

A Crossed Molecular Beams and Computational Study of the Formation of the Astronomically Elusive Thiosilaformyl Radical (HSiS , X^2A')

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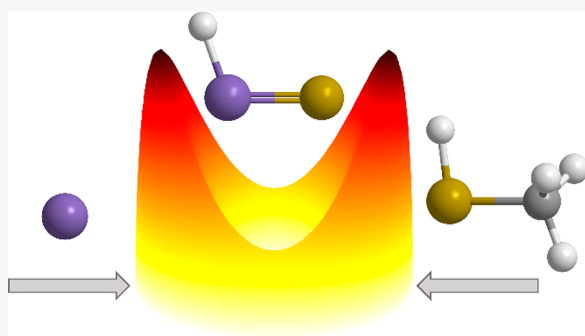


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Supporting Information

ABSTRACT: The formation pathways to silicon- and sulfur-containing molecules are crucial to the understanding of silicon–sulfur chemistry in interstellar and circumstellar environments. While multiple silicon- and sulfur-containing species have been observed in deep space, their fundamental formation mechanisms are largely unknown. The crossed molecular beams technique combined with electronic structure and Rice–Ramsperger–Kassel–Marcus (RRKM) calculations was utilized to study the bimolecular reaction of atomic silicon ($\text{Si}(^3P_j)$) with thiomethanol (CH_3SH , X^1A') leading to the thiosilaformyl radical (HSiS , X^2A') via an exclusive methyl radical (CH_3 , X^2A_2'') loss via indirect scattering dynamics which involves barrierless addition and hydrogen migration in an overall exoergic reaction, indicating the possibility that HSiS can form in cold molecular clouds. The astronomically elusive thiosilaformyl radical may act as a tracer of an exotic silicon–sulfur chemistry to be deciphered toward, for example, the star-forming region SgrB2, thus leading to a better understanding of the formation of silicon–sulfur bonds in deep space.



The investigation of the formation and reactivity of sulfur-bearing molecules in extraterrestrial environments represents an important instrument to understand the history and chemical evolution of star-forming regions, cold molecular clouds, and circumstellar envelopes of carbon stars.^{1–3} Compared to the cosmic carbon versus sulfur ratio of 15:1, sulfur is severely depleted in carbon-containing molecules. Thiomethanol (methylmercaptan, CH_3SH), the isovalent counterpart of methanol (CH_3OH), represents one of 20 sulfur–carbon-bearing molecules detected in the interstellar medium (ISM) (Figure 1). Identified for the first time by Linke et al. in the star-forming region SgrB2⁴ through its rotational spectrum⁵ and confirmed by Turner,⁶ Bellocche et al.,⁷ and Müller et al.,⁸ the thiomethanol molecule has emerged as a potential molecular building block leading to sulfur-containing amino acids like cysteine ($\text{HSCH}_2\text{CH}(\text{COOH})\text{NH}_2$) on low-temperature (10 K) ice-coated interstellar grains.⁹ On the basis of the detection of thiomethanol toward the solar type protostar IRAS 16293-2422¹⁰ and the HH 212 protostellar disk,¹¹ Majumdar et al. proposed a formation of thiomethanol on low-temperature icy grains followed by sublimation and/or reactive desorption¹² into the gas phase. Lamberts's computational model¹³ suggested that thiomethanol could be formed on grains from carbon monosulfide (CS) by stepwise hydrogenation via *cis/trans*-thiohydroxycarbene intermediates (HCSH) involving an analogous reaction

sequence from carbon monoxide (CO) to methanol (CH_3OH).¹⁴ However, once released from the grains into the gas phase, the chemistry and reactivity of thiomethanol is not well-understood. Heays et al. proposed that thiomethanol could be photodissociated and photoionized by the ultraviolet interstellar radiation field¹⁵ forming, e.g., CH_3S^+ , CH_2SH^+ , H_2SCS^+ , and HCS^+ . Ion flow studies revealed that thiomethanol could be rapidly protonated upon reaction with the hydronium ion (H_3O^+).¹⁶ Nevertheless, bimolecular reactions of thiomethanol in the gas phase involving two neutral species and their role in the formation of (hitherto astronomically unobserved) sulfur-bearing species have not been explored to date in laboratory experiments.

Crossed molecular beam experiments represent an ideal approach to untangle the outcome of elementary gas-phase reactions leading to sulfur-bearing molecules and their radicals of astrochemical relevance.^{17–19} Merging molecular beams and electronic structure calculations, Kaiser et al.²⁰ and Ochsenfeld

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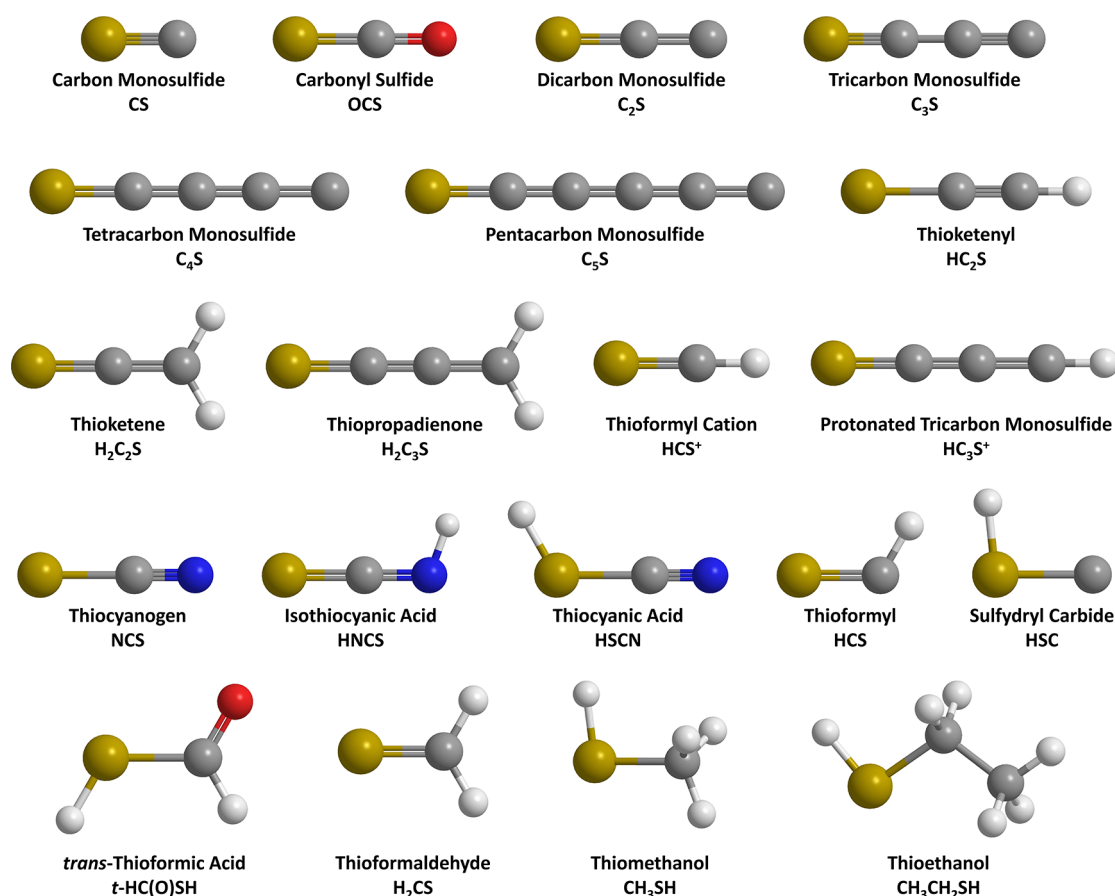
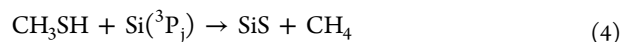
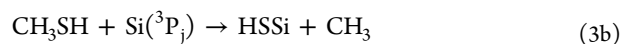
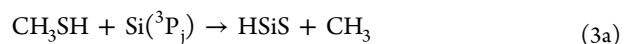
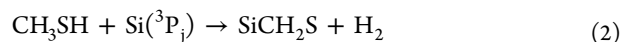
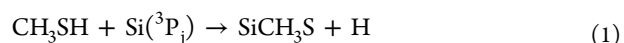


Figure 1. Sulfur–carbon-bearing molecules as detected in the interstellar medium. Atoms are color-coded as follows: sulfur (yellow); carbon (gray); oxygen (red); nitrogen (blue); hydrogen (white).

et al.²¹ revealed that the reaction of ground-state carbon atoms ($\text{C}(^3\text{P}_j)$) with hydrogen sulfide (H_2S) leads to the formation of the thioformyl radical (HCS , $\text{X}^2\text{A}'$) along with atomic hydrogen; reaction rates close to gas kinetics limits of a few $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ were derived.²² The thioketenyl radical (HCCS , $\text{X}^2\Pi$) was assigned as the product of the bimolecular gas-phase reaction of dicarbon (C_2 , $\text{X}^1\Sigma_g^+$) with hydrogen sulfide (H_2S).³ A recent chemical dynamics study of the rapid methylidyne (CH)–hydrogen sulfide (H_2S) reaction revealed the formation of thioformaldehyde (H_2CS) as well as thiohydroxycarbene (HCSH) under the elimination of atomic hydrogen,²³ thus demonstrating the unique power of the crossed molecular beam approach to unravel molecular mass growth processes by coupling interstellar carbon with sulfur chemistry. Here, we provide new knowledge on elementary reactions of sulfur-bearing molecules and unravel the chemical dynamics of the reaction of ground-state silicon atoms ($\text{Si}(^3\text{P}_j)$) with thiomethanol (CH_3SH) under single-collision conditions exploiting molecular beams. Coupling interstellar silicon with sulfur chemistry reveals the formation of at least the astronomically hitherto undetected thiosilaformyl (HSiS , $\text{X}^2\text{A}'$) isomer through the atomic silicon (Si) versus methyl (CH_3) exchange pathway. In deep space, these radicals might be photodissociated by the ultraviolet field, eventually forming interstellar and circumstellar silicon monosulfide (SiS),^{24–27} a molecular building block suggested to initiate a chain of reactions that lead ultimately to sulfide dust grains.^{28–30}

The crossed molecular beam experiments probed the atomic (H) and molecular hydrogen (H_2) loss pathways (reactions 1

and 2) as well as the methyl (CH_3) and methane (CH_4) elimination channels (reactions 3 and 4):



Accounting for the natural isotopic abundances of sulfur (^{32}S , 94.9%; ^{33}S , 0.8%; ^{34}S , 4.3%), silicon (^{28}Si , 92.2%; ^{29}Si , 4.7%; ^{30}Si , 3.1%), and carbon (^{12}C , 98.9%; ^{13}C , 1.1%), the reactive scattering signal was searched for at mass-to-charge ratios of $m/z = 75$ and 74 for the atomic and molecular hydrogen loss channels and at 61 and 60 for the methyl and methane loss channels, respectively. Despite scanning at the center-of-mass angle of 54° for 10 h, no definite signal for channels 1 or 2 was observable. However, signal was observable for the methyl loss channel (reaction (3)) as evidenced from ion counts recorded at $m/z = 61$ (HSiS^+) and 60 (SiS^+) (Figure S1). The TOF spectra at $m/z = 61$ and 60 are superimposable, i.e., they overlap after scaling, suggesting that only a single reaction channel is open in this elementary reaction, and the signal at $m/z = 60$ originates from dissociative electron impact ionization of the neutral reaction product at 61 amu. The

TOF spectra are very broad and extend over 500 μs (Figure 2). The corresponding laboratory angular distribution, which is

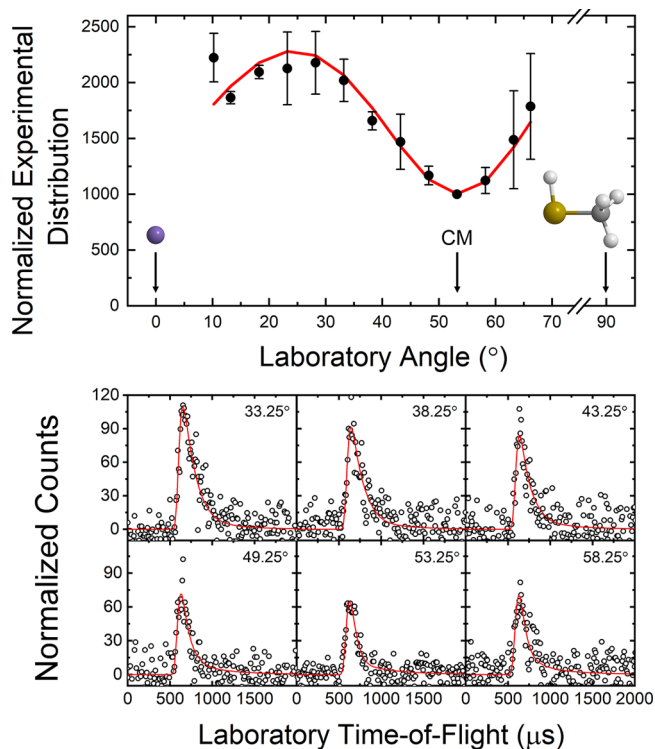


Figure 2. Laboratory angular distribution (top) and TOF spectra (bottom) for the reaction of atomic silicon ($\text{Si}(^3\text{P}_j)$) with thiomethanol (CH_3SH) recorded at $m/z = 61$. The directions of the silicon and thiomethanol beams are 0° and 90° , respectively. The black circles denote the experimental data, with the red lines given as the best-fits obtained from the CM functions shown in Figure 3.

spread over the accessible laboratory angular range from 10° to 67° in the scattering plane, reveals a dip close to the center-of-

mass angle. This finding suggests indirect scattering dynamics through involvement of SiCH_4S collision complex(es). An inspection of the corresponding Newton diagrams for the methyl and methane loss channels (reactions 3 and 4), respectively, reveals interesting findings (Figure S2). These diagrams correspond to the most probable velocities of the atomic silicon and thiomethanol reactants; the two-dimensional projection of the recoil spheres ("Newton circles") indicate the maximum velocities of the recoil vectors for channels 3 and 4 accounting for conservation of energy and momentum. Considering the predicted angular range of the $\text{H}^{28}\text{Si}^{32}\text{S}/\text{H}^{32}\text{S}^{28}\text{Si}$ and $^{28}\text{Si}^{32}\text{S}$ products, the Newton circles for the methyl and methane loss channels are distinct with the angular range of signal collected at $m/z = 61$ revealing close resemblance to the theoretically predicted distribution of the methyl group loss channel 3. The predicted angular range of the methane loss pathway (reaction 4) is significantly larger than the Newton circle of the methyl loss and could not account for the reactive scattering signal. Therefore, our laboratory data along with the Newton diagrams suggest the existence of the atomic silicon versus methyl group loss channel (reaction 3) and the absence of atomic and molecular hydrogen along with methane elimination pathways.

To offer quantitative evidence on the existence of the methyl loss channel (reaction 3) in the reaction of ground-state atomic silicon with thiomethanol and to reveal the chemical dynamics, we are transforming the experimental data from the laboratory to the center-of-mass (CM) reference frame.² First, fits of both the TOF spectra and the laboratory angular distribution could be achieved with a single channel for the reaction of silicon (^{28}Si ; 28 amu) with thiomethanol ($\text{CH}_3^{32}\text{SH}$; 48 amu). This yields reaction products with a mass combination of 61 amu ($\text{H}^{28}\text{Si}^{32}\text{S}$) and 15 amu (CH_3). In detail, fits were accomplished with a center-of-mass translational energy distribution with a maximum translational energy (E_{max}) of $83 \pm 9 \text{ kJ mol}^{-1}$. Energy conservation dictates that for those reaction products formed without internal excitation, the high

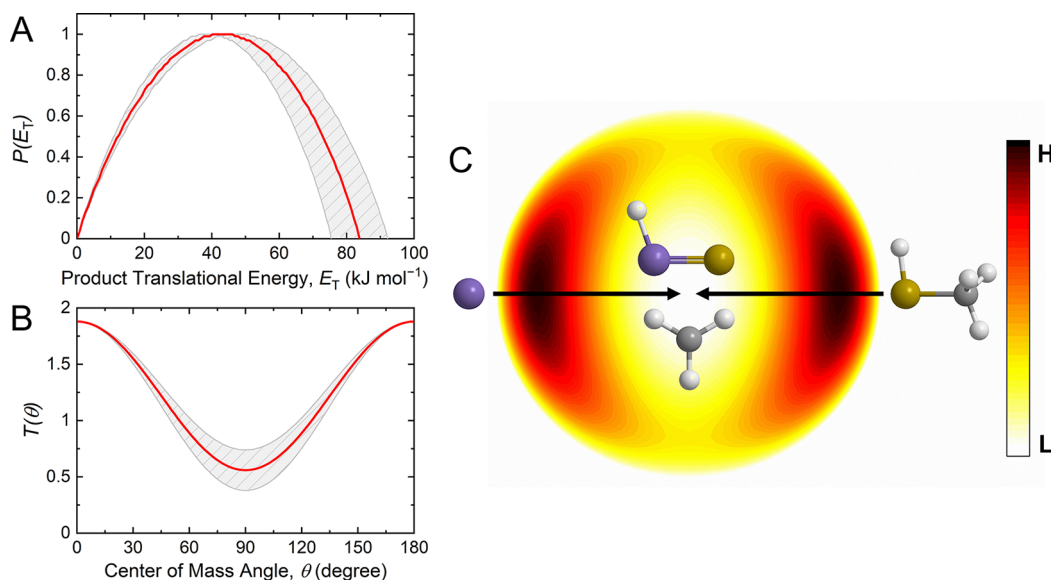


Figure 3. Center-of-mass product translational energy (A) and angular (B) flux distributions, as well as the corresponding flux contour map (C) of the reaction of atomic silicon ($\text{Si}(^3\text{P}_j)$) with thiomethanol (CH_3SH) leading to the formation of HSiS ($m/z = 61$). Red lines define the best-fit functions while shaded areas denote the error limits. Atoms are colored as follows: silicon (purple); sulfur (yellow); carbon (gray); hydrogen (white).

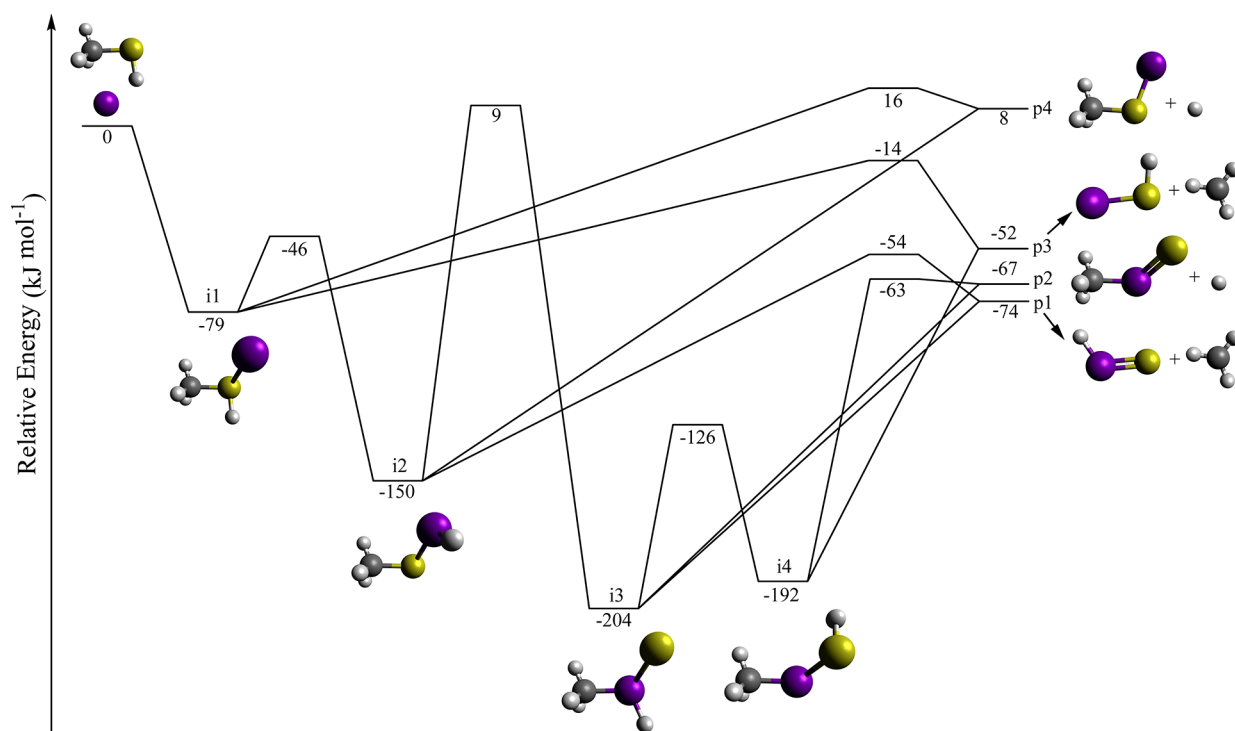


Figure 4. Schematic representation of the potential energy surface for the reaction between ground-state atomic silicon and thiomethanol calculated at the CCSD(T)-F12/aug-cc-pV(T+d)Z//M06-2X/cc-pV(T+d)Z+ZPE(M06-2X/cc-pV(T+d)Z) level of theory. The surface has been simplified by removing products above the reaction collision energy of 12.8 kJ mol^{-1} ; the full diagram is shown in Figure S3. Atoms are colored as follows: silicon (purple); sulfur (yellow); carbon (gray); hydrogen (white). Cartesian coordinates and vibrational frequencies are compiled in Table S2.

energy cutoff represents the sum of the reaction exoergicity plus the collision energy E_c ($12.8 \pm 0.5 \text{ kJ mol}^{-1}$). Therefore, by subtracting the collision energy from E_{max} , the methyl group loss channel is exoergic by $70 \pm 10 \text{ kJ mol}^{-1}$. Further, the $P(E_T)$ peaks away from zero translational energy at about 43 kJ mol^{-1} , suggesting a tight exit transition state of the decomposing reaction intermediate. This goes along with a substantial rearrangement of the electron density to form HSiS/HSSi plus the methyl radical. Finally, the $T(\theta)$ is forward-backward symmetric and depicts intensity from 0° to 180° . These findings reveal indirect scattering dynamics through long-lived CH_4SSi intermediate(s) with lifetimes longer than or at least comparable with their rotation periods. The distribution minimum at 90° proposes geometrical limitations and an emission of the methyl group nearly perpendicularly to the total angular momentum vector nearly within the rotational plane of the fragmenting complex(es).³¹ These findings are also compiled in the flux contour maps (Figure 3).

What are the underlying reaction dynamics of the elementary reaction of atomic silicon with thiomethanol? First, we are contrasting the experimentally derived reaction energy of $-70 \pm 10 \text{ kJ mol}^{-1}$ with the theoretically predicted reaction energies to form the thiosilaformyl (HSiS , X^2A') and isothiosilaformyl (HSSi , X^2A') isomers of -74 ± 5 and $-52 \pm 5 \text{ kJ mol}^{-1}$ for reactions 3a and 3b, respectively. This comparison suggests that at least the thermodynamically more stable thiosilaformyl isomer (HSiS , X^2A') is formed; the preparation of the less stable isothiosilaformyl isomer (HSSi , X^2A') cannot be excluded at the present stage. Further, considering the molecular structures of the polyatomic reactant ($\text{CH}_3\text{-S-H}$) and products (CH_3 , H-Si=S), it is evident that

the reacting silicon atom forms a bond with the sulfur atom and that the hydrogen atom is migrating from the sulfur atom to the silicon atom. Considering these experimental findings, we propose that ground-state atomic silicon interacts with one of the nonbonding electron pairs of the sulfur atom forming a sulfur-silicon bond via indirect (complex-forming) reaction dynamics. This leads to a $\text{CH}_3(\text{H})\text{SSi}$ reaction intermediate which undergoes atomic hydrogen migration from the sulfur to the silicon atom yielding a $\text{CH}_3\text{-S-Si-H}$ intermediate. The latter could undergo unimolecular decomposition through the loss of a methyl group accompanied by formation of the thiosilaformyl isomer (HSiS , X^2A') in an overall exoergic reaction ($-70 \pm 10 \text{ kJ mol}^{-1}$). The tight exit transition state can be rationalized through a significant electron reorganization from a sulfur-silicon single bond in the decomposing $\text{CH}_3\text{-S-Si-H}$ intermediate to a silicon-sulfur double bond in the thiosilaformyl radical product (HSiS , X^2A'). It should be noted that intersystem crossing (ISC) from the triplet to the singlet surface might be relevant if "heavy" reactants such as silicon and/or sulfur are involved in elementary reactions. However, our experimental data alone neither support nor refute the involvement of nonadiabatic reaction dynamics, and the data presented here can be explained through reaction on the triplet surface only.

The experimental findings and reaction mechanisms proposed above are fully supported by the results from our electronic structure calculations (Figure 4). Ground-state atomic silicon adds barrierlessly to one of the two nonbonding electron pairs of the sulfur atom of hydrogen sulfide forming a weakly stabilized reaction intermediate i1 on the triplet surface. This intermediate can decompose via methyl loss by overcoming a barrier of 38 kJ mol^{-1} with respect to the

separated products to **p3** ($\text{HSSi}; X^2A'$) in an overall exoergic reaction by -52 kJ mol^{-1} . Alternatively, **i1** isomerizes via hydrogen shift from the sulfur to the silicon atom yielding **i2**; the barrier for the hydrogen shift is lower by 32 kJ mol^{-1} compared to the exit barrier to form the methyl radical plus **p3** ($\text{HSSi}; X^2A'$). Note that atomic hydrogen losses from **i1** and **i2** to **p4** (H_3CSSi) are predicted to be endoergic by 8 kJ mol^{-1} . Intermediate **i2** can also undergo unimolecular decomposition via methyl loss to yield **p1** ($\text{HSiS}; X^2A'$) after overcoming a tight transition state located 20 kJ mol^{-1} above the separated products. Finally, our calculations also predict that a methyl group migration from **i2** to **i3** followed by hydrogen shift to **i4** is likely unfavorable energetically upon comparing the energies of the transition state of **i2** $\rightarrow$ **i3** and of **i2** $\rightarrow$ **p1** + CH_3 , which favor the methyl loss exit channel by 63 kJ mol^{-1} . The methyl group migration is accompanied by a significant elongation of the C–S bond from 183 to 217 pm; following this stretching mode of the methyl loss to **p1** represents a much more favorable pathway. Therefore, although the atomic hydrogen loss channel to **p2** (H_3CSiS) is thermodynamically favorable compared to the formation of **p1** ($\text{HSiS}; X^2A'$) plus methyl, the hydrogen loss pathway is closed considering the unfavorable barrier for the methyl migration (**i2** $\rightarrow$ **i3**), which cannot compete compared to the unimolecular decomposition of **i2** (**i2** $\rightarrow$ **p1** + CH_3). This conclusion gains full support from our experimental findings and the lack of observation of the atomic hydrogen loss pathway (reaction 1) to form **p2**. The Rice–Ramsperger–Kassel–Marcus (RRKM) calculations also support these conclusions. Because the rate constants were evaluated with a collision energy of 0 kJ mol^{-1} to simulate cold molecular cloud conditions, intermediates **i3** and **i4**, as well as products **p2** and **p4**, are inaccessible within the branching ratio calculations. This leaves products **p1** and **p3**, which were predicted to be formed with a branching ratio of 98 to 2%, respectively. Consequently, it follows that the most prominent reaction pathway involves the addition of ground-state atomic silicon to the sulfur atom, hydrogen migration from **i1** to **i2** through a barrier 33 kJ mol^{-1} above **i1**, and methyl loss through a tight exit transition state 20 kJ mol^{-1} above the separated products (**p1** + CH_3). Note that the geometry of the exit transition state from **i2** and **p1** plus methyl depicts the methyl group ejected at angles of 74.9° and 89.7° with respect to the O–X and O–Y principal axes, respectively (Figure 5). This in-plane emission matches the

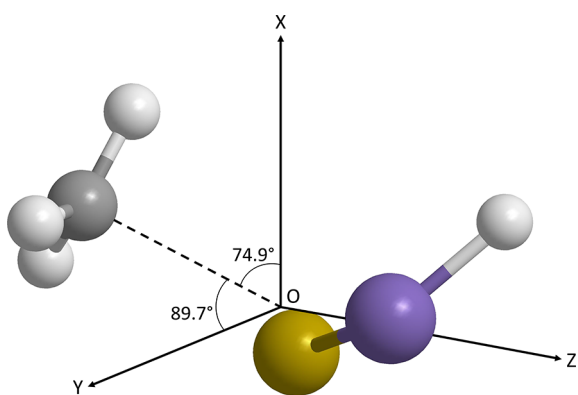


Figure 5. Orientation of the methyl leaving group in the transition state leading to the formation of product **p1** from intermediate **i2**. The center of mass is located at the origin, O.

experimental prediction of the ejection direction of the methyl group based on the $T(\theta)$ and flux contour map shown in Figure 3 very well. This calculated reaction energy of $-74 \pm 5 \text{ kJ mol}^{-1}$ is also in agreement with the experimentally derived reaction energy of $-70 \pm 10 \text{ kJ mol}^{-1}$ for the formation of the thiosilaformyl radical (HSiS) plus methyl.

The crossed molecular beam experiments of the elementary reaction of ground-state silicon atoms ($\text{Si}(^3P_j)$) with thiomethanol (CH_3SH) revealed the formation of at least the hitherto astronomically elusive thiosilaformyl isomer (HSiS, X^2A') via indirect scattering dynamics. This isomer can be visualized as the “double heavy” substituted formyl radical (HCO, X^2A'), which is known to exist in the interstellar medium since 1976.³² Likewise, the thiosilaformyl isomer (HSiS, X^2A') can be connected to the recently observed thioformyl isomer (HCS, X^2A')³³ by formally replacing the carbon atom through the isovalent silicon atom, hence providing the homologous series of isovalent $^2A'$ doublet radicals formyl, thioformyl, and thiosilaformyl: HCO , HCS , and HSiS . The H–E bond lengths of the formyl (HCO), thioformyl (HCS), and thiosilaformyl (HSiS) radicals of 1.120, 1.089, and 1.509 Å, respectively, as well as the E=Y double-bond lengths of 1.183, 1.568, and 1.967 Å,³⁴ indicate weaker and less energetic bonding involving silicon in comparison to carbon, especially with respect to the double bond between the heavy atoms.

With formyl (HCO) and thioformyl (HCS) observed toward, e.g., NGC 2024³⁵ and L483,³³ respectively, and the microwave spectrum of thiosilaformyl (HSiS) known from rotational spectroscopy studies,³⁶ the thiosilaformyl radical would represent an ideal target for prospective astronomical searches in, for example, the star-forming region SgrB2, where thiomethanol (CH_3SH) has been observed;⁴ the atomic silicon reactant is the degradation product of silane (SiH_4) by the internal vacuum ultraviolet photon field and energetic galactic cosmic rays.³⁷ The thiosilaformyl radical (HSiS) could act as a tracer to constrain the chemical and physical conditions of the hitherto poorly constrained silicon and sulfur chemistries and the formation of the very first silicon–sulfur bond in deep space. Here, the thiosilaformyl radical (HSiS) could eventually be photolyzed to silicon monosulfide (SiS) or react with atomic hydrogen to yield molecular hydrogen and silicon monosulfide (SiS), which has been predicted computationally to occur barrierlessly with rate constants of a few $10^{-10} \text{ cm}^3 \text{ s}^{-1}$.^{38,39} Note that models advocate that silicon monosulfide ($\text{SiS}(X^1\Sigma^+)$) represents the critical molecular building block initiating the chain of reactions that lead ultimately to sulfide dust grains.^{28–30}

EXPERIMENTAL METHODS

The experiments were performed with a universal crossed molecular beam machine.⁴⁰ Briefly, a pulsed supersonic ground-state atomic silicon beam ($\text{Si}(^3P_j)$) seeded in neon (Ne, 99.999%, Airgas) carrier gas was generated via laser ablation of a silicon rod kept in helical motion.⁴¹ Typically, 3 mJ of the 266 nm fourth harmonic output of a Nd:YAG laser are tightly focused onto a rotating silicon rod (Si, 99.999%, Goodfellow Cambridge Limited). The pulsed silicon atom beam with a velocity (v_p) of $948 \pm 13 \text{ m s}^{-1}$ and speed ratio (S) of 6.0 ± 0.3 crossed a pulsed thiomethanol (CH_3SH , 98.0%, Sigma-Aldrich) beam ($v_p = 740 \pm 18 \text{ m s}^{-1}$, $S = 10.2 \pm 0.8$) kept at 550 Torr backing pressure perpendicularly in the interaction region of the scattering chamber. This resulted in a

collision energy of 12.8 ± 0.5 kJ mol⁻¹ and center-of-mass angle of $54.0 \pm 1.1^\circ$. Reactively scattered species were monitored using a triply differentially pumped quadrupole mass spectrometer (QMS) with an electron-impact ionizer operated at 80 eV and 2 mA in 5° steps in the time-of-flight (TOF) mode. Up to 1.2×10^6 TOF spectra were recorded at each angle. To gain information on the reaction dynamics, the TOF spectra and laboratory angular distribution were fit exploiting a forward convolution routine; this approach yielded the center-of-mass translational energy flux distribution $P(E_T)$ along with the center-of-mass angular flux distribution $T(\theta)$. These functions were exploited to derive the flux contour map, denoted as $I(u, \theta) \sim P(u) \times T(\theta)$, which depicts an overall image of the outcome of the reaction.

■ COMPUTATIONAL METHODS

The GAMESS-US⁴² and MOLPRO⁴³ packages were employed in all calculations presented throughout this work. First, geometry optimizations and frequency analyses were performed at the density functional theory (DFT)⁴⁴ level employing the M06-2X⁴⁵ exchange and correlation functional, together with the cc-pV(T+d)Z basis set.^{46,47} This functional was chosen for its performance in barrier heights (both hydrogen-transfer and non-hydrogen-transfer).⁴⁸ The calculations employed unrestricted wave functions; no symmetry restrictions were imposed. All transition states were confirmed to have a single imaginary frequency, and intrinsic reaction coordinate (IRC) calculations were performed for each of them to ensure the correct connection paths. To enhance the accuracy of the computed energies, we performed single-point energy calculations at the explicitly correlated coupled cluster^{49,50} (CCSD(T)-F12) level, using the cc-pVTZ-F12 basis set⁵¹ for all geometries previously optimized. The reported energies are always zero-point energy (ZPE) corrected at the DFT level, and the methodology is abbreviated as CCSD(T)-F12/aug-cc-pV(T+d)Z//M06-2X/cc-pV(T+d)Z+ZPE(M06-2X/cc-pV(T+d)Z). This methodology usually yields energies with an accuracy of ± 5 kJ mol⁻¹. Energy-dependent rate constants (Table S1) were derived for the unimolecular reaction steps on the triplet CH₄SiS PES following formation of the initial collision complex utilizing RRKM theory.⁵² The available internal energy is the sum of the collision and chemical activation energies, where the value of the former used was 0 kJ mol⁻¹ to better simulate bimolecular reactions in cold molecular clouds. The rate constants were evaluated within the harmonic approximation with CCSD(T)-F12 energies and M06-2X/cc-pV(T+d)Z vibrational frequencies. Statistical branching ratios between products were obtained from RRKM rate constants using the steady-state approximation.⁵³

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c01706>.

TOF spectra taken at the CM angle for $m/z = 60$ and 61 (Figure S1); Newton circle diagram for the title reaction (Figure S2); PES including all calculated products (Figure S3); energy-dependent rate constants derived from RRKM calculations (Table S1); computed Cartesian coordinates and vibrational frequencies of all

reactants, transition states, intermediates, and products (Table S2) (PDF)

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Notes

The authors declare no competing financial interest.

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