

COMMUNICATION

Interstellar Ice Chemistry Yields Elusive Sulfinothioic Acid (HS(O)SH)

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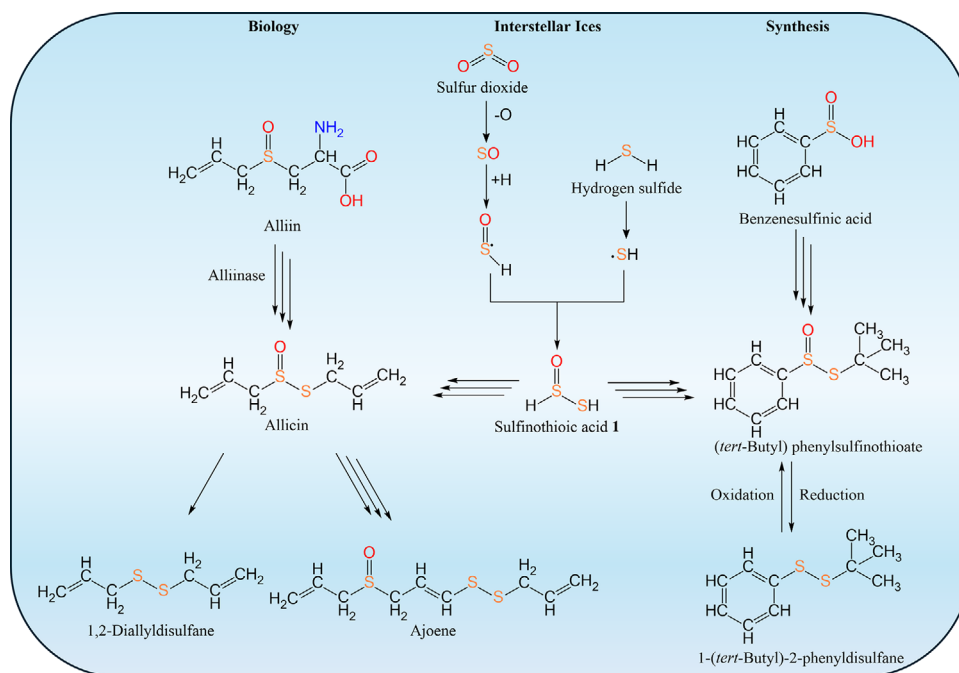
ABSTRACT

Low-oxidation-state sulfur oxyacids are key yet experimentally elusive intermediates in interstellar sulfur chemistry; even the simplest member, sulfinothioic acid (HS(O)SH), has neither been detected in space nor isolated terrestrially. The S–S(O) motif, also present in biological systems, can be reduced to form disulfide bridges (RSSR'), suggesting potential astrobiological relevance. Here, we report the first formation of sulfinothioic acid in astrophysically relevant sulfur dioxide (SO₂)–water (H₂O) ices and its identification via isomer-selective photoionization reflectron time-of-flight mass spectrometry combined with isotopic labeling. Irradiation of these ices at 5 K under ultrahigh vacuum with galactic cosmic-ray proxies yields sulfinothioic acid. These results establish a missing link in interstellar sulfur chemistry and reveal a previously unrecognized class of astrochemically accessible sulfur oxyacids formed via radical-mediated, non-equilibrium processes driven by energetic particles in cold interstellar environments.

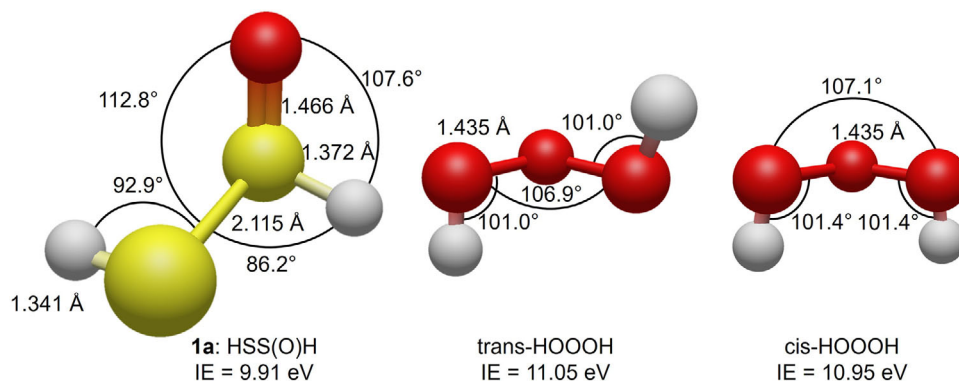
Low-oxidation-state sulfur oxyacids represent an understudied class of inorganic molecules bridging fundamental redox chemistry with the molecular evolution of sulfur in extraterrestrial environments [1, 3]. Sulfinothioic acid (**1**, HS(O)SH, Scheme 1) is the simplest member of this family and has remained elusive despite quantum-chemical predictions of its stability [4, 5]. Unlike well-characterized high-oxidation sulfur acids such as sulfuric acid (H₂SO₄), sulfur oxyacids are inherently unstable under terrestrial conditions but can be stabilized through deprotonation to sulfinothoates (RS(O)S–R) or substitution with bulky organic groups (RS(O)SR'), where R is an organic side chain such as benzene or tert-butyl (Scheme 1) [6, 7]. These analogues display diverse redox behavior, including reduction to disulfide bridges (RSSR'), formation of sulfinic acids (RSOH), and nucleophilic substitution reactions [8–12]. Such reactivity occurs in biological systems; for example, organosulfinothoates like allacin—formed

from alliin by alliinase—exhibit antibacterial and antiviral activity [13–16]. Despite this rich chemistry, the simplest neutral representative—sulfinothioic acid **1** (HS(O)SH)—has neither been isolated in the laboratory nor identified in extraterrestrial environments. Within the broader chalcogen family, comparison to the oxygen chemistry provides a fundamental conceptual framework for evaluating the stability of such reduced sulfur oxyacids.

The synthesis of hydrogen trioxide (H₂O₃) in cryogenic ices at 5 K demonstrates that a three-atom oxygen chain (O–O–O) can be stabilized within low-temperature matrices [17–20]. Following Langmuir's concept of isovalency [21], hydrogen trioxide serves as the oxygen analogue of the sulfur species H₂S₂O, where the O–O–O backbone corresponds to an S–S–O chain (Scheme 2). Although the S–S bond in sulfinothioic acid **1** is longer (2.115 Å) than the



SCHEME 1 | Overview of biological pathways to produce allicin and its products like ajoene, proposed interstellar reactions to produce the simplest sulfinothioic acid **1**, and synthetic applications to produce sulfinothioates and disulfide crosslinks.



SCHEME 2 | Comparison of isovalent species including sulfinothioic acid (**1a**, HSS(O)H) and recently detected hydrogen trioxide (trans-/cis-HOOH). The calculated geometries of **1a** were completed at the CCSD(T)-F12/cc-pVTZ-F12 level of theory. This geometry is compared with calculated geometries of hydrogen trioxide from Bai et al. [17].

O–O bonds in H₂O₃ (1.435 Å), the S–O bond length (1.466 Å) remains comparable, highlighting the structural analogy. Nevertheless, H₂S₂O has never been experimentally observed.

Here, we report the first formation and detection of sulfinothioic acid **1** (HS(O)SH) via high-energy electron irradiation of sulfur dioxide (SO₂) and water (H₂O) ices under ultra-high vacuum (10^{−11} Torr) at 5 K [22]. This ice mixture, representing a model interstellar ice, is inert at 5 K, limiting chemistry to quantum-tunneling processes [21–24]. In space, galactic cosmic rays drive non-equilibrium chemistry by generating cascades of secondary electrons that chemically modify interstellar grains [25–27], which is simulated experimentally using energetic electrons [28, 29]. Tunable soft photoionization (PI) selectively ionizes newly formed molecules based on their ionization energies (Figure 1),

allowing detection via reflectron time-of-flight mass spectrometry (ReToF-MS). This approach provides direct insight into the formation of previously unknown low-oxidation sulfur species, offering a window into unstable redox sulfur oxyacids, the chemical evolution of interstellar ices, and filling a longstanding gap in the isovalent chalcogens between hydrogen trioxide (H₂O₃) and trisulfane (H₂S₃).

Soft photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) was exploited to identify isomer specific reaction products during temperature-programmed desorption (TPD) based on the adiabatic ionization energies (IEs, Figure 1) [23–26]. As molecules sublime into the gas phase from the ice, they are isomer-selectively ionized with vacuum ultraviolet (VUV) light. This process does not produce di-cations and minimizes

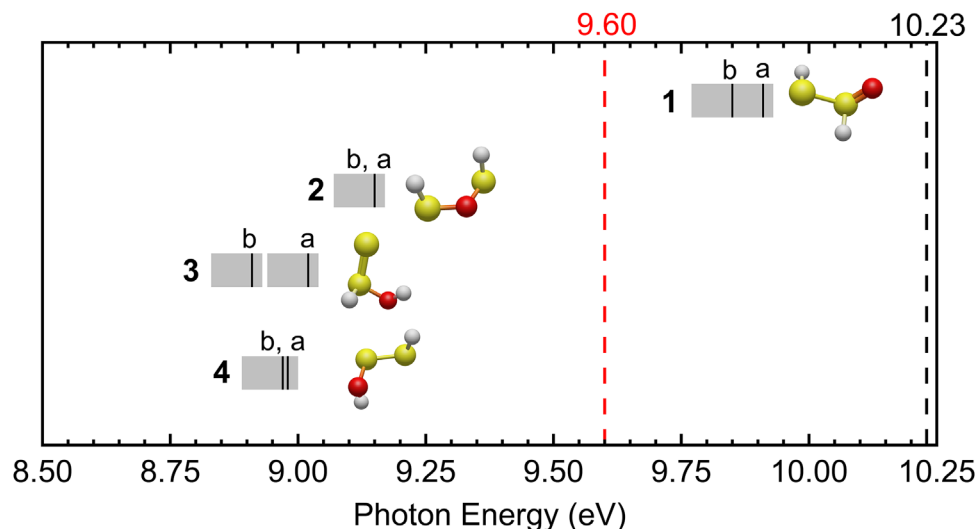


FIGURE 1 | Experimental photon energies (dashed line) overlaid with the adiabatic ionization energy (solid black) of each isomer and calculated error (gray box). The error includes the Stark effect (-0.03 eV) and the error in computation calculations of ± 0.05 eV.

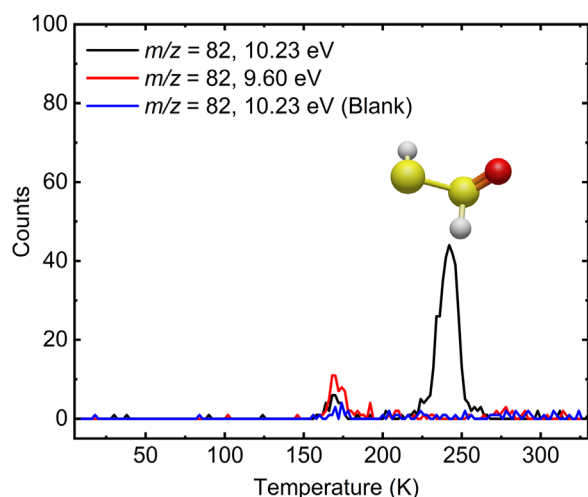


FIGURE 2 | TPD-PI-ReToF-MS profiles of $\text{SO}_2/\text{H}_2\text{O}$ ices after processing by energetic electrons (100 nA, 1 hr). Ion counts measured by the ReToF-MS of the $m/z = 82$ channel during TPD (5–330 K) with a photon energy of 10.23 eV (black), 9.60 eV (red), and compared with the unirradiated $\text{SO}_2/\text{H}_2\text{O}$ ice (10.23 eV; blue).

fragmentation resulting in an intact parent cation with a mass-to-charge (m/z) equivalent to the molecular mass of the product (amu). Since $\text{H}_2\text{S}_2\text{O}$ has four different isomers, experiments were selectively designed to disambiguate between each isomeric form (Figure 1). For a comprehensive overview of all m/z channels observed during TPD see Figure S1.

Using photons with an energy of 10.23 eV, which can photoionize all isomers 1–4 (Figure 1), the temperature-programmed desorption (TPD) profile of $m/z = 82$ ($\text{H}_2\text{S}_2\text{O}^+$) recorded from the electron-irradiated $\text{SO}_2/\text{H}_2\text{O}$ ice exhibits a distinct desorption peak at 242 K (Figure 2). The $m/z = 82$ signal at 242 K does not co-desorb with high-mass sulfur products, separating it from lower-order sulfanes such as H_2S_2^+ ($m/z = 66$) and larger sulfur-rich species such as S_8^+ ($m/z = 256$) (Figure S1). This feature is

absent in the blank $\text{SO}_2/\text{H}_2\text{O}$ experiment conducted under identical conditions but without electron irradiation demonstrating that the observed signal during the exposure to ionizing radiation originates from electron-induced processing of the ice. To further constrain the carrier of this signal, the photon energy was tuned to 9.60 eV. At this energy, isomer 1 (IE = 9.93–9.77 eV) can no longer be photoionized, whereas isomers 2–4 remain accessible. Under these conditions, the $m/z = 82$ peak disappears (Figure 2). This result demonstrates that the signal observed at 10.23 eV arises from photoionization of sulfinthioic acid ($\text{HS}(\text{O})\text{SH}$, 1).

Since the starting ice mixture contains SO_2 and H_2O , the $m/z = 82$ mass channel could in principle correspond to alternative molecules such as H_2O_5^+ or H_2SO_3^+ . Therefore, additional isotopic analyses were performed to confirm the molecular formula of the detected species. First, the number of sulfur atoms was evaluated using the natural isotopic distribution of sulfur. The isotopes ^{32}S and ^{34}S occur in a natural abundance ratio of 22:1. For a molecule containing two sulfur atoms, such as $\text{H}_2\text{S}_2\text{O}$, the expected isotopic abundance ratio between $m/z = 82$ ($^{32}\text{S}_2$) and $m/z = 84$ ($^{32}\text{S}^{34}\text{S}$) is therefore 11:1. Experiments conducted at 10.23 and 10.49 eV were used to evaluate this distribution (Figure 3A,B). At 10.23 eV, the integrated ion signals yield an m/z 82:84 ratio of 12.1:1, closely matching the expected 11:1 value. Similarly, data at 10.49 eV produce a ratio of 10.5:1, again consistent with the theoretical isotopic distribution for a two-sulfur species. The number of hydrogen atoms was confirmed using isotopic substitution experiments with D_2O . Replacement of H_2O with D_2O results in the substitution of hydrogen by deuterium, producing $\text{D}_2\text{S}_2\text{O}$, which would shift the molecular ion from $m/z = 82$ to $m/z = 84$. In the irradiated $\text{SO}_2/\text{D}_2\text{O}$ ice experiment conducted at 10.49 eV, no desorption signal is observed at $m/z = 82$ (Figure 3C). Instead, the desorption peak shifts to $m/z = 84$, confirming the presence of two hydrogen atoms in the detected molecule. This shift cannot be explained by the presence of $\text{H}_2\text{S}^{34}\text{SO}$ as the signal in $m/z = 82$ for $\text{H}_2\text{S}_2\text{O}$ is insufficient to explain the signal strength in $m/z = 84$. Overall, the sulfur isotopic distribution and deuterium labeling experiments unambiguously demonstrate that the desorbing species

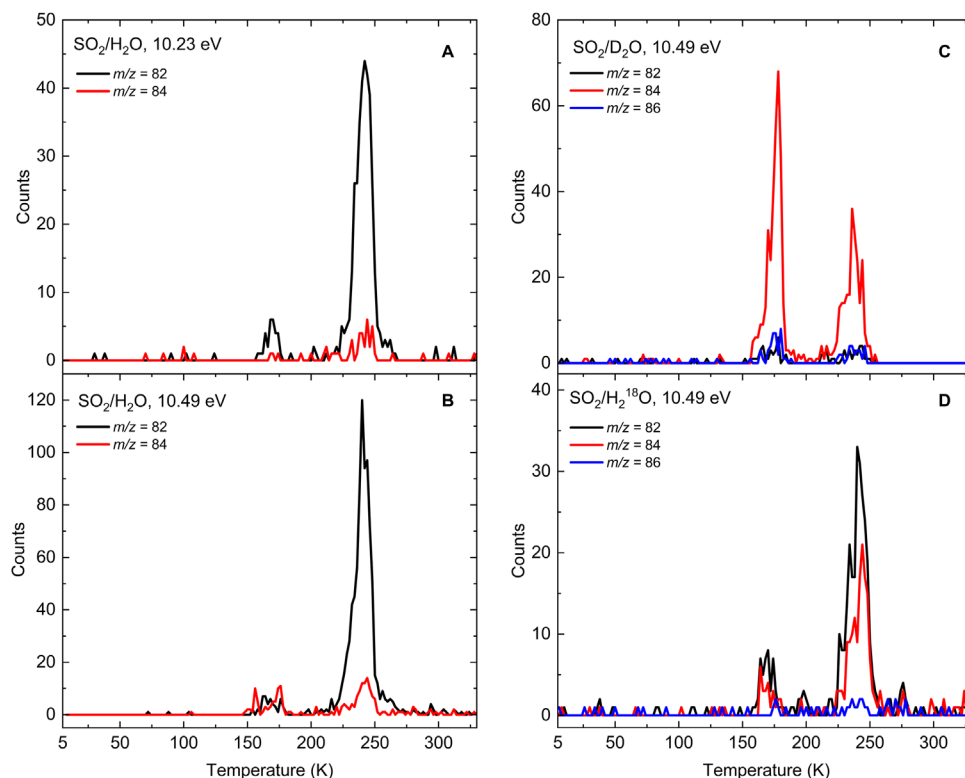


FIGURE 3 | TPD-ReToF-MS profiles of the $\text{SO}_2/\text{H}_2\text{O}$, $\text{SO}_2/\text{D}_2\text{O}$, and $\text{SO}_2/\text{H}_2^{18}\text{O}$ ices after processing by energetic electrons (100 nA, 1 h). Ion counts were measured for the photon energy 10.23 eV (A) and 10.49 eV (B) in the $\text{SO}_2/\text{H}_2\text{O}$ ices and 10.49 eV in the $\text{SO}_2/\text{D}_2\text{O}$ (C) and $\text{SO}_2/\text{H}_2^{18}\text{O}$ (D) ice by the ReToF-MS. The mass profiles include $m/z = 82$, 84, and 86 which corresponds to the parent and isotopologue channels of $\text{H}_2\text{S}_2\text{O}$.

responsible for the $m/z = 82$ signal contains two sulfur atoms and two hydrogen atoms. Combined with the photon-energy dependent ionization experiments, these results confirm that the product observed in the irradiated $\text{SO}_2/\text{H}_2\text{O}$ ice is sulfinothioic acid ($\text{HS}(\text{O})\text{SH}$, **1**).

Previous matrix-isolation studies have demonstrated that hydrogen atoms and hydroxyl atoms generated by photolysis can react with SO_2 in rare-gas matrices, establishing the feasibility of low-temperature sulfur oxide hydrogenation and hydroxylation chemistry [27–29]. However, the experimental formation of neutral $\text{H}_2\text{S}_2\text{O}$ and mechanistic investigation of its formation have remained unexplored.

To unravel the mechanism of formation of sulfinothioic acid **1**, additional isotopically labeled ice experiments were conducted. An ice composed of $\text{SO}_2/\text{H}_2^{18}\text{O}$ provides a mass shift of two if the oxygen primarily originates from water; however, if the oxygen in sulfinothioic acid **1** originates from SO_2 , no isotope shift will be observed. During TPD, one sublimation event is observed occurring at 242 K at $m/z = 82$ and $m/z = 84$ (Figure 3D). Counter to the previous non-isotopically labeled ice, the $m/z = 84$ channel is enhanced suggesting that at least some of the sulfinothioic acid **1** does contain ^{18}O . The presence of $m/z = 82$ as the dominant peak illustrates oxygen is likely preserved from SO_2 in the main synthetic pathway. Typical branching ratios of both pathways can be derived as 67% retain the oxygen from SO_2 and 33% incorporate the oxygen from ^{18}O -labeled water (H_2^{18}O). Therefore, the principal route to formation of sulfinothioic acid

1 likely only requires water as a hydrogen source. Based on the observed formation of $\text{HS}(^{16}\text{O})\text{SH}$ and $\text{HS}(^{18}\text{O})\text{SH}$, three potential reaction pathways can be proposed (Figure 4).

The dominant formation pathway retains the oxygen atom originating from sulfur dioxide. Accordingly, **Pathway 1** (Figure 4) commences with endoergic cleavage of an $\text{S}=\text{O}$ bond in SO_2 , producing sulfur monoxide (SO). The resulting sulfur monoxide triplet diradical can barrierlessly recombine with suprathermal hydrogen atoms generated in the ice through electron-induced O–H bond cleavage in H_2O . This reaction forms the sulfinyl radical (HSO), which subsequently undergoes barrierless radical–radical recombination with the sulfhydryl radical (SH) to sulfinothioic acid **1**. Although hydrogen sulfide (H_2S) is not an initial reagent, both the present experiments and previous studies demonstrate that H_2S forms efficiently in $\text{SO}_2/\text{H}_2\text{O}$ ices and serves as a major source of SH radicals. Consequently, H_2S likely plays a key role in supplying the sulfhydryl radicals required for this recombination step. The $\text{SO}_2/\text{H}_2^{18}\text{O}$ labeling experiment indicates that this pathway accounts for approximately 67% of the total production of sulfinothioic acid **1** within the ice.

Two additional pathways may contribute to the formation of the isotopically labeled product $\text{HS}(^{18}\text{O})\text{SH}$ observed in the oxygen-labeled experiment. In **Pathway 2**, hydrogen disulfide (H_2S_2)—as observed during TPD (Figure S1)—first forms within the ice and subsequently reacts with an oxygen atom generated from water dissociation. This mechanism therefore provides a plausible route to oxygen incorporation from water.

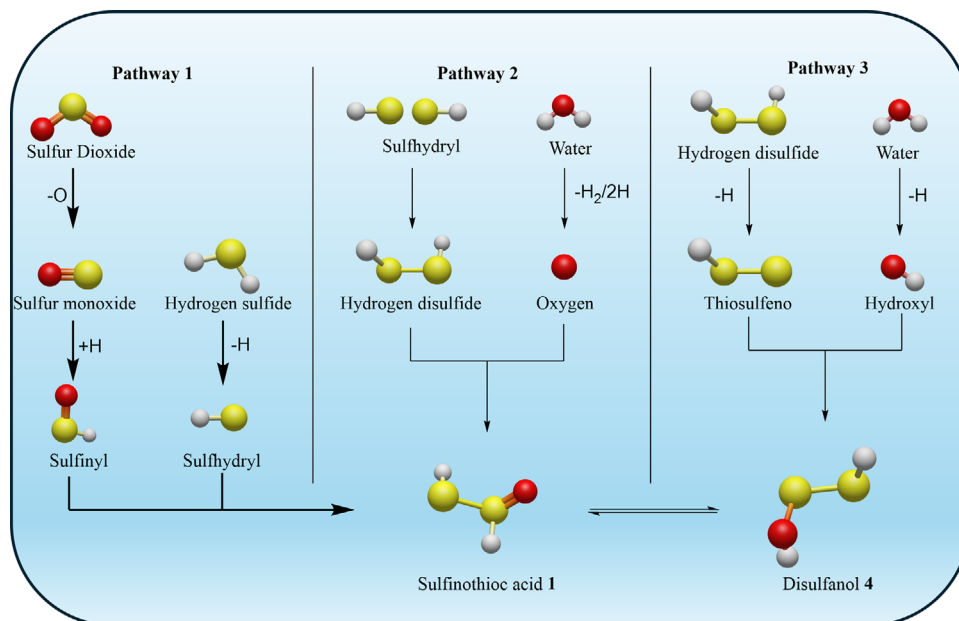


FIGURE 4 | Three potential pathways for the formation of sulfinothioic acid **1** species available within the ice ($\text{SO}_2/\text{H}_2\text{O}$) and constrained by the branching ratios produced in the $\text{SO}_2/\text{H}_2^{18}\text{O}$ experiments.

Pathway 3 invokes chemistry commonly observed in low-oxidation-state sulfur oxyacids, where tautomerization facilitates interconversion between isomeric forms [4]. In this scheme, the thiosulfeno radical (HS_2) recombines barrierlessly with the hydroxyl radical (OH) to form disulfanol (HSSOH , **4**). Subsequent intramolecular hydrogen transfer from oxygen to the central sulfur atom would then generate sulfinothioic acid **1**. This tautomerization is calculated to be endoergic by 59 kJ mol^{-1} ; however, initiation by energetic electrons or quantum tunneling processes could potentially enable the rearrangement. Since disulfanol **4** is not detected in the present experiments, this pathway is considered less probable.

Overall, the isotopic labeling results indicate that **Pathway 1** dominates the formation chemistry, consistent with the observed 67% retention of the oxygen atom from SO_2 . **Pathway 2** and **Pathway 3**, which incorporate oxygen derived from water, likely contribute to the remaining 33% of sulfinothioic acid **1** production, although their relative importance appears to be secondary compared with the sulfur dioxide-derived pathway (Supporting Information).

The detected sulfinothioic acid **1** represents a mixed chalcogen molecule between hydrogen trioxide (H_2O_3) and trisulfane (H_2S_3) which contains the $\text{S}-\text{S}(\text{O})$ motif, where one sulfur is in the +2 oxidation state (sulfinyl) and the other is a thiol ($-\text{SH}$). This molecule can be seen as the thiol derivative of a sulfinic acid, where the sulfinyl sulfur is directly bonded to another sulfur atom. Quantum chemical calculations reveal that the $\text{S}-\text{S}$ bond distance ($2.115 \text{ \AA}$) is significantly longer than typical $\text{O}-\text{O}$ bonds. In hydrogen trioxide, the $\text{O}-\text{O}$ bond length is $1.435 \text{ \AA}$, reflecting the smaller covalent radius of oxygen. Further, the $\text{S}-\text{S}$ bond found in sulfinothioic acid **1** is slightly elongated when compared to polysulfanes which typically fall in the range of $2.05\text{--}2.10 \text{ \AA}$ [30]. Thus, the electron-withdrawing character of the adjacent sulfinyl group likely elongates the $\text{S}-\text{S}$ bond. In contrast,

the $\text{S}=\text{O}$ bond of the sulfinyl group is substantially shorter at $1.466 \text{ \AA}$, reflecting the double-bond character arising from highly polarized π interaction dominant in oxygen–sulfur bonds [31, 32]. This bonding also highlights key differences between oxygen and sulfur chemistry. While H_2O_3 involves compact bonding with limited isomer and conformational flexibility, substitution of sulfur introduces longer bonds, increased polarizability, and alternate bonding motifs as observed by the sulfinyl moiety. Consequently, sulfinothioic acid can be interpreted as a sulfur-expanded analogue of hydrogen trioxide in which the central chalcogen chain is lengthened and electronically polarized by the sulfinyl functionality.

Overall, this study marks the first experimental detection of sulfinothioic acid ($\text{HS}(\text{O})\text{SH}$, **1**). Utilizing isomer-selective PI-ReToF-MS, we unambiguously identify sulfinothioic acid **1** through its sublimation at 242 K in tandem with sulfur-isotope distribution analysis, and deuterium labeling. These data confirm both the molecular formula and specific isomeric identity of $\text{H}_2\text{S}_2\text{O}$ in interstellar ices, broadening knowledge on low-oxidation state sulfur acid chemistry and on stable structures in the chalcogen isovalent series. Isotopically labeled water (H_2^{18}O) reveals that sulfinothioic acid **1** primarily forms through retention of the $\text{S}=\text{O}$ moiety of SO_2 , with water serving chiefly as a hydrogen source. Incorporation of ^{18}O from water at a level of 33% demonstrates the presence of secondary pathways wherein oxygen atoms from water oxidize disulfane (H_2S_2). Together, these results support a reaction network dominated by radical–radical recombination—particularly between hydrogen sulfinyl (HSO) and thiol (SH) radicals—induced by energetic electrons, and augmented by hydrogen disulfide (H_2S_2) and thiosulfeno (HS_2). The formation of sulfinothioic acid **1** widens the inventory of low-oxidation sulfur compounds that may be present in molecular clouds. These findings demonstrate that even formally unstable, reduced sulfur oxyacids can be synthesized and stabilized within cold ices processed by energetic particles, offering new

perspectives on the long-standing sulfur depletion problem in the interstellar medium [30, 33–37] as well as on sulfur redox cycling in low-temperature environments. More broadly, the generation of reactive sulfur–oxygen species through high-energy processing may influence prebiotic chemistry via reduction of sulfinothioic acid **1** to disulfides, contribute to atmospheric chemical cycles on Earth [38] and sulfur-rich planetary bodies such as Venus [39, 40], and play a role in the evolving chemistry of molecular clouds that ultimately give rise to star-forming regions.

Author Contributions

R.I.K. designed the experiments. M.M., Z.W., C.Z., and J.W. performed the experiments. R.F. performed and analyzed the computational calculations. M.M. and R.I.K. analyzed the experimental data; M.M. and R.I.K. wrote the paper.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: Additional references are given in the Supporting Information [41–71].