THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JPCL Letter

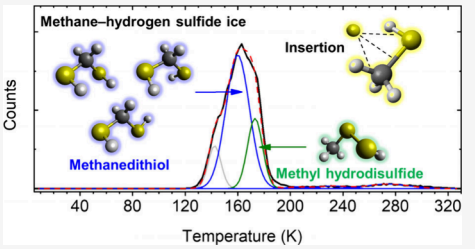
Bottom-Up Formation of the Simplest Geminal Thiol—Methanedithiol ($CH_2(SH)_2$)—and the Methyl Hydrodisulfide (H_3CSSH) Isomer in Interstellar Analogue Ices

Jia Wang,[#] Ashanie Herath,[#] Andrew M. Turner, Mason McAnally, Ryan C. Fortenberry,* André K. Eckhardt,* and Ralf I. Kaiser*

Cite This: *J. Phys. Chem. Lett.* 2026, 17, 8090−8097 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Geminal dithiols—organic molecules bearing two thiol groups on the same carbon atom—are versatile synthons in organic and atmospheric chemistry, exhibiting significantly greater stability than their oxygen analogues. Here, we report the first formation of the smallest geminal dithiol, methanedithiol ($CH_2(SH)_2$), and its structural isomer, methyl hydrodisulfide (CH_3SSH), in low-temperature model interstellar ices composed of methane and hydrogen sulfide via energetic electron irradiation, simulating secondary electrons generated by galactic cosmic rays. Both isomers were identified in the gas phase using isomer-selective vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS), guided by quantum chemically computed adiabatic ionization energies, and confirmed through isotopic labeling and ultraviolet photolysis studies. These results not only demonstrate that methanedithiol and methyl hydrodisulfide can form on ice-coated interstellar nanoparticles and represent promising candidates for future astronomical detection, but they also provide fundamental insights into the nonequilibrium synthesis of geminal dithiols in extraterrestrial environments.

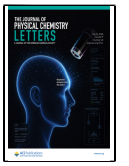


Langmuir's concept of isovalency highlights the remarkable similarities in chemical reactivity of atoms and molecular entities sharing the same number of valence electrons.[1] Oxygen and sulfur—both group VI nonmetals with ns^2np^4 configurations—play central roles in terrestrial atmospheric chemistry and biochemistry.[2,3] While oxygen exists primarily as diatomic molecular oxygen (O_2) and triatomic ozone (O_3), sulfur exhibits extensive catenation, forming a rich variety of solid allotropes, with octasulfur (S_8) as the most stable form.[4] The significantly larger atomic radius of sulfur (88 pm) compared to oxygen (48 pm), combined with differences in the energies of bonding and nonbonding orbitals along with energetically accessible d-orbitals for sulfur, leads to notable deviations from isovalent predictions.[5−7]

Similar to Langmuir and isovalency, Erlenmeyer is attributed with his own rule. This heuristic states that geminal diols—carbon centers bearing two hydroxyl groups—are unstable. However, recent studies have reported the formation of such geminal diols in low-temperature interstellar ice analogues (Figure 1).[8] In contrast, sulfur analogues, geminal dithiols (gem-dithiols), are substantially more stable and widely employed as versatile synthons in organic and atmospheric chemistry.[9] Since Cairns et al.'s first preparative synthesis of gem-dithiols including methanedithiol ($CH_2(SH)_2$, **1**) via aldehyde and ketone reactions with pressurized hydrogen sulfide (H_2S), their potential role in astrochemical processes has remained largely unexplored.[10] Meanwhile, the interstellar medium (ISM) hosts a nonthermal sulfur chemistry that produces complex organosulfur molecules, following the first sulfuretted species, carbon monosulfide (CS), detected in 1971.[11−13] Additionally, methane has now been confirmed in interstellar ices via infrared observations from the James Webb Space Telescope (JWST), while hydrogen sulfide is inferred from astrochemical models and cometary detections.[14−17] These discoveries underscore the potential value for exploring sulfur analogues of geminal diols under astrochemical conditions.

Herein, we report the first formation of the simplest geminal dithiol, methanedithiol ($CH_2(SH)_2$, **1**), and its structural isomer methyl hydrodisulfide (CH_3SSH, **2**), in low-temperature methane−hydrogen sulfide (CH_4−H_2S) ices exposed to energetic electrons as proxies of galactic cosmic rays (GCRs). Quantum chemical computations on gas phase molecules provide adiabatic ionization energies (IEs) and relative energies of CH_4S_2 isomers, guiding isomer-selective identification via vacuum ultraviolet (VUV) photoionization during temperature-programmed desorption (TPD).

Received: May 30, 2026
Revised: June 24, 2026
Accepted: June 25, 2026
Published: July 2, 2026



https://doi.org/10.1021/acs.jpclett.6c01781
J. Phys. Chem. Lett. 2026, 17, 8090−8097

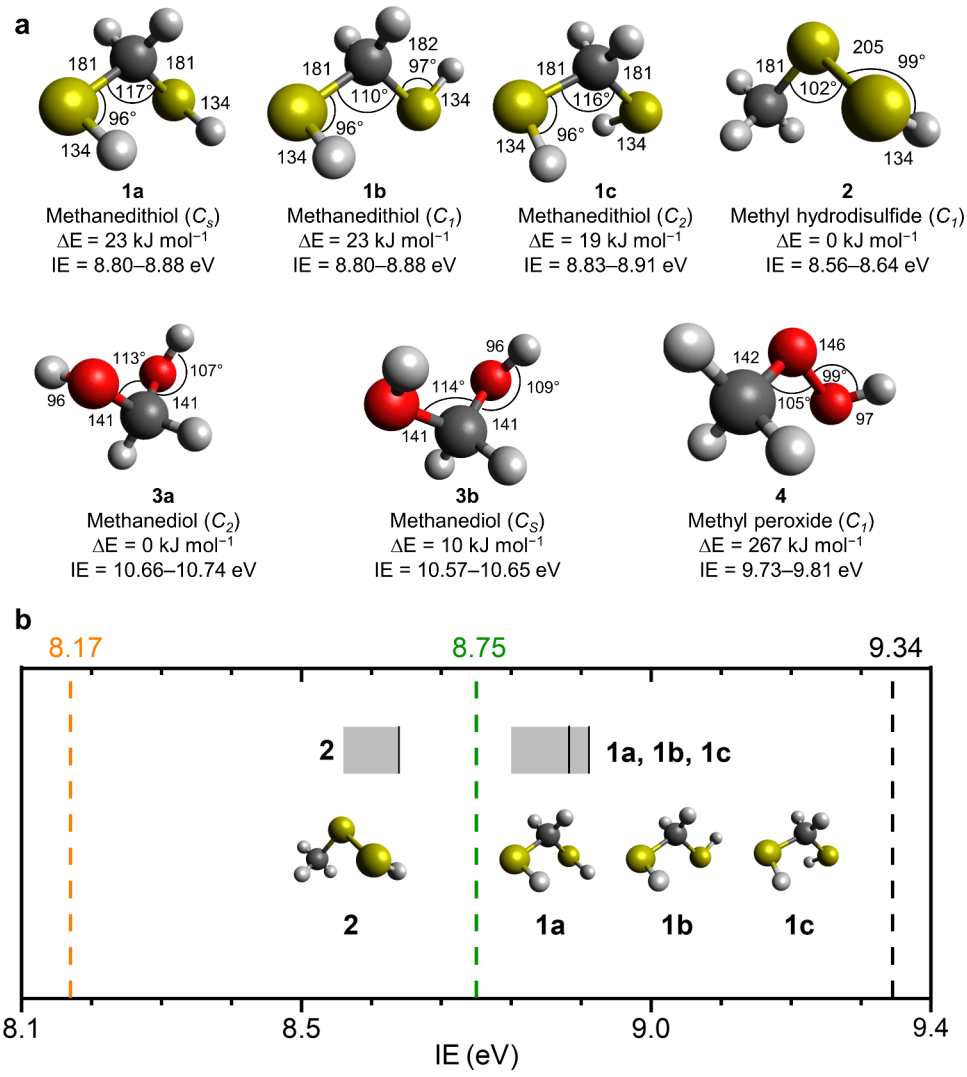


Figure 1. (a) Comparison of calculated molecular structures, relative energies (ΔE), and adiabatic ionization energies (IEs) of CH_4S_2 and CH_4O_2 isomers.[8] Bond lengths are indicated in pm and bond angles in degrees. Structural parameters are omitted where redundant. (b) Computed IEs (solid black line) of CH_4S_2 isomers and the photon energies (colored dashed lines) utilized for the ReToF-MS experiments (Tables S1 and S2). IE ranges are corrected for thermal and Stark effects by −0.03 eV and combined uncertainty ranges of −0.05/+0.03 eV.[8] Uncertainty range is indicated in gray.

Comparison with the isovalent oxygen analogues, methanediol ($CH_2(OH)_2$) and methyl peroxide (CH_3OOH), highlights fundamental divergence in stability and energetics between isovalent species. It is worth noting that the synthesis of methyl hydrodisulfide (**2**) was reported by Böhme and Zinner,[18] and a convenient preparative method for **2** and **2**-d_1 was later developed by Bauder and co-workers, who also performed their microwave and infrared spectroscopic characterization.[19,20] In the present study, we focus on the bottom-up formation of methanedithiol (**1**) and methyl hydrodisulfide (**2**) in low-temperature interstellar analog ices composed of methane and hydrogen sulfide upon energetic electron irradiation, followed by their isomer-selective identification in the gas phase during TPD. These results demonstrate that methanedithiol (**1**) and methyl hydrodisulfide (**2**) can form on ice-coated interstellar nanoparticles, with both disulfide molecules appearing to be promising targets for future astronomical detection in hot molecular cores such as Sagittarius B2 (Sgr B2). Furthermore, in combination with isotopic labeling experiments, this work provides fundamental insights into the nonequilibrium formation pathways of geminal dithiols in deep space.

The experiments were carried out in an ultrahigh vacuum chamber operating at pressures of a few 10^{-11} Torr.[21,22] Gas mixtures of hydrogen sulfide (H_2S) and methane (CH_4) with a H_2S:CH_4 ratio of 3:7 were deposited onto a polished silver substrate cooled to 5 K, resulting in a CH_4:H_2S ratio of 0.2 ± 0.1:1.[23] The ice thicknesses were determined to be 1100 ± 200 nm using laser interferometry.[7] The deposited ices were irradiated with 5 keV electrons at 5 K with a current of 100 nA for 60 min, corresponding to effective doses of 7.3 ± 0.3 eV molecule^{-1} for methane and 15.6 ± 0.3 eV molecule^{-1} for hydrogen sulfide.[23] Fourier transform infrared (FTIR) spectra were recorded to characterize the deposited ices of methane and hydrogen sulfide (CH_4–H_2S), before, during, and after electron irradiation at 5 K at a resolution of 4 cm^{-1}. Infrared absorption features observed in pristine and irradiated methane–hydrogen sulfide ices have been reported previously.[23] Briefly, ethane (C_2H_6) formation was evident via multiple fundamental vibrations at 2974 cm^{-1} (ν_1), 2960 cm^{-1}

https://doi.org/10.1021/acs.jpclett.6c01781
J. Phys. Chem. Lett. 2026, 17, 8090−8097

(ν_{10}), 2881 cm^{-1} (ν_5), 1462 cm^{-1} (ν_{11}), and the $\nu_8 + \nu_{11}$ mode at 2939 cm^{-1}.[24] The absorption at 1437 cm^{-1} was assigned to ethene (C_2H_4, ν_{12}).[24] Carbon disulfide (CS_2) was identified via its prominent asymmetric stretch ν_3, at 1513 cm^{-1}.[25]

The main IR features of methyl hydrodisulfide (**2**) were reported to include the CH_3 stretching at 2930 cm^{-1} and CH_3 deformation at 1437 and 1419 cm^{-1}.[19] However, the CH_3 stretching overlaps with the $\nu_8 + \nu_{11}$ mode of ethane (C_2H_6) at 2939 cm^{-1}, while the CH_3 deformation feature coincides with the ν_{12} mode of ethene (C_2H_4) at 1437 cm^{-1}. Additional absorption at 1429 cm^{-1} and 1414 cm^{-1} can be attributed to asymmetric CH_3 deformation vibrations of CH_3−S− groups and/or CH_2 deformation vibrations of CH_2−S− groups.[23,26] In particular, the absorption at 1414 cm^{-1} may also originate from methyl hydrodisulfide (**2**). The new absorption feature at 2495 cm^{-1} shouldering to the symmetric/asymmetric S−H stretching modes of hydrogen sulfide, can be assigned to polysulfanes (H_2S_n; $n > 2$).[17] Due to the overlapping infrared absorption features of molecules in the irradiated ices, unambiguous identification of **1** and **2** cannot be achieved via infrared spectroscopy alone. Moreover, the low product abundances formed under the relatively low-dose irradiation conditions make the unambiguous identification of CH_4S_2 isomers challenging. Thereby, the need for a more sensitive, isomer-selective analytical technique is essential.

Single photon ionization (PI) of subliming molecules, coupled with the detection of the ions utilizing reflectron time-of-flight mass spectrometry (ReToF-MS), represents a valuable tool to identify structural isomers of molecules formed during the exposure of astrophysical model ices to proxies of GCRs in the TPD phase.[21,27] Following irradiation, the ices were warmed from 5 to 330 K at a heating rate of 1 K min^{-1}. During this process, subliming species were photoionized in the gas phase using pulsed (30 Hz) VUV photoionization, separated by their mass-to-charge ratios with a reflectron time-of-flight mass spectrometer, and detected using a microchannel plate detector. Each mass spectrum was obtained by integrating 3600 sweeps, corresponding to an integration time of 2 min. The PI-ReToF-MS requires accurate knowledge of the IEs of the structural isomers of interest (Figure 1a). Three conformers of the geminal dithiol (**1**) were identified at the CCSD(T)-F12/cc-pVTZ-F12 level of theory as implemented in the MOLPRO 2025.1 program.[28−32] The methyl hydrodisulfide isomer (CH_3SSH, **2**)—also known as methyl hydrogen disulfide or methyldisulfane—is thermodynamically favored by some 23 kJ mol^{-1} compared to the three conformers **1a**, **1b**, and **1c** of methanedithiol ($CH_2(SH)_2$). Such a finding differs from the oxygen analogue, which energetically favors two conformers of methanediol ($CH_2(OH)_2$) by 267 kJ mol^{-1} (**3a**) and 257 kJ mol^{-1} (**3b**) compared to the methyl peroxide isomer (CH_3OOH, **4**).[8] Only one conformer of the geminal dithiol cation exists, the **1c** form. The cations of the remaining conformers exhibit imaginary frequencies; following the corresponding coordinates downhill for each cation produces the **1c** cation structure. The neutral geometries of conformers **1a** and **1b** are nearly degenerate in energy, but they are distinctly separated into their own minimum energy wells. These data guide the selection of the experimental photon energies: VUV photon energies of 10.49 and 9.34 eV can ionize both isomers **1** and **2**. Photon energy of 8.75 eV can selectively ionize isomer **2** (IE = 8.56−8.64 eV), but not **1** (IE = 8.80−8.91 eV) (Table S1). At 8.17 eV, which is below the IEs of **1** and **2**, neither of the two isomers can be ionized. Figure 1b compiles the adiabatic IEs and the photon energies utilized in the experiments.

The sublimation profile of m/z = 80 observed at 9.34 eV with an onset sublimation temperature of 121 K and a peak at 163 K is shown in Figure 2a. Possible molecular species that

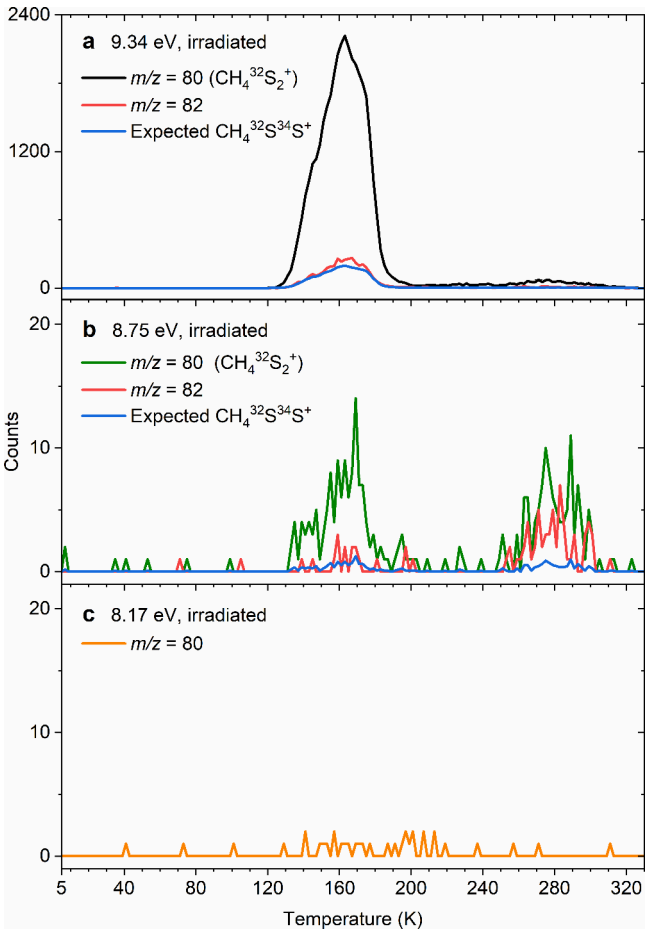


Figure 2. $^{32}S/^{34}S$ ratio comparisons for the two-sulfur system—CH_4S_2 (m/z = 80)—in irradiated CH_4−H_2S ices at photon energies of (a) 9.34 eV, (b) 8.34 eV, and (c) 8.17 eV in high dose irradiation experiments.

can bear a mass-to-charge ratio (m/z) of 80 in these ices containing only carbon−hydrogen-sulfur are $CH_4S_2^+$, C_4S^+, and $C_6H_8^+$. To confirm the molecular formula of this ion signal, the natural isotopic distribution ratio among the sulfur isotopes ^{32}S and ^{34}S was utilized. The expected ion counts at m/z = 82 for $CH_4{}^{32}S^{34}S$ were predicted utilizing the ion signal at m/z = 80 ($CH_4{}^{32}S_2{}^+$). This expected integrated signal of m/z = 82 versus 80 of 9% matches well with the signal observed of 11 ± 2% (Figure 2a). Thereby, the ion signal observed at m/z = 80 at 9.34 eV peaking at 163 K is originating from species carrying two sulfur atoms: CH_4S_2. This signal collected at 9.34 eV was compared to ion counts collected at photon energies of 8.75 and 8.17 eV. When the photon energy was lowered to 8.75 eV, the integrated signal counts dropped from 70 820 ± 400 to 310 ± 100. Figure 2b compares the expected isotopic contribution at m/z = 82 ($CH_4{}^{32}S^{34}S^+$) to the signal observed at m/z = 82 at 8.75 eV, confirming that the molecular carrier contains two sulfur atoms—CH_4S_2—for the sublimation event peaking at 169 K, but not for the sublimation event with a peak

https://doi.org/10.1021/acs.jpclett.6c01781
J. Phys. Chem. Lett. 2026, 17, 8090−8097

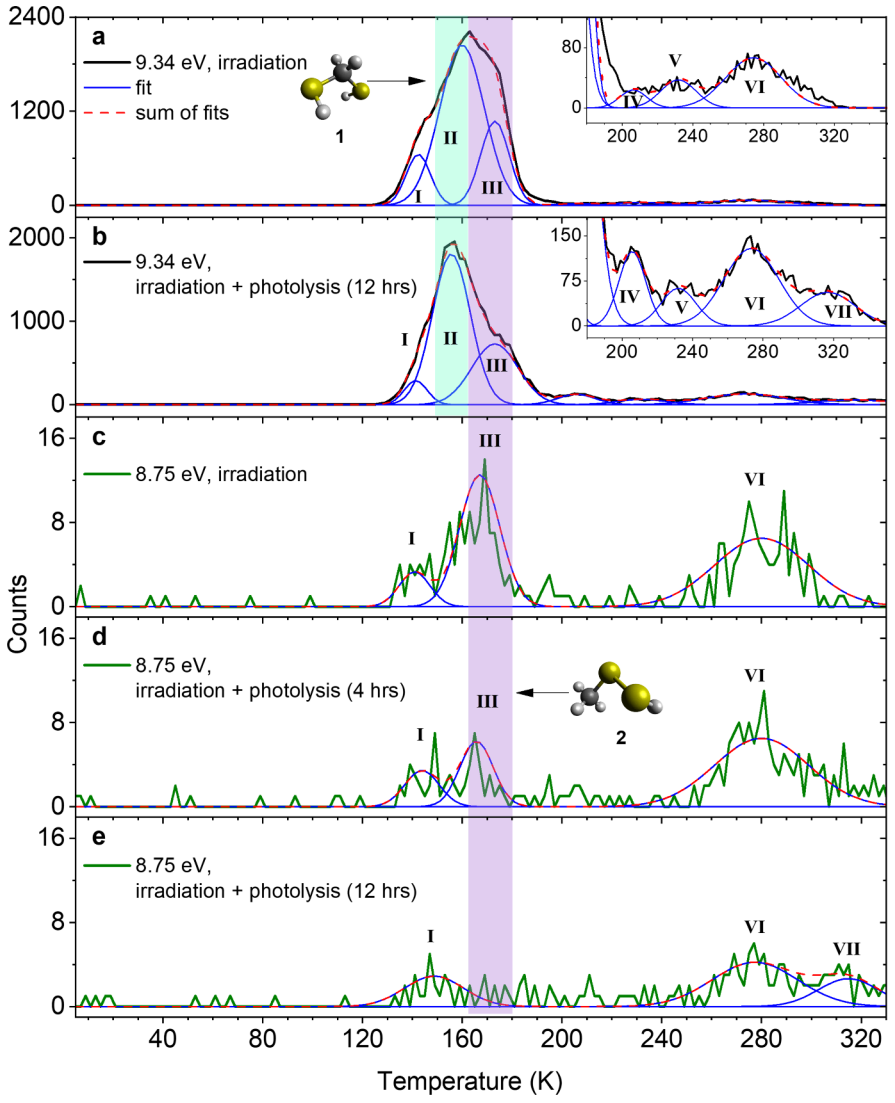


Figure 3. Deconvoluted ion signals at m/z = 80 recorded during TPD of irradiated CH_4–H_2S ices. Ion signal for irradiation-only ice observed at 9.34 eV (a) and 8.75 eV (c). Irradiation followed by photolysis at 282 nm for 12 h, recorded at 9.34 eV (b). TPD signal after photolysis at 282 nm for 4 h (d) and 12 h (e), recorded at 8.75 eV. The sublimation events are deconvoluted into peaks I–VII. The sublimation signals between 180–330 K in panels (a) and (b) are shown in magnified view. The green and violet shaded regions indicate sublimation events corresponding to isomers **1** and **2**, respectively.

sublimation temperature of 280 K. No ion signal was observed at 8.17 eV (Figure 2c). These results suggest that ion signal observed at 8.75 eV can be linked to isomer **2** subliming at 163 K. Since the absolute photoionization cross sections of **1** versus **2** are unknown, no conclusion can be made at this stage if the drop of ion counts from 9.34 to 8.75 eV is the result of **1** or originates from the reduced photoionization cross section of **2**. Therefore, the photoionization experiments provide compelling evidence for **2**, but not (yet) of **1**.

To evaluate the potential presence of **1**, isomer-selective photolysis experiments were carried out. The ultraviolet (UV) spectra of both isomers were calculated at the TD-B3LYP/aug-cc-pVTZ level of theory using the Gaussian 16 program (Figure S1).[33−38] Calculated spectra revealed that UV bands below 259 nm overlap significantly among the two isomers, whereas isomer **2** can be selectively photolyzed at 282 nm. For the photolysis experiments, methane-hydrogen sulfide ices were first exposed to energetic electrons to synthesize CH_4S_2 isomer(s), and subsequently subjected to UV photolysis at 282 nm to selectively photolyze and hence destroy isomer **2**. The resulting changes in the TPD profiles of m/z = 80 at 9.34 and 8.75 eV can be used to identify any remaining contributions from isomer **1**: a complete loss of the m/z = 80 signal in the TPD profile at 8.75 eV after photolysis indicates the destruction of isomer **2**, whereas persistence of the signal at 9.34 eV requires deconvolution of contributions from both isomers. Figure 3 compares the m/z = 80 ion signal from irradiated ices with and without 282 nm photolysis. Three sublimation events (peaks I, II, and III) were identified at 9.34 eV, whereas two sublimation events (peaks I and III) were observed at 8.75 eV, both assigned to species with the molecular formula CH_4S_2. At 8.75 eV, the signal intensity of peak III decreased after 4 h of photolysis (Figure 3d) and disappeared after 12 h (Figure 3e), indicating selective destruction consistent with isomer **2**. In contrast, peak II observed only at 9.34 eV showed no measurable change upon 12 h of photolysis (Figures 3a and 3b). Since isomer **1** cannot be photolyzed at 282 nm, its persistence indicates that peak II

https://doi.org/10.1021/acs.jpclett.6c01781
J. Phys. Chem. Lett. 2026, 17, 8090−8097

is assigned to **1**. Note that peak I remained even after photolysis and the deconvoluted peaks between 200 and 330 K are labeled IV through VIII; these weak peaks may be attributed to the fragments of higher mass species. A blank experiment without irradiation was conducted at 10.49 eV under otherwise identical conditions; no sublimation event was observed at m/z = 80,[23] confirming that the ion signal responsible for these molecules is caused by the energetic electron irradiation of processed ices. All detected mass channels of ion signals and their proposed molecular formulas are summarized in Table S3.

Having provided evidence for the formation of methanedithiol (**1**) and methyl hydrodisulfide (**2**) in irradiated methane−hydrogen sulfide ices, we now consider their potential formation pathways. Previous laboratory studies have demonstrated the formation of disulfane (HSSH) and methanethiol (CH_3SH) in electron-irradiated hydrogen sulfide and methane−hydrogen sulfide ices, respectively.[17,23] Methanedithiol (**1**) may form either via insertion of an electronically excited sulfur atom ($S(^1D)$) into the C−H bond of methanethiol (reaction 1) or through methylene (CH_2) insertion into the S−S bond of disulfane (reaction 2) (Figure S2). In contrast, methyl hydrodisulfide (**2**) could form through sulfur atom insertion into the C−S or S−H bond of methanethiol (reaction 3) or via methylene insertion into the S−H bond of disulfane (reaction 4). The insertion reactions leading to **1** and **2** are expected to be barrierless for electronically excited sulfur atoms and for electronically excited singlet carbene. This behavior is analogous to the oxygen system, in which methanediol (**3**) and methyl peroxide (**4**) are formed barrierlessly via insertion of excited oxygen atom ($O(^1D)$) into the C−H and C−O bonds of methanol (CH_3OH), releasing 626 and 359 kJ mol^{-1}, respectively.[8]

$$CH_3SH + S \rightarrow CH_2(SH)_2(\mathbf{1}) \quad (1)$$

$$HSSH + CH_2 \rightarrow CH_2(SH)_2(\mathbf{1}) \quad (2)$$

$$CH_3SH + S \rightarrow CH_3SSH(\mathbf{2}) \quad (3)$$

$$HSSH + CH_2 \rightarrow CH_3SSH(\mathbf{2}) \quad (4)$$

To further elucidate the formation mechanisms, additional *low dose* irradiation experiments were conducted at 10.49 eV using CH_4−H_2S ice and isotopically labeled ice mixtures (CH_4−D_2S and CD_4−H_2S). In the low dose CH_4−H_2S ice experiment, the TPD profile of m/z = 80 exhibits three sublimation events peaking at 85 K, 140 K (peak VIII), and 181 K (peak IX) (Figure 4a). The weak feature at 85 K was attributed to detector saturation caused by intense H_2S desorption. In contrast, high dose experiments at 9.34 eV exhibit a broad sublimation event peaking at 163 K (Figure 2). Integrated intensity ratios of m/z = 82 to m/z = 80 for peaks VIII and IX are 10% ± 2% and 19% ± 2%, respectively. Only peak VIII matches the natural isotopic abundance ratio of ^{32}S:^{34}S (9%) and is therefore assigned to CH_4S_2 isomers, whereas peak IX at 180 K likely arises from fragment ions of higher mass species formed via dissociative photoionization at 10.49 eV. Accordingly, only peak VIII is used for isotopic analysis in deuterated ice mixtures.

In the irradiated CD_4−H_2S ice, TPD profiles of m/z = 82, 83, and 84 all exhibit peak VIII, whereas no corresponding signal is observed at m/z = 80 (Figure 4b). The m/z = 82 signal ($CH_2D_2S_2^+$) is assigned to **1**-d_2 and/or **2**-d_2, formed via

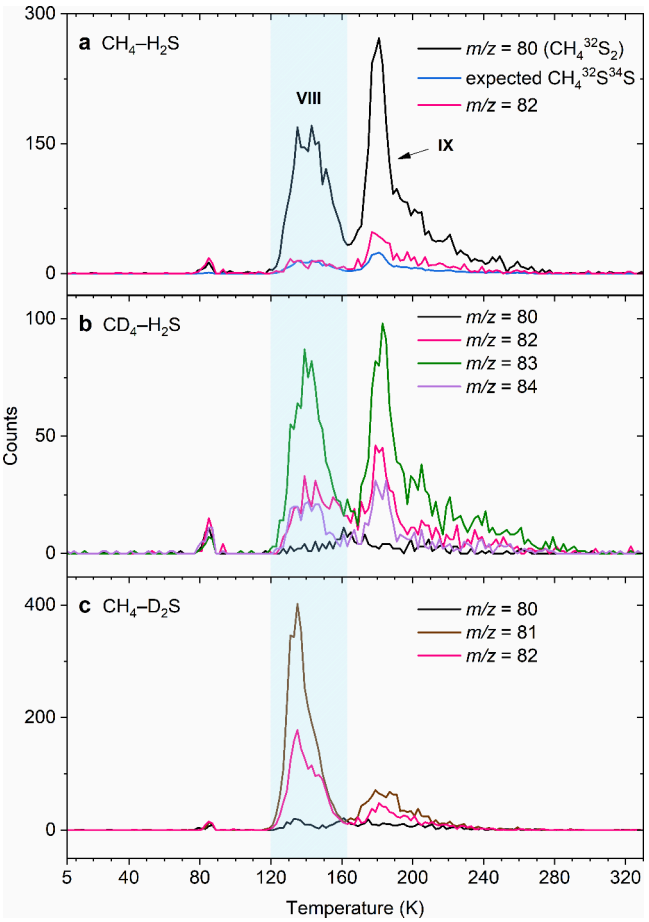


Figure 4. (a) TPD profiles for CH_4S_2 (m/z = 80) under low dose irradiation and photoionization at 10.49 eV. TPD profile for m/z = 80 in CH_4−H_2S ice is compared to the signal observed at m/z = 82 and the expected signal for $CH_4{}^{32}S^{34}S$. Isotopic mass shifts are observed in the TPD profiles of the deuterated ice mixtures (b) CD_4−H_2S and (c) CH_4−D_2S.

insertion of methylene-d_2 (CD_2) into the S−H bonds of disulfane or sulfur atom insertion into methanethiol-d_2 (HCD_2SH) (Figure S3). Mass shifts of 3 amu (m/z = 83) and 4 amu (m/z = 84) indicate the formation of CHD_3S_2 and CD_4S_2 species, respectively. The m/z = 83 signal is assigned to **1**-d_3 and/or **2**-d_3 arising from sulfur atom insertion into C−D bonds of methanethiol-d_3 (CD_3SH), while the m/z = 84 feature is attributed to **1**-d_4 and/or **2**-d_4 formed via sulfur atom insertion into C−S or S−D bonds of methanethiol-d_4 (CD_3SD). Among these mass channels, the strongest signal is observed at m/z = 83, indicating preferential formation of methanethiol-d_3 (CD_3SH) in the CD_4−H_2S system. Similar behavior is observed in the irradiated CH_4−D_2S ice (Figure 4c), where TPD profiles of m/z = 80, 81, and 82 all display peak VIII. The CH_4S_2 isomers at m/z = 80 can form through two successive sulfur atom insertions into methane (Figure S4). Sulfur insertion into the C−H, C−S, or S−D bonds of methanethiol-d_1 (CH_3SD) produces **1**-d_1 and/or **2**-d_1, contributing to the m/z = 81 signal. The insertion of methylene into disulfane-d_2 (DSSD) or sulfur insertion into methanethiol-d_2 (CH_2DSD) yields **1**-d_2 and/or **2**-d_2 detected at m/z = 82. The dominant intensity at m/z = 81 indicates that methanethiol-d_1 (CH_2DSH) is formed preferentially in the CH_4−D_2S ice. Overall, isotopic substitution experiments

https://doi.org/10.1021/acs.jpclett.6c01781
J. Phys. Chem. Lett. 2026, 17, 8090−8097

support the formation pathways involving sequential sulfur atom insertion and methylene insertion processes mediated by methanethiol and disulfane intermediates. The dominant partially deuterated products further indicate that sulfur insertion into methanethiol is a major pathway leading to isomers **1** and **2** (Figure 5).

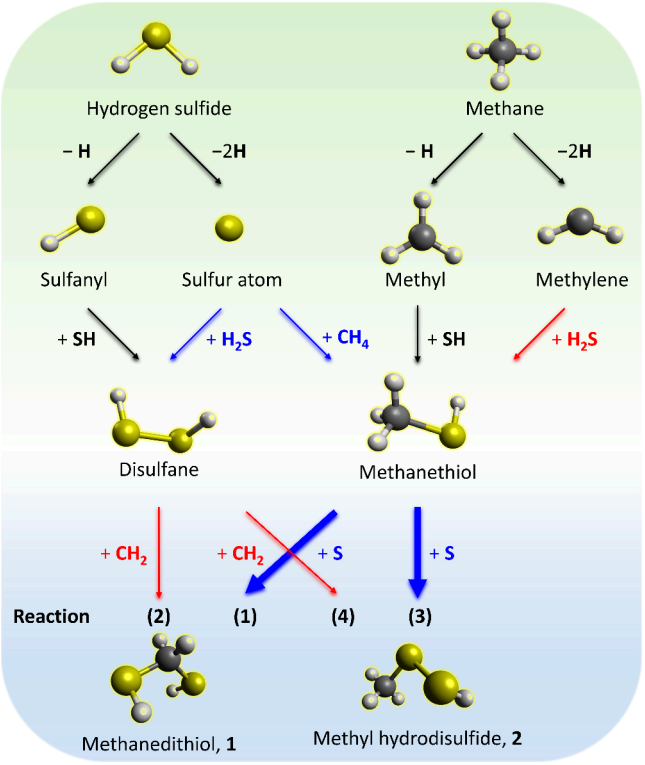


Figure 5. Proposed formation pathways of isomers **1** and **2** in irradiated methane–hydrogen sulfide ices. Red and blue arrows indicate methylene and sulfur atom insertions, respectively.

In conclusion, we present the first formation of the simplest geminal dithiol molecule, methanedithiol (**1**), together with its isomer methyl hydrodisulfide (**2**), in low-temperature model interstellar ices composed of methane and hydrogen sulfide. The ice mixtures were exposed to energetic electrons, simulating the secondary electrons produced in tracks of GCRs on the lifetime of a typical cold molecular cloud of a few 10^7 years.[39] These molecules were identified in the gas phase using VUV photoionization time-of-flight mass spectrometry combined with UV photolysis. Deuterium-labeled ice mixtures provide mechanistic evidence for the preferred formation routes leading to **1** and **2** as the barrierless radical–radical recombination of methyl and sulfanyl radicals followed by S atom insertion processes, in these low-temperature ices. Although thermodynamically most stable structures differ between oxygen and sulfur analogues in CH_4O_2 and CH_4S_2 systems, the observation of both isomers **1** and **2** in the gas phase resembles the oxygen analogues, methanediol (**3**) and methyl peroxide (**4**).[8] The low temperature of 5 K and ultrahigh vacuum conditions of 10^{-11} Torr utilized here can be extrapolated to extraterrestrial interstellar cloud environments, explicitly from the surface of interstellar dust grains in dense molecular clouds to star-forming regions. Even the low dose experiments carried out with exposure doses as low as 0.16 ± 0.04 eV molecule^{-1} for methane and 0.28 ± 0.04 eV molecule^{-1} for hydrogen sulfide, amounting to 1–10% of total GCR exposure to interstellar ices over a lifetime in a cold molecular cloud,[39] the formation of these molecules is observed. Once formed, these molecules can sublime into the gas phase during the warm-up phase of star-forming regions. Most recently, Merino and co-workers computationally characterized the structures, spectroscopy, and energies of CH_4S_2 isomers as astrochemically relevant sulfur-bearing molecules,[40] motivated by the sulfur depletion problem in the ISM.[41,42] Earlier theoretical studies also reported the low-temperature spectroscopic predictions for methyl hydrodisulfide,[43] and the reactivity of alkyl hydropersulfides with hydrogen sulfide.[44] Notably, methanethiol (CH_3SH) has been observed toward the Sgr B2 molecular cloud[45] and multiple star-forming regions such as the hot cores Orion KL[46] and G327.3–0.6[47] and that isomers **1** and **2** are only a sulfur-atom insertion step away from methanethiol. Given that the microwave and infrared spectra of methyl hydrodisulfide (**2**) have been previously measured[19,20] and that isomers **1** and **2** possess relatively large dipole moments of up to 2.0 D[40] and 1.796 D,[20] respectively, methanedithiol (**1**) and methyl hydrodisulfide (**2**) represent promising targets for future astronomical searches in these interstellar environments using telescopes such as the Atacama Large Millimeter/submillimeter Array (ALMA) and the James Webb Space Telescope (JWST). Alternatively, these simple organosulfur molecules may serve not only as potential reservoirs of the missing sulfur[40] but also as precursors to complex sulfur-containing molecules such as dithioformic acid (HC(S)SH), recently detected toward the hot corino NGC 1333 IRAS 4A2,[48] highlighting nonequilibrium pathways that drive the emergence of increasingly complex sulfur chemistry in extraterrestrial environments and shedding light to the sulfur depletion problem.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.6c01781.

Experimental and computational methods, simulated UV spectra of isomers **1** and **2** (Figure S1), proposed formation pathways leading to **1** and **2** in CH_4–H_2S ice (Figure S2), CD_4–H_2S ice (Figure S3), CH_4–D_2S ice (Figure S4), uncertainty analysis of IEs (Table S1), VUV generation parameters (Table S2), proposed molecular formula for all observed mass channels (Table S3), Cartesian coordinates, vibrational frequencies, computed UV frequencies and intensities (Tables S4 and S5) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Ryan C. Fortenberry – *Department of Chemistry and Biochemistry, University of Mississippi, Oxford, Mississippi 38677, United States;* orcid.org/0000-0003-4716-8225; Email: r410@olemiss.edu

André K. Eckhardt – *Lehrstuhl für Organische Chemie II, Ruhr-Universitat Bochum, Bochum 44801, Germany;* orcid.org/0000-0003-1029-9272; Email: Andre.Eckhardt@ruhr-uni-bochum.de

Ralf I. Kaiser – *Department of Chemistry and W. M. Keck Laboratory in Astrochemistry, University of Hawai'i at*

https://doi.org/10.1021/acs.jpclett.6c01781
J. Phys. Chem. Lett. 2026, 17, 8090–8097

Mānoa, Honolulu, Hawaii 96822, United States; orcid.org/0000-0002-7233-7206; Email: ralfk@hawaii.edu

Authors

Jia Wang − *Department of Chemistry and W. M. Keck Laboratory in Astrochemistry, University of Hawai'i at Mānoa, Honolulu, Hawaii 96822, United States*

Ashanie Herath − *Department of Chemistry and W. M. Keck Laboratory in Astrochemistry, University of Hawai'i at Mānoa, Honolulu, Hawaii 96822, United States*

Andrew M. Turner − *Department of Chemistry and W. M. Keck Laboratory in Astrochemistry, University of Hawai'i at Mānoa, Honolulu, Hawaii 96822, United States*

Mason McAnally − *Department of Chemistry and W. M. Keck Laboratory in Astrochemistry, University of Hawai'i at Mānoa, Honolulu, Hawaii 96822, United States;* orcid.org/0009-0000-7799-9914

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.6c01781

Author Contributions

#J. Wang and A. Herath contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation (NSF) Division of Astronomical Sciences (NSF-AST 2403867). The authors thank the W. M. Keck Foundation (R.I.K) for financing the experimental setup and the University of Hawai'i for providing teaching assistantships (A.H., M.M.). The computational work employed the Mississippi Center for Supercomputing Research, which is gratefully acknowledged for its use herein. The work by R.C.F. is supported by NSF grant AST 2407815. The work in Bochum was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy − EXC 2033 − 390677874 − RESOLV.

■ REFERENCES

(1) Langmuir, I. The arrangement of electrons in atoms and molecules. *J. Am. Chem. Soc.* **1919**, *41*, 868−934.

(2) Wagner, P. D. The biology of oxygen. *Eur. Respir. J.* **2008**, *31*, 887−890.

(3) Francioso, A.; Baseggio Conrado, A.; Mosca, L.; Fontana, M. Chemistry and biochemistry of sulfur natural compounds: Key intermediates of metabolism and redox biology. *Oxid. Med. Cell. Longev.* **2020**, *2020*, 8294158.

(4) Eckert, B.; Steudel, R. Elemental sulfur and sulfur-rich compounds II. *Top. Curr. Chem.* **2003**, *231*, 31−98.

(5) Parker, D. S. N.; Wilson, A. V.; Kaiser, R. I.; Labrador, T.; Mebel, A. M. Gas-phase synthesis of the silaisocyanoethylene molecule (C_2H_3NSi). *J. Org. Chem.* **2012**, *77*, 8574−8580.

(6) Parker, D. S. N.; Mebel, A. M.; Kaiser, R. I. The role of isovalency in the reactions of the cyano (CN), boron monoxide (BO), silicon nitride (SiN), and ethynyl (C_2H) radicals with unsaturated hydrocarbons acetylene (C_2H_2) and ethylene (C_2H_4). *Chem. Soc. Rev.* **2014**, *43*, 2701−2713.

(7) Turner, A. M.; Abplanalp, M. J.; Chen, S. Y.; Chen, Y. T.; Chang, A. H. H.; Kaiser, R. I. A photoionization mass spectroscopic study on the formation of phosphanes in low temperature phosphine ices. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27281−27291.

(8) Zhu, C.; Kleimeier, N. F.; Turner, A. M.; Singh, S. K.; Fortenberry, R. C.; Kaiser, R. I. Synthesis of methanediol [$CH_2(OH)_2$]: The simplest geminal diol. *Proc. Natl. Acad. Sci. U.S.A.* **2022**, *119*, No. e2111938119.

(9) Voronkov, M.; Shagun, L.; Ermolyuk, L.; Timokhina, L. Geminal dithiols. *J. Sulfur Chem.* **2004**, *25*, 131−153.

(10) Cairns, T. L.; Evans, G. L.; Larchar, A. W.; McKusick, B. C. gem-Dithiols. *J. Am. Chem. Soc.* **1952**, *74*, 3982−3989.

(11) Penzias, A. A.; Solomon, P. M.; Wilson, R. W.; Jefferts, K. B. Interstellar carbon monosulfide. *Astrophys. J.* **1971**, *168*, L53.

(12) Sanz-Novo, M.; Rivilla, V. M.; Endres, C. P.; Lattanzi, V.; Jiménez-Serra, I.; Colzi, L.; Zeng, S.; Megías, A.; López-Gallifa, Á.; Martínez-Henares, A.; et al. On the abiotic origin of dimethyl sulfide: Discovery of dimethyl sulfide in the interstellar medium. *Astrophys. J. Lett.* **2025**, *980*, L37.

(13) Cabezas, C.; Vávra, K.; Molpeceres, G.; Kolesniková, L.; Agúndez, M.; Vylitová, G.; Marcelino, N.; Hrubčík, L.; Fuentetaja, R.; Uhlíková, T.; et al. Discovery of propenethial (CH_2CHCHS) in TMC-1. *Astron. Astrophys.* **2025**, *698*, L24.

(14) McClure, M. K.; Rocha, W. R. M.; Pontoppidan, K. M.; Crouzet, N.; Chu, L. E. U.; Dartois, E.; Lamberts, T.; Noble, J. A.; Pendleton, Y. J.; Perotti, G.; et al. An ice age JWST inventory of dense molecular cloud ices. *Nat. Astron.* **2023**, *7*, 431−443.

(15) Shingledecker, C. N.; Lamberts, T.; Laas, J. C.; Vasyunin, A.; Herbst, E.; Kästner, J.; Caselli, P. Efficient production of S_8 in interstellar ices: The effects of cosmic-ray-driven radiation chemistry and nondiffusive bulk reactions. *Astrophys. J.* **2020**, *888*, 52.

(16) Vidal, T. H. G.; Loison, J.-C.; Jaziri, A. Y.; Ruaud, M.; Gratier, P.; Wakelam, V. On the reservoir of sulphur in dark clouds: chemistry and elemental abundance reconciled. *Mon. Not. R. Astron. Soc.* **2017**, *469*, 435−447.

(17) Herath, A.; McAnally, M.; Turner, A. M.; Wang, J.; Marks, J. H.; Fortenberry, R. C.; Garcia-Alvarez, J. C.; Gozem, S.; Kaiser, R. I. Missing interstellar sulfur in inventories of polysulfanes and molecular octasulfur crowns. *Nat. Commun.* **2025**, *16*, 5571.

(18) Böhme, H.; Zinner, G. Über Darstellung und Eigenschaften von Alkyl-hydro-polysulfiden. *Justus Liebigs Ann. Chem.* **1954**, *585*, 142−149.

(19) Grassi, G.; Tyblewski, M.; Bauder, A. Convenient preparation and spectroscopic characterization of methyl hydrodisulfide and methyl deuterodisulfide. *Helv. Chim. Acta* **1985**, *68*, 1876−1879.

(20) Tyblewski, M.; Ha, T. K.; Bauder, A. Microwave spectrum, electric dipole moment, internal rotation barrier, and molecular structure of methyl hydrodisulfide. *J. Mol. Spectrosc.* **1986**, *115*, 353−365.

(21) Abplanalp, M. J.; Forstel, M.; Kaiser, R. I. Exploiting single photon vacuum ultraviolet photoionization to unravel the synthesis of complex organic molecules in interstellar ices. *Chem. Phys. Lett.* **2016**, *644*, 79−98.

(22) Wang, J.; Zhang, C.; Marks, J. H.; Evseev, M. M.; Kuznetsov, O. V.; Antonov, I. O.; Kaiser, R. I. Interstellar formation of lactaldehyde, a key intermediate in the methylglyoxal pathway. *Nat. Commun.* **2024**, *15*, 10189.

(23) Herath, A.; Turner, A. M.; McAnally, M.; Wang, J.; Kaiser, R. I. Formation of dimethyl sulfide (CH_3SCH_3) and ethanethiol (CH_3CH_2SH) in interstellar analog ices of methane (CH_4) and hydrogen sulfide (H_2S). *Phys. Chem. Chem. Phys.* **2026**, *28*, 5094−5110.

(24) Bennett, C. J.; Jamieson, C. S.; Osamura, Y.; Kaiser, R. I. Laboratory studies on the irradiation of methane in interstellar, cometary, and solar system ices. *Astrophys. J.* **2006**, *653*, 792−811.

(25) Maity, S.; Kim, Y. S.; Kaiser, R. I.; Lin, H. M.; Sun, B. J.; Chang, A. H. H. On the detection of higher order carbon sulfides (CSx; x = 4−6) in low temperature carbon disulfide ices. *Chem. Phys. Lett.* **2013**, *577*, 42−47.

(26) Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*; John Wiley & Sons, Ltd., 2004.

(27) Turner, A. M.; Kaiser, R. I. Exploiting photoionization reflectron time-of-flight mass spectrometry to explore molecular

mass growth processes to complex organic molecules in interstellar and solar system ice analogs. *Acc. Chem. Res.* **2020**, *53*, 2791−2805.
(28) Adler, T. B.; Knizia, G.; Werner, H.-J. A simple and efficient CCSD(T)-F12 approximation. *J. Chem. Phys.* **2007**, *127*, 221106.
(29) Knizia, G.; Adler, T. B.; Werner, H.-J. Simplified CCSD(T)-F12 methods: Theory and benchmarks. *J. Chem. Phys.* **2009**, *130*, No. 054104.
(30) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A fifth-order perturbation comparison of electron correlation theories. *Chem. Phys. Lett.* **1989**, *157*, 479−483.
(31) Peterson, K. A.; Adler, T. B.; Werner, H.-J. Systematically convergent basis sets for explicitly correlated wavefunctions: The atoms H, He, B−Ne, and Al−Ar. *J. Chem. Phys.* **2008**, *128*, No. 084102.
(32) Werner, H.; Knowles, P.; Knizia, G.; Manby, F.; Schütz, M.; Celani, P.; Györffy, W.; Kats, D.; Korona, T.; Lindh, R. MOLPRO, version 2025.1, a package of ab initio programs (see http://www.molpro.net 2025).
(33) Yang, W.; Parr, R. G.; Lee, C. Various functionals for the kinetic energy density of an atom or molecule. *Phys. Rev. A* **1986**, *34*, 4586−4590.
(34) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785−789.
(35) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(36) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.
(37) Adamo, C.; Jacquemin, D. The calculations of excited-state properties with Time-Dependent Density Functional Theory. *Chem. Soc. Rev.* **2013**, *42*, 845−856.
(38) Frisch, M. J.; Trucks, G. W., Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16, Rev. C.01.*; Gaussian, Inc.: Wallingford, CT, 2016.
(39) Yeghikyan, A. G. Irradiation of dust in molecular clouds. II. Doses produced by cosmic rays. *Astrophysics* **2011**, *54*, 87−99.
(40) Flores-Larrañaga, R.; Gonzalez-Ortiz, L. A.; Ortíz-Chi, F.; Castro, M. E.; Melendez, F. J.; Noriega, L.; Merino, G. Computational characterization of CH_4S_2 isomers as key candidates in interstellar sulfur chemistry. *ACS Earth Space Chem.* **2026**, *10*, 110−119.
(41) Jiménez-Escobar, A.; Muñoz Caro, G. M. Sulfur Depletion in Dense Clouds and Circumstellar Regions. *Astron. Astrophys.* **2011**, *536*, A91.
(42) Ruffle, D. P.; Hartquist, T. W.; Caselli, P.; Williams, D. A. The sulphur depletion problem. *Mon. Not. R. Astron. Soc.* **1999**, *306*, 691−695.
(43) Dalbouha, S.; Senent, M. L.; Komiha, N. Theoretical spectroscopic characterization at low temperatures of methyl hydroperoxide and three S-analogs. *J. Chem. Phys.* **2015**, *142*, 074304
(44) Zhang, L.; Zhang, X.; Wu, Y.-D.; Xie, Y.; Fukuto, J. M.; Schaefer, H. F. The reaction of alkyl hydropersulfides (RSSH, R = CH_3 and ^{t}Bu) with H_2S in the gas phase and in aqueous solution. *Phys. Chem. Chem. Phys.* **2019**, *21*, 537−545.
(45) Linke, R. A.; Frerking, M. A.; Thaddeus, P. Interstellar methyl mercaptan. *Astrophys. J.* **1979**, *234*, L139−L142.
(46) Kolesniková, L.; Tercero, B.; Cernicharo, J.; Alonso, J. L.; Daly, A. M.; Gordon, B. P.; Shipman, S. T. Spectroscopic characterization and detection of ethyl mercaptan in ORION. *Astrophys. J.* **2014**, *784*, L7.
(47) Gibb, E.; Nummelin, A.; Irvine, W. M.; Whittet, D. C. B.; Bergman, P. Chemistry of the organic-rich hot core G327.3−0.6. *Astrophys. J.* **2000**, *545*, 309.
(48) Manna, A.; Pal, S. First identification and chemical modeling of new thiol (−SH) bearing molecule in the interstellar medium: Dithioformic acid. *ACS Earth Space Chem.* **2024**, *8*, 2401−2410.

https://doi.org/10.1021/acs.jpclett.6c01781
J. Phys. Chem. Lett. 2026, 17, 8090−8097