A chemical dynamics study on the gas phase formation of thioformaldehyde (H₂CS) and its thiohydroxycarbene isomer (HCSH)

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Complex organosulfur molecules are ubiquitous in interstellar molecular clouds, but their fundamental formation mechanisms have remained largely elusive. These processes are of critical importance in initiating a series of elementary chemical reactions, leading eventually to organosulfur molecules—among them potential precursors to iron-sulfide grains and to astrobiologically important molecules, such as the amino acid cysteine. Here, we reveal through laboratory experiments, electronic-structure theory, quasi-classical trajectory studies, and astrochemical modeling that the organosulfur chemistry can be initiated in star-forming regions via the elementary gas-phase reaction of methylidyne radicals with hydrogen sulfide, leading to thioformaldehyde (H₂CS) and its thiohydroxycarbene isomer (HCSH). The facile route to two of the simplest organosulfur molecules via a single-collision event affords persuasive evidence for a likely source of organosulfur molecules in star-forming regions. These fundamental reaction mechanisms are valuable to facilitate an understanding of the origin and evolution of the molecular universe and, in particular, of sulfur in our Galaxy.

Significance
Since the detection of carbonyl monosulfide (CS) in star-forming regions, about 200 molecules as complex as fullerences have been detected in interstellar and circumstellar environments, but the formation routes to organosulfur molecules have remained essentially elusive. Exploiting thioformaldehyde (H₂CS) and its thiohydroxycarbene isomer (HCSH), we deliver compelling testimony via laboratory experiments, electronic-structure theory, astrochemical modeling, and quasi-classical trajectory studies that these organosulfur species can be efficiently formed in star-forming regions such as Sagittarius B2 through bimolecular reactions involving hydrogen sulfide and methylidyne radicals. These elementary mechanisms are of fundamental importance to aid our understanding of how carbon and sulfur chemistries are connected in deep space, thus expanding our view on the sulfur cycle in the Galaxy.


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regions such as Orion KL and Sgr B2. The reaction of ground-state methylidyne radicals (CH) with hydrogen sulfide was investigated under single-collision conditions revealing the preparation of distinct organosulfur isomers: thioformaldehyde and thiohydroxycarbene (HCSH) (reaction 1). This system represents the prototype reaction of the simplest closed shell hydride of sulfur–hydrogen sulfide, as detected with fractional abundances of up to $10^{-3}$ in star-forming regions (23, 24)—with the simplest benchmark of an organic radical—methylidyne (CH) generated through photolysis of methane (CH$_4$) (25)—to prepare key organosulfur molecules via a single-collision event through the coupling of the sulfur and carbon chemistries in star-forming regions. Our investigations also provide dynamical information on the elementary steps to both thioformaldehyde and thiohydroxycarbene isomers. Since the laboratory data strongly depend on the structures of the initially formed collision complexes, along with the products of the reaction, we first calculated the geometries of energetically accessible reaction intermediates and products and identified the transition states connecting them, and then compared our crossed-beam data and experimental dynamics with those arising from QCT states connecting them, and then compared our crossed-beam data and experimental dynamics with those arising from QCT. The laboratory angular distribution was relatively broad and spread over at least 45° within the scattering plane; the nearly forward–backward symmetry around the center-of-mass (CM) angle of 48.9° suggests indirect reaction dynamics involving the formation of HCS complex(es).

Having established that in the reaction of ground-state methylidyne radicals with hydrogen sulfide, the atomic hydrogen-loss channel results in the formation of H$_2$CS isomer(s) (reaction 1a), we then elucidated to what extent the hydrogen atom is lost from the methylidyne radical, from the hydrogen sulfide reactant, or from both. Therefore, we conducted the crossed-beam reactions of methylidyne (CH; X$^2$Π; 13 amu) with deuterium sulfide (D$_2$S; X$^2$A$_1$; 36 amu) and of D$_1$-methylidyne (CD; X$^2$Π; 14 amu) with hydrogen sulfide (H$_2$S; X$^2$A$_1$; 34 amu) to explore the position of the atomic hydrogen loss. Any ejection of a loss of a hydrogen atom should result in reactive scattering signal at m/z 48 (D$_2$CS$^+$) and m/z 47 (HDSC$^+$), respectively (reactions 2a and 3a). In the CD/H$_2$S system, reactive scattering signal was observed at m/z 47 and 46 at a ratio of 0.57 ± 0.31 (SI Appendix, Fig. S1). Signal at m/z 47 unequivocally demonstrated the elimination of atomic hydrogen and formation of HDCS isomer(s) (reaction 3a). Ion counts at m/z 46 could arise from an atomic deuterium-loss pathway (reaction 3b) and/or dissociative-electron-impact ionization of the neutral

![Image](134x532 to 455x730)

**Fig. 1.** Neutral sulfur-bearing molecules detected in the ISM. In addition, four molecular ions (SH$^+$, NS$^+$, SO$^+$, and HCS$^+$) were also detected in interstellar clouds.
HDCS. Considering the CH/D2S system, only weak ion counts were detected at \( m/z 48 \) (reaction 2a); signal at \( m/z 47 \) was of similar intensity as in the CD/H2S system and can only be explained via atomic deuterium loss leading to the formation of DHCS 47 (reaction 2b), but not from dissociative electron-impact ionization of D2CS. Note that the ratio of the ion counts of \( m/z 48 \) vs. 47 is only 0.08 ± 0.02; this finding suggests that signal at \( m/z 48 \) not only originates from DH13CS, but also from atomic hydrogen loss. In summary, the isotopic substitution experiments reveal that the ejected atomic hydrogen/deuterium predominantly originates from the (deuterated) hydrogen sulfide reactant and to a smaller fraction from the (deuterated) methylidyne radical.

CH(13 amu) + D2S (36 amu) → D2CS (48 amu) + H (1 amu),

[2a] CH(13 amu) + D2S (36 amu) → DHCS (47 amu) + D (2 amu),

[2b] CD(14 amu) + H2S (34 amu) → HDCS (47 amu) + H (1 amu),


[3b]

Crossed Molecular Beams Studies—CM Frame. The analysis of the raw data revealed compelling evidence that, for the reaction of ground-state methylidyne radicals with hydrogen sulfide, a molecule with the chemical formulae H2CS is formed via atomic hydrogen elimination, with the hydrogen originating predominantly from the hydrogen sulfide reactant. To gain information on the underlying reaction dynamics, we transformed the experimental data from the laboratory to the CM reference frame (26, 27); this process yielded the CM translational energy-flux distribution \( P(E_T) \) and the CM angular-flux distribution \( T(\theta) \) (Fig. 3). Best fits of the laboratory data could be accomplished with a single-channel fit yielding products with a mass combination of 46 amu (H2CS) and 1 amu (H). The \( P(E_T) \) supported in the identification of the product isomer(s). For reaction products formed without internal excitation, the high-energy cutoff of 275 ± 25 kJ·mol⁻¹ represents the sum of the absolute value of the reaction exoergicity plus the collision energy \( E_c \) (18.9 ± 0.4 kJ·mol⁻¹). Based on energy conservation, a subtraction of the collision energy suggests that the...
reaction is highly exoergic with an energy of $-256 \pm 25$ kJ·mol$^{-1}$. The $P(E_{\text{f}})$ peaks away from zero translational energy at around 30 to 50 kJ·mol$^{-1}$; this finding proposes the existence of a tight exit transition state for the decomposition of the H$_2$CS complex(es) accompanied by a significant electron-density rearrangement upon the atomic hydrogen loss (28). Finally, the $T(0)$ is forward–backward symmetric and extends over the complete angular range from 0° to 180° with a forward–backward symmetry. These findings propose indirect scattering dynamics via long-lived H$_2$CS intermediates whose lifetimes are longer than, or at least competitive with, their rotation periods. The distribution minimum at 90° suggests geometrical constraints with the hydrogen atom emitted perpendicularly to the total angular momentum vector almost within the rotational plane of the decomposing H$_2$CS complex(es) (28, 29).

Electronic Structure and Dynamics Calculations. With the identification of the H$_2$CS isomer(s) as the product of the bimolecular gas-phase reaction of the methylidyne radical with hydrogen sulfide along with the preferential emission of the hydrogen atom from the hydrogen sulfide reactant, it is our goal to elucidate the underlying chemical dynamics and reaction mechanism(s). This is achieved by combining our experimental findings with electronic structure and molecular-dynamics calculations. Reactants, products, intermediates, and transition-state structures relevant to the reaction of ground-state methylidyne radicalcals with hydrogen sulfide were characterized and compiled in the potential energy surface (Fig. 4 and SI Appendix, Fig. S2). These calculations predicted the existence of eight reaction channels. The atomic hydrogen loss leads to the thermodynamically most stable thioformaldehyde isomer (H$_2$CS, X$^1$A$^1$, p1), which is energetically favorable by 183 kJ·mol$^{-1}$ compared to its trans thiohydroxycarbene structure (HCSH, X$^1$A$^1$, p2trans); owing to the repulsion of both hydrogen atoms, the cis thiohydroxycarbene species (HCSH, X$^1$A$^1$, p2cis) is destabilized by 5 kJ·mol$^{-1}$. These energy differences are in excellent agreement with a previous computational investigation of the thioformaldehyde (p1)–trans/cis thiohydroxycarbene (p2trans/cis) isomer pair of 183 and 4 kJ·mol$^{-1}$, respectively (30). Suto et al. (31) and Guest and coworkers (32) predicted trans thiohydroxycarbene (p2trans) to be less stable by 186 and 198 kJ·mol$^{-1}$ compared to thioformaldehyde (p1). The first excited triplet state of thiohydroxycarbene (HCSH, $^3$A$^1$, p2trip) lies 33 kJ·mol$^{-1}$ above the energy of the separated reactants and, hence, is energetically not accessible, considering a collision energy of 18.9 kJ·mol$^{-1}$ in the present experiments. The computed singlet–triplet gap of thiohydroxycarbene of 78 kJ·mol$^{-1}$ agrees well with the prediction of Schreiner and coworkers (33) of about 71 kJ·mol$^{-1}$. The molecular hydrogen loss is accompanied by the formation of the thioformyl (HCS, X$^2$A$^1$, p3) and iso-thioformyl (HSC, X$^2$A$^2$, p4) radicals with overall reaction exoergicities of 283 and 121 kJ·mol$^{-1}$ with respect to the separated reactants. The energy difference of both isomers of 162 kJ·mol$^{-1}$ is in line with previous calculations by Ochsenfeld, Head-Gordon, and coworkers (30) revealing a thioformyl isomer, which lies 166 kJ·mol$^{-1}$ lower in energy than iso-thioformyl. Finally, two carbon–sulfur bond-cleavage channels lead to ground-state atomic sulfur (S, $^3$P) plus the methyl radical (CH$_3$, X$^2$A$^1$, p5) and thioxo-dihydro (HS, X$^2$T$^1$) plus triplet carbene (CH$_2$, X$^2$B$_2$) (p6); the direct hydrogen-abstraction channel forming thioxo-dihydro plus carbene has to pass a transition state located 25 kJ·mol$^{-1}$ above the separated reactants; hence, this pathway is closed under our experimental conditions at collision energies of 18.9 kJ·mol$^{-1}$.

Our computations revealed further the existence of three doublet reaction intermediates (i1–i3). The reaction of methylidyne with hydrogen sulfide can be initiated by the barrierless addition to the sulfur atom and/or insertion into the sulfur–hydrogen bond, leading to collision complexes i1 and i2, respectively. Both intermediates can be interconverted along a transition state located about 50 kJ·mol$^{-1}$ below the energy of the separated reactants. The thiohydroxymethyl radical intermediate i2 may undergo a hydrogen shift from the sulfur to the carbon atom, yielding the thiomethoxy radical (i3). The thiohydroxymethyl–thiomethoxy system is isovalent to the hydroxymethyl–methoxy radical pair. Among these three intermediates, i2 and i3 can both eject a hydrogen atom forming thioformaldehyde (p1). Four reaction pathways may connect to singlet cis/trans thiohydroxycarbene (HCSH) (i1$\rightarrow$p2trans/p2cis; i2$\rightarrow$p2trans/p2cis). Interestingly, besides the atomic hydrogen loss, our computations also located two molecular hydrogen-loss pathways leading from intermediates i3 and i2 to thioformyl (HCS, X$^1$A$^1$, p3) and iso-thioformyl (HSC, X$^1$A$^2$, p4) via tight exit transition states. The aforementioned intermediates are also linked to carbon–sulfur bond-rupture channels forming atomic sulfur (S, $^3$P) plus methyl (CH$_3$, X$^2$A$^1$, p5) and thioxo-dihydro (HS, X$^2$T$^1$) plus triplet carbene (CH$_2$, X$^2$B$_2$, p6).

An association of these computations with our experimental data leads to interesting findings. A comparison of these data with the experimental reaction energy for the atomic hydrogen-loss pathway of $-256 \pm 25$ kJ·mol$^{-1}$ suggests an excellent correlation with the computed reaction exoergicity of $233 \pm 10$ kJ·mol$^{-1}$, leading at least to thioformaldehyde (H$_2$CS, X$^1$A$^1$, p1) via direct scattering dynamics through the involvement of CH$_3$S intermediate(s) i2 and/or i3 holding a lifetime longer than the(ir) rotational period(s). This reveals that thioformaldehyde can be formed in the gas phase as a result of a reaction between two neutral species under controlled experimental conditions via a single-collision event. It is important to highlight that the formation of the less
stable singlet cis/trans thiohydroxy carbene isomers (HCSH, p2cis/trans) cannot be ruled out at the present stage, since their contribution can be “hidden” in the low-energy part of the CM translational energy distribution. Further, the computationally predicted molecular hydrogen-loss channel could not be verified experimentally; this suggests that the molecular hydrogen-loss pathway(s) only holds a minor fraction at a level of some percent within the detection limit of our experimental setup. Finally, the accessible reaction channel opening up from carbon–sulfur bond cleavage (p5 and p6) cannot be probed in our setup because the m/z values of the ionized products would overlap with fragment ions of the reactants along with their isotopically labeled counterparts.

These open queries call for QCT calculations (34, 35), thus bridging the dynamics experiments with the theoretical understanding of the methylidyne–hydrogen sulfide system (SI Appendix). In QCT, the reactants are propagated by solving classical equations of motion with the accelerations calculated with an ab initio method on-the-fly. It is important to note that millions of ab initio calculations are involved in QCT; therefore B3LYP/aug-cc-pVDZ (36, 37) was employed for its balance between computation cost, accuracy, and trajectory stability (SI Appendix). Overall, 500 trajectories were sampled at collision energies of 18 kJ·mol⁻¹ by systematically varying the impact parameter from 100 to 500 pm in steps of 100 pm; since no reactions were observed at impact parameters of 500 pm, simulations with larger impact parameters were not conducted (SI Appendix, Table S3). These trajectory studies revealed simulating results and provided explicit evidence on two distinct entrance channels via methylidyne addition to the sulfur atom of hydrogen sulfide and methylidyne insertion into the sulfur–hydrogen bond, yielding intermediates i1 and i2, respectively (Fig. 5 and Movies S1–S7). Considering the larger acceptance of the non-bonding electron pairs of sulfur, nearly two out of three trajectories led to addition (63 ± 3%), while only one out of three trajectories proceeded via insertion (SI Appendix, Table S4; 37 ± 3%). Considering the barrier heights, collision complex i1 isomerizes to i2 via hydrogen shift from the sulfur to the carbon atom and may also eject atomic hydrogen-forming cis/trans thiohydroxy carbene isomers (HCSH; p2) with fractions of 55 ± 4% (isomerization) and 45 ± 4% (hydrogen-atom loss) averaged over all impact parameters. The thiohydroxymethyl intermediate i2 may eliminate atomic hydrogen to yield thioformaldehyde (H₂CS; p1) (18 ± 4%) and may also add to the sulfur atom of hydrogen sulfide isomers (HCSH; p2) (6 ± 2%); considering the barrier of only 121 kJ·mol⁻¹ the hydrogen-atom migration from the sulfur to the carbon atom leading to the thiomethylic radical i3 dominates (75 ± 4%). It is important to highlight that the trajectory calculations reveal the formation of thioformaldehyde (H₂CS; p1) and of singlet cis/trans thiohydroxycarbene (HCSH; p2). Considering the atomic hydrogen loss, 70 ± 3% of the trajectories lead to thioformaldehyde (H₂CS; p1) and 30 ± 3% to cis/trans thiohydroxy carbene isomers (HCSH; p2) with the reaction sequences i1 → i2 → p1 + H and i1 → p2 + H dominating the formation of thioformaldehyde (H₂CS; p1) and of singlet cis/trans thiohydroxycarbene (HCSH; p2), respectively (Fig. 5). Interestingly, these results closely match statistical branching ratios obtained by RRKM (Rice–Ramsperger–Kassel–Marcus) calculations at the collision energy of 19 kJ·mol⁻¹, 66% and 32% for p1 and p2trans/p2cis, respectively (SI Appendix, Table S6), assuming the 63%/37% initial formation of i1/i2 in the entrance channel, as evaluated by the trajectory calculations. The trajectory calculations also allowed us “tagging” the hydrogen atoms at the methylidyne and hydrogen sulfide reactants. Overall, the hydrogen atom was emitted preferentially from the hydrogen sulfide reactant (86 ± 2%) compared to the methylidyne radical (14 ± 2%) (SI Appendix, Table S5). Finally, we also explored the potential importance of molecular hydrogen loss (p3/p4) and carbon–sulfur bond cleavage processes (p5 and p6) compared to atomic hydrogen loss. The overall product-branching ratios are: 77 ± 3% for the atomic hydrogen loss, 7 ± 1% for the molecular hydrogen loss, and 15 ± 2% for the carbon–sulfur bond cleavage (SI Appendix, Table S3). These results correlate well with our findings of a dominating hydrogen-loss pathway leading to thioformaldehyde (H₂CS; p1) and singlet cis/trans thiohydroxycarbene (HCSH; p2) with branching ratios of the molecular hydrogen loss to be too low to be observed in our scattering experiments. Optimized Cartesian coordinates and vibrational frequencies of reactants, intermediates, transition states, and dissociation products are given in SI Appendix, Table S7.

Astrochemical Modeling and Implications. Having established the formation of thioformaldehyde (H₂CS; p1) and of singlet cis/trans thiohydroxy carbene (HCSH; p2) under single-collision conditions in the laboratory along with electronic structure and QCT calculations, we then deliberated on potential astrochemical implications. It is vital to transfer these findings to “real” interstellar environments since experiments conducted under well-defined laboratory conditions can scarcely replicate the chemical complexity of the ISM. Our studies revealed explicitly that the reaction has no entrance barrier, that all barriers involved in the formation of thioformaldehyde and thiohydroxycarbene are well below the energy of the separated reactants, and that the overall reactions to prepare both isomers are exergonic. These results represent crucial requirements for this reaction to be important, not only in low-temperature molecular clouds (10 K) (38), but also in star-forming regions where the newborn stars drive the sublimation of the icy grains at temperatures as high as 300 K (17). The entrance barrier would prohibit these reactions in low-temperature interstellar environments. Consequently, our findings can be universally related to any interstellar environment, such as molecular clouds and also star-forming regions, where ice mantles and, most importantly, sufficient hydrogen sulfide can be removed from grains by sublimation (20) and where adequate concentrations of methylidyne radicals and hydrogen sulfide exist. This conclusion also
gains full support from earlier kinetics studies of the methylidyne–hydrogen sulfide system, revealing high rate constants at 295 to 300 K from $2 \times 10^{-31}$ to $3 \times 10^{-10}$ cm$^3$ s$^{-1}$ (39). Consequently, barrierless reactions between methylidyne radicals and hydrogen sulfide are very fast, close to the collisional kinetic limit, at astrochemically relevant temperatures.

We performed astrochemical model simulations exploiting a network of gas-phase reactions in the Orion Hot Core utilizing the chemical kinetic data of the University of Manchester Institute of Science and Technology (UMIST) Database for Astrochemistry (40). Chemical and physical parameters for the simulations were extracted from Esplugues et al. (17) and were operated at typical densities of $2 \times 10^{-3}$ cm$^{-3}$ at temperatures of 100 to 200 K (40). This reaction network was updated by the additional reactive chemistry of the methylidyne radical with hydrogen sulfide and removing all ion–molecule and neutral–neutral reactions leading to thioformaldehyde, which were not studied experimentally in any laboratory. The hot molecular core (HMC) model starts with an initial fractional abundance of hydrogen sulfide of $2 \times 10^{-6}$ as sublimed from the grains; this is about 10% of the elemental sulfur. These HMC models resulted in intriguing findings. First, the fractional abundances derived for thioformaldehyde ($H_2CS; p_1$) in the range of the chemical processing of the Hot Core of 10$^5$ y to a few hundred thousand years are consistent with the astronomical observations defined by the gray bars of (0.1 to 4.0) $\times 10^{-9}$ (Fig. 6). One should note that, although the chemistry is simulated for up to 10$^7$ y, HMCs are young objects with ages in the range of 10$^5$ y to a few hundred thousand years. Second, at ages of less than a few hundred thousand years, the bimolecular reaction of methylidyne with hydrogen sulfide provides the dominating route to thioformaldehyde ($H_2CS; p_1$). Third, since our experiments revealed that thioformaldehyde ($H_2CS; p_1$) and cis/trans thiohydroxycarbene (HCSH; $p_2$) are formed simultaneously, we may predict that cis/trans thiohydroxycarbene (HCSH; $p_2$) should be present in HMCs, such as the Orion core at fractional abundances of about 0.3 to 0.5 times that of thioformaldehyde ($H_2CS; p_1$). It should be noted that, once formed, thioformaldehyde ($H_2CS; p_1$) cannot isomerize to trans thiohydroxycarbene (HCSH; $p_2$), since a barrier of isomerization of 85 kJ mol$^{-1}$ above the energy of the separate reactants separates both isomers (SI Appendix).

Conclusions

Our investigations provide a solid foundation on the formation of two of the simplest closed-shell organosulfur molecules—thioformaldehyde ($H_2CS; p_1$) and the previously astronomically unobserved singlet cis/trans thiohydroxycarbene (HCSH; $p_2$)—via elementary neutral–neutral reactions. Previous routes have predominantly speculated on the involvement of unstudied and, hence, unconfirmed chains of ion–molecule reactions (18) terminated by dissociative recombination and hypothetical formation of thioformaldehyde ($H_2CS; p_1$). Consequently, our results challenge conventional wisdom that the organosulfur chemistry in star-forming regions is dictated by complex networks of ion–molecule reactions with previous astrochemical models hardly reproducing observed fractional abundances of thioformaldehyde of up to $4 \times 10^{-9}$ in the Orion Hot Core star-forming region (40). Consequently, the ability of barrierless, exoergic, neutral–neutral reactions between methylidyne and hydrogen sulfide suggests that this elementary reaction might trigger complex chains of elementary reactions, leading to a rich sulfur chemistry in star-forming regions. Combined experimental and computational studies as provided here also represent a template to shed light on the nature of the molecular carriers of the unknown sulfur reservoir in the gas phase (41, 42)—among them perhaps thiohydroxycarbene (HCSH; $p_2$), as detected here—which are critically required to account for the missing sulfur budget in our Galaxy. Structural isomers in particular, such as the thioformaldehyde ($H_2CS; p_1$)–thiohydroxycarbene (HCSH; $p_2$) isomer pair, can be exploited as molecular tracers to define the physical and chemical conditions in star-forming regions (23, 43). With thioformaldehyde ($H_2CS; p_1$) residing ubiquitously in star-forming regions and branching ratios of thioformaldehyde to thiohydroxycarbene of typically three to one derived from the present study, fractional abundances of thiohydroxycarbene of up to $10^{-9}$ with respect to molecular hydrogen are predicted. Consequently, the prospective detection of trans/cis thiohydroxycarbene, which have dipole moments of 1.8 and 2.6 Debye, respectively (33), would be invaluable to test future chemical models of the organosulfur chemistry in star-forming regions. In terrestrial laboratories, all previous attempts to detect trans/cis-thiohydroxycarbene spectroscopically in the gas phase or in low-temperature matrices were unsuccessful, although Lamberts suggested that thiohydroxycarbene should represent a reactive intermediate in the hydrogenation of carbonyl monosulfide (CS) on interstellar grains (44). The high reactivity, even in low-temperature matrices, might be linked to the molecular structure of thiohydroxycarbene, suggesting that thiohydroxycarbene is not a true carbene, but, rather, a ylide with a negatively charged carbon atom and a positively charged sulfur atom (33). However, the vast regions of space represent a unique natural laboratory on a macroscopic scale and, hence, an unprecedented opportunity to search for highly reactive molecules such as thiohydroxycarbene. With the commission of the Atacama Large Millimeter/Submillimeter Array, the detection of exotic organosulfur molecules, such as thiohydroxycarbene, will intensify. An understanding of these data will rely on critical advances in experimental and computational chemical dynamics as achieved here, thus closing the gap between observational and laboratory data on the extraterrestrial sulfur chemistry that has existed for decades and, hence, changing the way we think about the organosulfur chemistry in the ISM.

Materials and Methods

Experimental. Reactive scattering experiments were carried out under single-collision conditions, as provided in a crossed molecular beam machine (45) by intersecting supersonic beams of electronically ground-state methylidyne (CH, $X'\Pi$) and D1-methylidyne radicals (CD, $X'\Pi$) with hydrogen sulfide ($H_2S; X'\Pi$) and deuterium sulfide ($D_2S; X'\Pi$) perpendicularly at collision energies of 19 kJ mol$^{-1}$. A pulsed supersonic beam of methylidyne radicals (CH; $X'\Pi$)
was generated by photolysis of bromoform (99%; Sigma-Aldrich Chemistry) at 248 nm (KrF; Coherent) seeded in helium (He, 99.9999%; Gaspro) at back pressure of 1 atm in the gas phase. The laser kinetic energy density, laser temporal pulse shape and laser spatial pulse shape were chosen to achieve a maximum in the ion yield. The lasers were temporally pulsed at a frequency of 10 Hz and were set to collide with each other with a relative translational energy of 18 kJ mol⁻¹. The timestep of the ab initio molecular dynamics simulation was 0.05 fs and was subject to further reduction until the total energy of the trajectories became stable. The position of the atoms was updated with the velocity Verlet algorithm. The trajectory was halted after it formed a product or went back to the reactant, however long it took. A total of 100 trajectories were sampled at each impact parameter (b), starting from 1.0 Å, with an increment of 1.0 Å, to detect b_{mean} the largest impact parameter of which a trajectory is reactive. The trajectories were weighted with respect to b to ensure that the cross-section of the collision was properly sampled.

### Astrochemical Modeling

We modeled those interstellar sources in which hydrogen sulfide is abundant, namely, HMCs, which have typical molecular hydrogen-number densities in the range 10⁹ to 10¹⁰ cm⁻³ and kinetic temperatures between 100 and 300 K. Such sources are found in regions of high-mass star formation and contain such large column densities of molecular hydrogen and dust that photo-processing of the gas is unimportant, even though very luminous, young hot stars provide the heating necessary to get to these high temperatures. We calculated the time-dependent chemical kinetic evolution of the hot gas using the full set of reactions and rate coefficients contained in the UMIST Database for Astrochemistry 2012 (47), with additional reactions to describe the formation of silicon dioxide (SiO₂) (48) and, here, thioformaldehyde. As initial conditions for these calculations, molecules were injected into the hot gas from the sublimation of the ice mantles from the grains. The adopted initial abundances were consistent with those observed in ices in cold dark clouds. Abundances relative to molecular hydrogen were extracted from the model and plotted against time.

### Data Availability

All data that were generated during the current research are available in the paper and S1 Appendix.

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