

Supplementary Information for:

**Formation of Dimethyl sulfide (CH_3SCH_3) and Ethanethiol ($\text{CH}_3\text{CH}_2\text{SH}$) in
Interstellar Analog Ices of Methane (CH_4) and Hydrogen Sulfide (H_2S)**

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Supplementary Note: Identification of sulfanes (H_2S_n ; $n = 2-11$) and elemental octasulfur (S_8)

Temperature programmed desorption (TPD) analysis revealed the presence of both sulfanes (H_2S_n , $n = 2-11$) and elemental octasulfur S_8 . Overlapping TPD profiles of ions at different mass-to-charge ratios (m/z) indicate lower-mass ions from fragmentation of the parent molecular ion, as indicated in Figure S4. Sulfane (H_2S_n) fragmentation to H_2S and an S_{n-1}^+ elemental sulfur fragment was observed for higher order sulfanes (H_2S_n , $n > 5$). Experiments with isotopically labeled ice mixtures $\text{CH}_4\text{-D}_2\text{S}$, and $\text{CD}_4\text{-H}_2\text{S}$ ices confirmed the assigned molecular formula at each m/z . Adiabatic ionization energies (IEs) for H_2S_n , ($n = 2-8$) molecules calculated at the F12-TZ//B3LYP/aug-cc-pVTZ and F12-TZ//B3LYP/aVTZ levels of theory including zero-point vibrational energy (ZPVE) corrections were utilized in identification of these molecules in the gas phase.¹ Sulfanes up to H_2S_{11} were identified and confirmed via deuterated ice experiments by a mass shift of 2 amu. In addition, the natural isotopic distribution of signal was observed in mass channels differing by 2 amu for ^{32}S versus ^{34}S for sulfanes and deuterated sulfanes, where the respective $\text{H}_2^{34}\text{S}^{32}\text{S}_{n-1}$ or $\text{D}_2^{34}\text{S}^{32}\text{S}_{n-1}$ are expected. TPD profiles of sulfanes H_2S_7 , H_2S_8 and H_2S_9 observed in methane and hydrogen sulfide ice at 9.34 eV photons in Figure S4 are replotted in Figure S5 as the signal intensities of the sulfanes H_2S_7 to H_2S_9 are relatively very low compared to the corresponding elemental sulfur fragments S_7^+ , S_8^+ and S_9^+ . At 9.34 eV, fragmentation of the parent ion is less intense in small sulfanes up to H_2S_5 . However, larger sulfanes exhibit fragmentation in which the fragment ions show greater intensity than their parent signals. Using the peak sublimation temperature of the S_9^+ fragment, the sublimation temperature of its predicted parent sulfane, H_2S_{10} , was determined to be 285 K. Likewise, exploiting the sublimation peak of S_{10}^+ fragment, the peak sublimation temperature of H_2S_{11} was determined to be 299 K. The sharp sublimation event with a peak at 313 K is due to the co-sublimation with subliming octasulfur (S_8).

The IEs and relative energies of six conformers and isomers of S_8 calculated at the F12-TZ single point level of theory with B3LYP/aug-cc-pVTZ geometries with a maximum error of ± 0.05 eV were used in analyzing octasulfur.¹ Top panel of Figure S6 displays the signal observed for $m/z = 256$ at each photon energy utilized in the irradiated methane (CH_4) and hydrogen sulfide (H_2S) ices at photon energies 10.49 eV, 9.34 eV, 8.75 eV, and 8.17 eV. At 9.34 eV and photon energies above, two-sublimation peaks are present, indicating the possibility of S_8 conformers/isomers.

Upon lowering the photon energy to 8.75 eV, which is below the IE of the *crown* conformer, no ion signal was observed. Therefore, only the *crown* isomer was formed and identified in the processed ices. In the deuterated ice experiment, $m/z = 256$ showed two sublimation peaks arranged the same as in the non-deuterated ice as well as in pure hydrogen sulfide ices reported before by Herath et. al.¹ A comparison of sublimation profiles of octasulfur in pure hydrogen sulfide ice versus mixed ices at varied photoionization energies is in Figure S6.

Overlapping sublimation temperatures and sublimation profiles were used to identify the contribution from sulfanes to the signal channels of elemental sulfur fragments (Figure S7). The deconvolution of the sublimation events of S_7^+ ($m/z = 224$), S_6^+ ($m/z = 192$) and S_5^+ ($m/z = 160$) was utilized to identify the origins of sublimation events at temperature ranges in the TPD phase of the experiment amongst the subliming elemental sulfur and the contribution from the fragmentation of sulfanes (H_2S_n) to H_2S and S_{n-1}^+ fragments (Figure S7). In $m/z = 160$ corresponding to S_5^+ ions, the first sublimation event with an onset sublimation temperature of 183 K was observed subliming earlier than H_2S_5 , where the onset sublimation temperature is at 195 K and H_2S_6 , with an onset at 219 K. The second sublimation event for $m/z = 160$ with a peak sublimation temperature of 243 K overlaps with the sublimation of H_2S_6 sublimation peak at the same temperature. The contribution from H_2S_6 fragmentation for S_5^+ ($m/z = 160$) are indicated with green deconvoluted peaks in Figure S7. This sublimation signal at $m/z = 160$ with the 183 K sublimation event therefore cannot be originated from the fragmentation from higher order sulfanes. Signal at $m/z = 158$, (2 amu below $m/z = 160$) observed a sublimation event that coincides with the sublimation profile of $m/z = 160$ at 183 K. A possible species that can contribute to the signal at $m/z = 158$ is $C_2H_6S_4$. Considering the natural isotopic distribution of sulfur, the expected distribution of $C_2H_6S_4$ signal to $m/z = 160$ via $C_2H_6S_3^{34}S$ was calculated. Within the error, the 183 K sublimation event of $m/z = 160$ signal matches the calculated profile of $C_2H_6S_3^{34}S$ (Figure S7). Likewise, the sublimation event with the onset sublimation temperature of 205 K in $m/z = 192$ can be due to $C_2H_6S_4^{34}S^+$ ions and at $m/z = 224$, $C_2H_6S_5^{34}S^+$ ions may contribute to the 227 K sublimation event. The contributions of sulfanes on S_7^+ ($m/z = 224$), S_6^+ ($m/z = 192$) and S_5^+ ($m/z = 160$) are indicated in Figure S7.

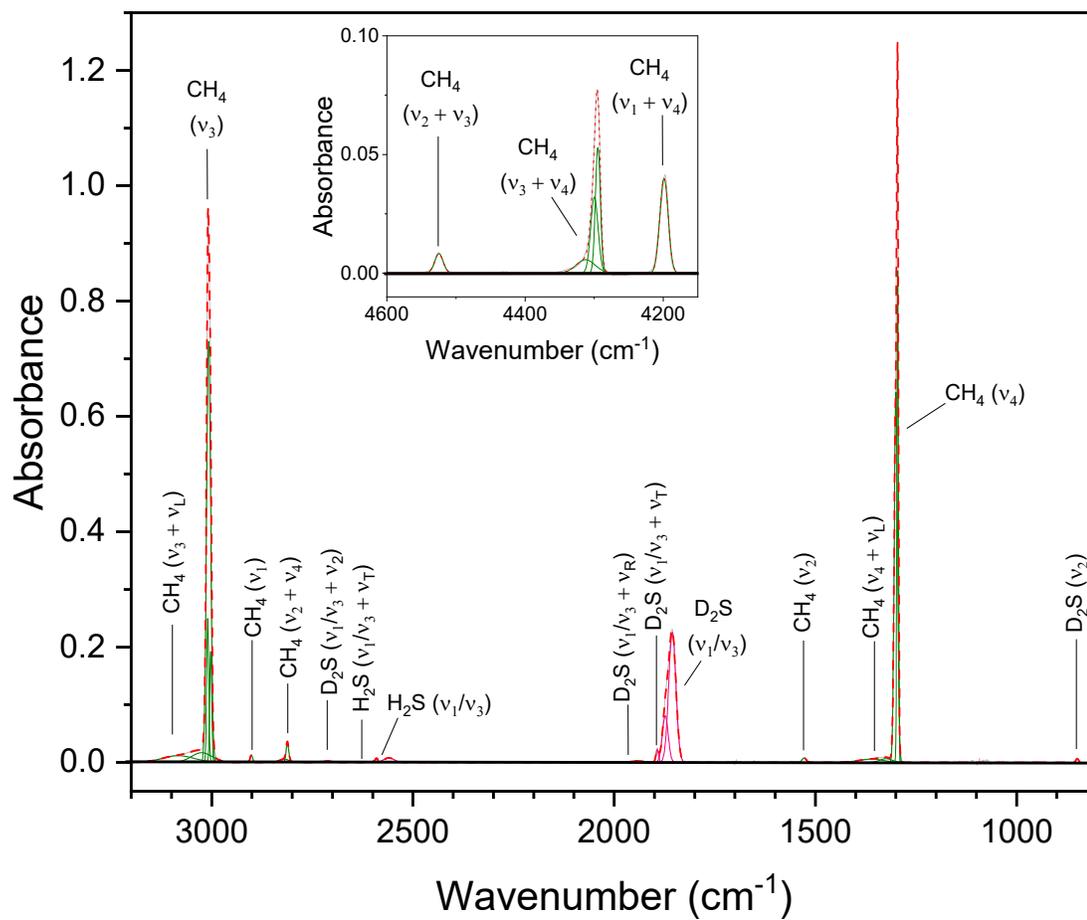


Figure S1. FTIR spectrum of pristine CH₄-D₂S ice at 5 K.

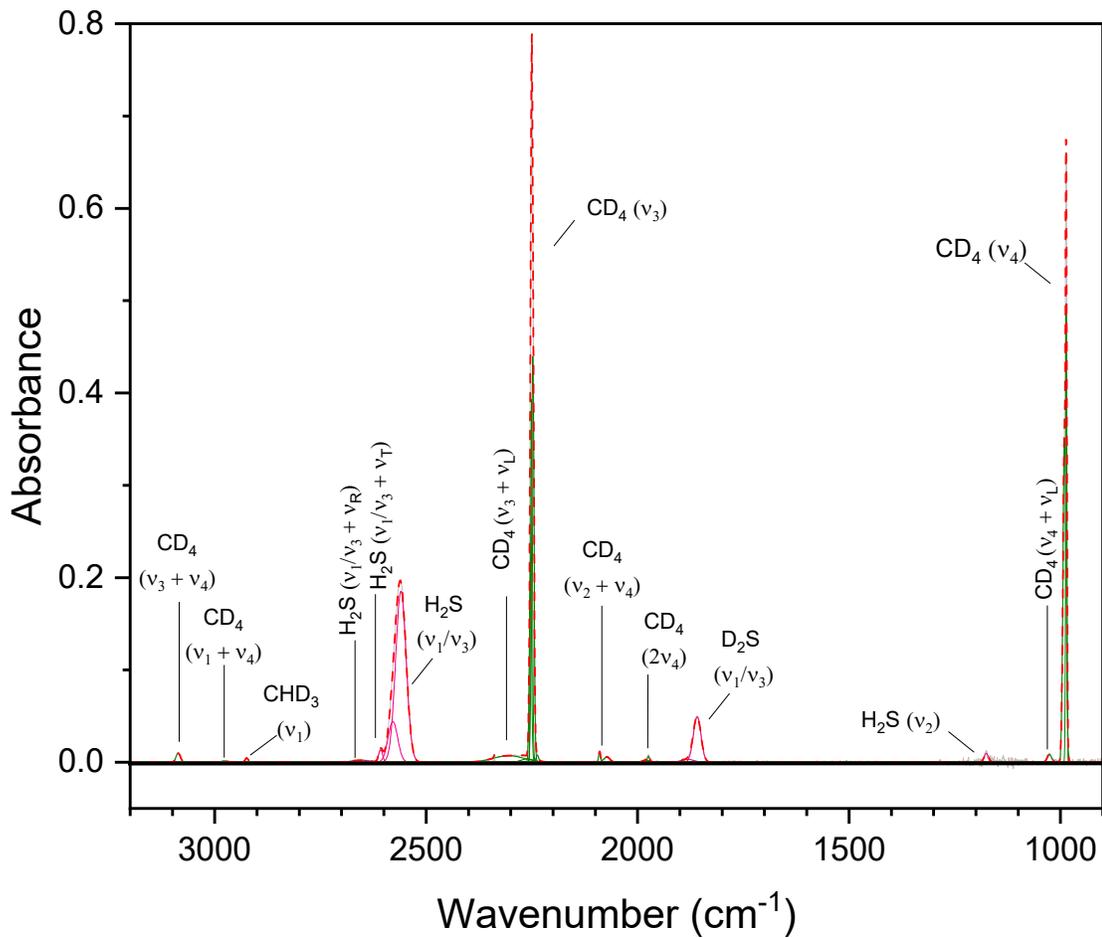


Figure S2. FTIR spectrum of pristine CD₄-H₂S ice at 5 K.

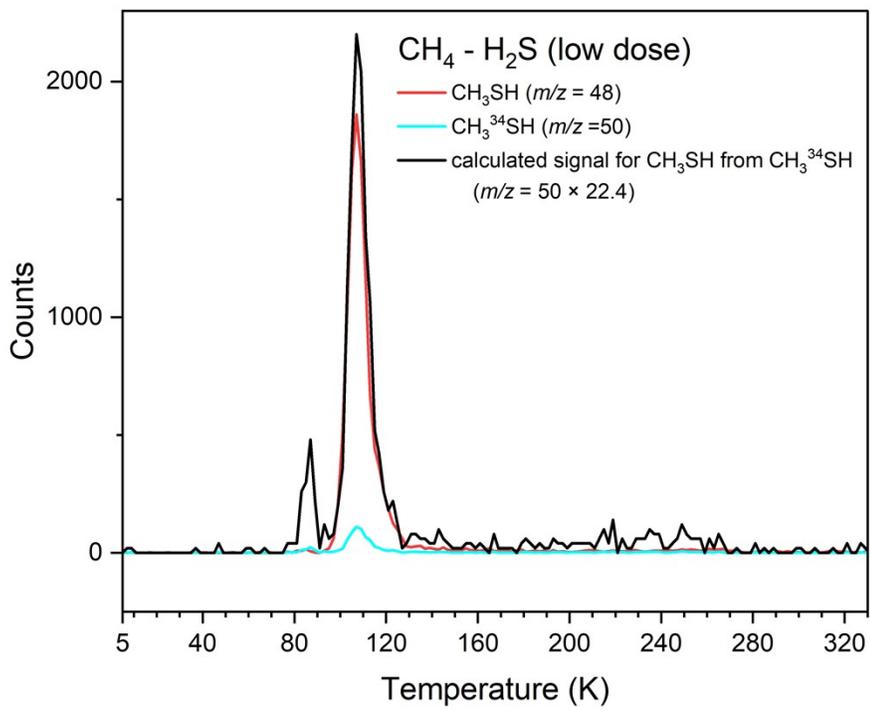


Figure S3. ReToF-MS data collected for methanethiol identification. Signal at $m/z = 48$ in the CH₄-H₂S ice photoionized at 10.49 eV during TPD was identified as a single sulfur species by comparing with $m/z = 50$. Signal at $m/z = 50$ (CH₃³⁴SH) is scaled back to CH₃³²SH.

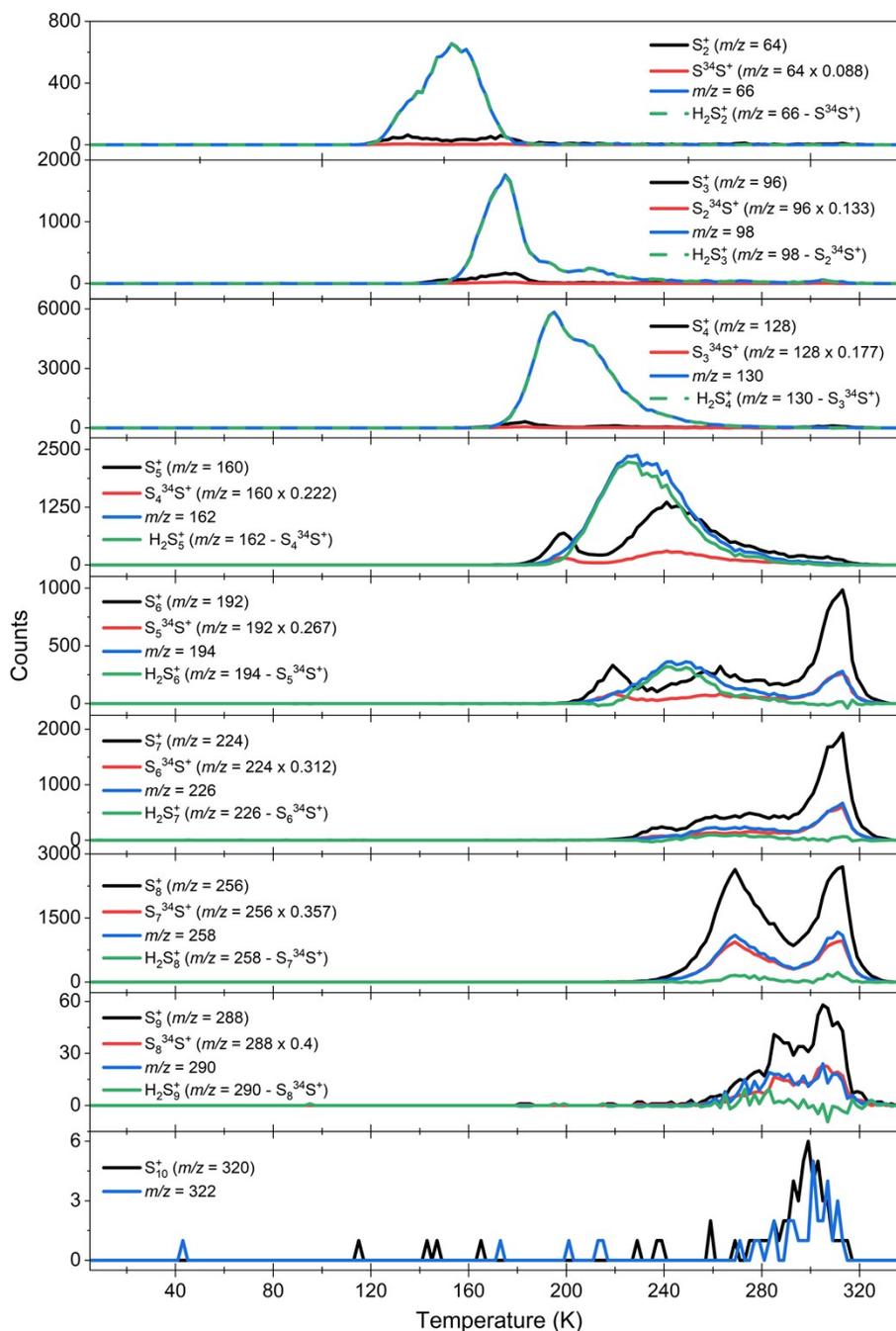


Figure S4. ReToF-MS signal for sulfanes and the molecular fragments with same number of sulfur atoms subliming at different temperatures for methane and hydrogen sulfide ice at 9.34 eV photons. Black lines indicate signal observed for S_n^+ ions, whereas green lines: sulfanes. The green traces for sulfanes H_2S_2 , H_2S_3 and H_2S_4 are in dashed lines to enhance the visibility. Deuterated ice confirmed the assigned mass formulae at each mass via a mass shift. Signal for sulfanes H_2S_7 , H_2S_8 and H_2S_9 are replotted in Figure S4 in their corresponding signal count scales.

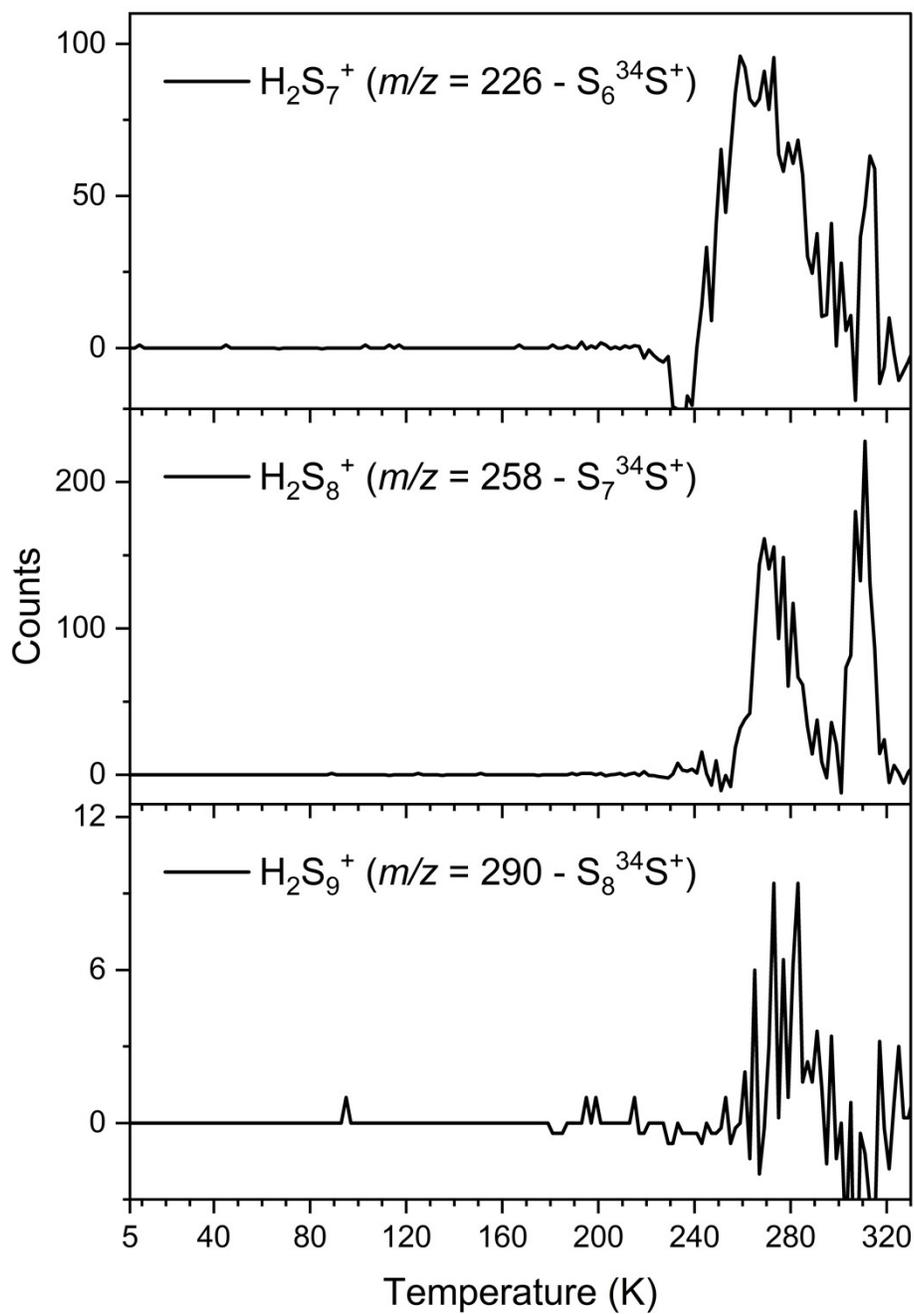


Figure S5. TPD profiles of sulfanes H_2S_7 , H_2S_8 and H_2S_9 observed in methane and hydrogen sulfide ice at 9.34 eV photons.

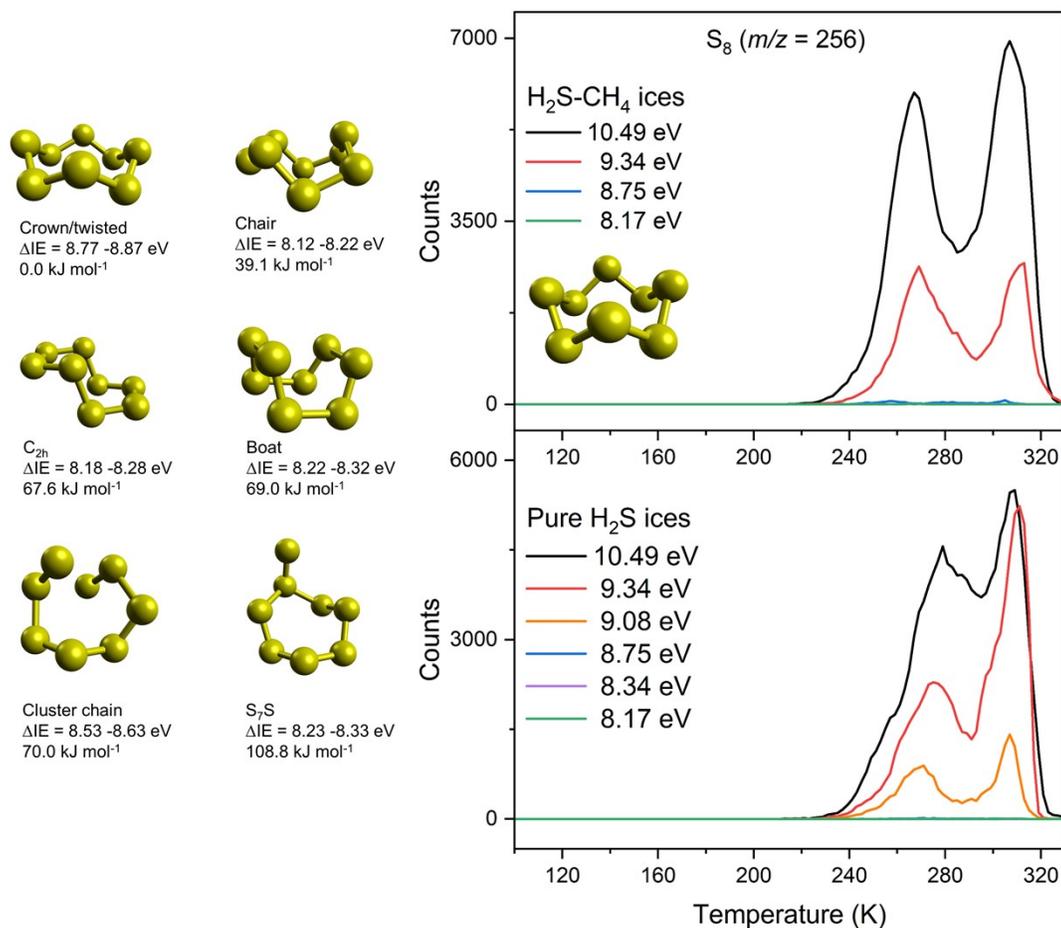


Figure S6. Comparison of ReToF-MS data for cyclic octasulfur (S_8) formed in the CH_4 - H_2S ice to the pure H_2S ices. The sublimation peaks are identified at 310 K and 268 K. The adiabatic ionization energies and relative energies of six conformers and isomers of S_8 calculated at the F12-TZ single point level of theory with B3LYP/aug-cc-pVTZ geometries with a maximum error of ± 0.05 eV were used in analyzing octasulfur.¹

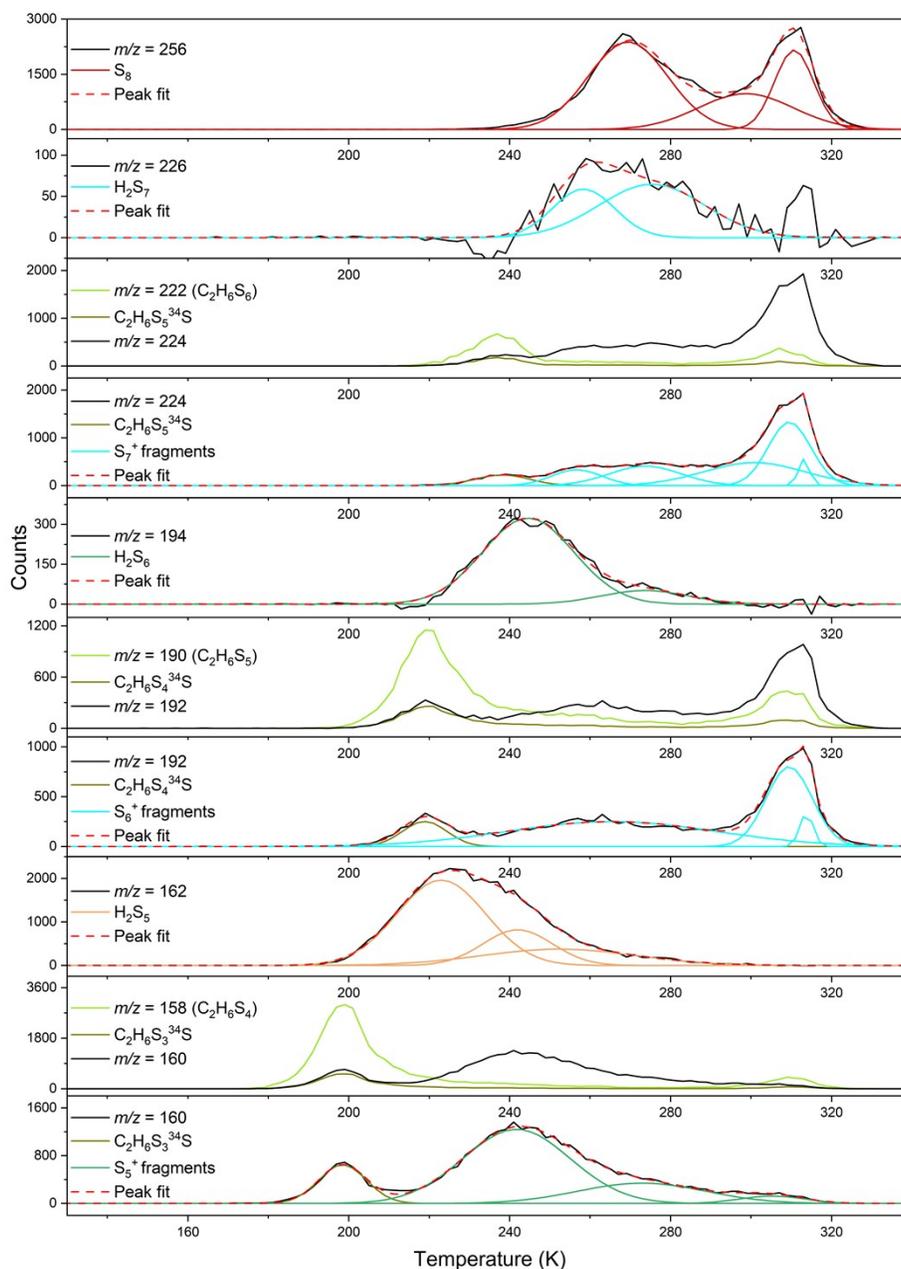


Figure S7. ReToF-MS identifications for octasulfur (S_8), and molecular sulfur fragments of S_7^+ , S_6^+ , and S_5^+ in the CH_4 - H_2S ice with 9.34 eV photons. Signal for each mass is indicated in black lines where the deconvoluted Gaussian peaks are color coded with molecules indicated in the key at each panel. The sum of fitted peaks are denoted with the dashed-red lines. S_8 shows two sublimation events with peak sublimation temperatures 269 K and 313 K. At $m/z = 160$, additional to S_5^+ ions, $C_2H_6S_3^{34}S^+$ ions may contribute to the sublimation event with an onset at 183 K. Likewise, at $m/z = 192$, $C_2H_6S_4^{34}S^+$ ions may contribute to the sublimation event with an onset sublimation temperature of 205 K and at $m/z = 224$, $C_2H_6S_5^{34}S^+$ ions may contribute to the 227 K sublimation event.

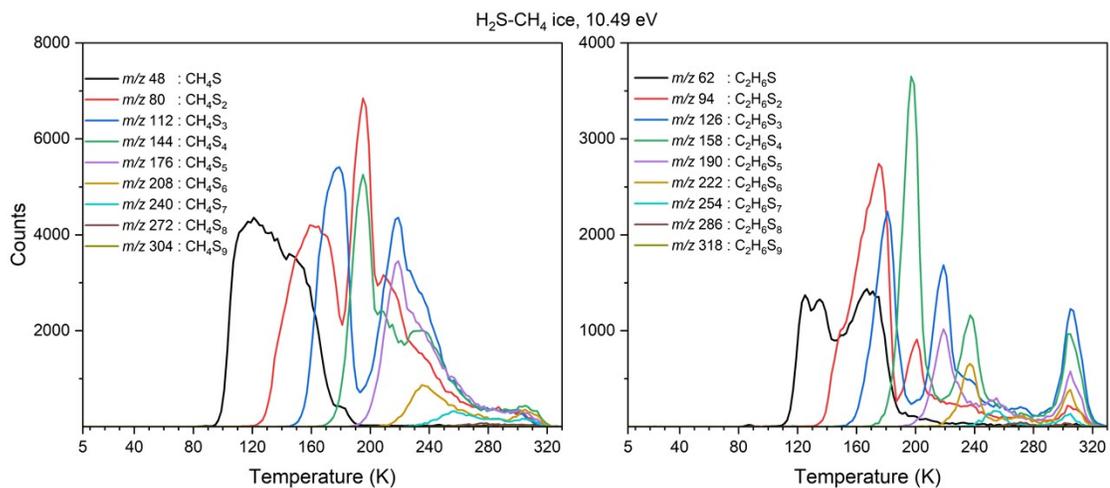


Figure S8. TPD Sublimation profiles in mass channels for alkylsulfane /ether series of CH₄S_n: n = 1-9 (*left*) and C₂H₆S_n: n = 2-9 (*right*) observed with 10.49 eV photons in the high irradiation dose CH₄-H₂S ice. The sublimation peak at 310 K is due to co-sublimation with cyclic octasulfur formed on the ice.

Supplementary References

- 1 A. Herath, M. McAnally, A. M. Turner, J. Wang, J. H. Marks, R. C. Fortenberry, J. C. Garcia-Alvarez, S. Gozem and R. I. Kaiser, Missing interstellar sulfur in inventories of polysulfanes and molecular octasulfur crowns, *Nat. Commun.* , 2025, **16**, 1–13.