVE(cc-pVTZ-F12), presumably implying “CCSD(T)-F12/cc-pVTZ-F12”. This inconsistency requires clarification.

**Reply**: Thank you for pointing it out. we have corrected it with “ZPVE(ωB97XD/aug-cc-pVTZ)” in the caption of Table 2.

8. In Table 2 only “dissociative ionization energy” should be used, not “dissociation ionization energy".

**Reply**: Thank you for the suggestion. We have fixed it.

9. The titles of Tables 1 and 2 should be slightly changed. This is not an “Error analysis”, that is why this phrase should be avoided. These tables simply show relative energies and IEs that you have obtained including error.

**Reply**: Thank you for the suggestion. We have removed the “Error analysis” phrase and revised the titles of Table 1 and Table 2.

**Referee: 2**

***Comments to the Author***

Coulaud et al. present the first preparation of thiocarbonic acid (H2CS3) and the potential 1c-1c dimer in interstellar ice analogs through simulated irradiation experiments, isomer-selective PI-ReToF-MS, and quantum chemistry calculations. This molecule serves as the counterpart to extraterrestrial carbonic acid (H2CO3), making it a promising candidate for future astronomical searches. Furthermore, its formation in the interstellar ices represents a significant step toward understanding the oxygen/sulfur chemistry in deep space, such as the sulfur depletion problem.  
The methods employed are state-of-the-art, and the manuscript is well written. I recommend its publication, contingent on the authors addressing the following comments:

**Reply**: Thank you very much for the careful review of our work and for providing us with suggestions. We replied to your comments or suggestions below. All changes are highlighted in yellow in the revised manuscript.

1)      On Page 9, in the second paragraph of mass spectrometry section. In Fig. 6a, the event I was assigned to the saturation of the MCP detector. Please include the TPD profile at m/z = 110 from the blank experiment.

**Reply**: Thank you for the suggestion. The TPD profile for *m/z* = 110 from the blank experiment has been added in Fig. S2.

Additionally, could author clarify why there are two peaks for the sublimation of CS2 in Fig. S2?

**Reply**: Thank you for the pointing it out. We noticed that the presence of two peaks for the sublimation of CS2 in Fig. S2 came from an error during the data plotting step. We have fixed it and the actual peak shape for CS2 at *m/z* = 76 was restored in Fig. S2. In our experiments, the saturation of the detector will likely happen when the number of counts is above 4000, leading to a nearly flat platform in the TPD profile. All three TPD profile (*m/z* = 34, 76, and 110) were superposed for added clarity. In addition, the caption of Fig. S2 have been modified as followed:

“**Fig. S2** TPD profiles of hydrogen sulfide (blue) at *m/z =* 34, carbon disulfide (green) at *m/z =* 76 and the co-desorption features at *m/z =* 110 (black) in unirradiated (blank) H2S−CS2 ice at 10.49 eV. For the TPD profiles of hydrogen sulfide and carbon disulfide, the unusual shape is caused by the saturation of the detector upon sublimation.”

2)      Please double-check the reference list, as some journal names are incorrect, for example, citation 21 should be “J. Phys. Chem. A”, not “J. Phys. Chem.”.

**Reply**: Thank you for your careful proofreading. This citation has been fixed and all the other references have been completely double-checked and corrected.