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Directed Gas-Phase Formation of the Germaniumsilylene Butterfly Molecule (Ge(μ -H₂)Si)

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Supporting Information

ABSTRACT: The hitherto elusive dibridged germaniumsilylene molecule $(Ge(\mu-H_2)Si)$ has been formed for the first time via the bimolecular gas-phase reaction of ground-state germanium atoms (Ge) with silane (SiH₄) under single-collision conditions. Merged with state-of-the-art electronic structure calculations, the reaction was found to proceed through initial formation of a van der Waals complex in the entrance channel, insertion of the germanium into a silicon-hydrogen bond, intersystem crossing from the triplet to the singlet surface, hydrogen migrations, and eventually elimination of molecular hydrogen via a tight exit transition state, leading to the germaniumsilylene "butterfly". This investigation provides an extraordinary peek at the largely unknown silicon-germanium chemistry on the molecular level and sheds light on the essential nonadiabatic reaction dynamics of germanium and silicon, which are quite distinct from those of the isovalent carbon system, thus offering crucial insights that reveal exotic chemistry and intriguing chemical bonding in the germanium-silicon system on the most fundamental, microscopic level.



F or one century, Langmuir's concept of isoelectronicity has been influential in expanding novel synthetic chemistry, in rationalizing the reactivity of isoelectronic systems, in developing modern concepts of chemical bonding, and in understanding basic concepts of molecular structure.¹ For the last decades, particular attention has been devoted to comparing the germanium and silicon chemistries with the analogous carbon chemistry.²⁻⁵ Residing in main group XIV, carbon, silicon, and germanium each have four valence electrons and hence are isovalent.⁶ Yet, their chemical bonding can be quite distinct, as demonstrated by the linear tricarbon molecule $[C_3; (1)]^7$ strongly differing from the cyclic silicon dicarbide molecule $[SiC_2; (2)]^8$ and the bent disilicon carbide $[Si_2C; (3)]^9$ and trisilicon $[Si_3; (4)]^{10}$ molecules (Figure 1). The diverse chemical bonding of carbon versus silicon and germanium is best reflected in a comparison of the homo- (E_2H_2) and heteronuclear $(EE'H_2)$ dihydrides (Figure 2). Whereas the linear acetylene molecule $(H-C\equiv C-H)$ (5)



Figure 1. Minimum-energy geometries and point groups of isovalent tricarbon (1), silicon dicarbide (2), disilicon carbide (3), and trisilicon (4); carbon and silicon atoms are color-coded in gray and purple, respectively.

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Figure 2. Structures, point groups, and relative energies (kJ mol⁻¹) of homo- and heteronuclear dihydrides of the main group XIV elements carbon (gray), silicon (purple), and germanium (green).

exemplifies the thermodynamically most stable isomer, with vinylidene carbene $(H_2C=C)$ (6) less stable by 186 kJ mol^{-1} ,¹¹ the sequence of stability is reversed for the SiCH₂ and GeCH₂ isomers. Here, the silavinylidene $(H_2C=Si)$ (7) and germavinylidene $(H_2C=Ge)$ (10) molecules represent the global minima and are thermodynamically favored by 145 and 177 kJ mol⁻¹ compared to the trans bent isomers silaacetylene (HC=SiH) (8) and germaacetylene (HC=GeH) (11).^{12,13} This departure can be understood from the reduced overlap of the valence s and p orbitals of the silicon and germanium atoms as compared to carbon, which hinders their ability to form the sp orbital hybrids responsible for the linear geometry of acetylene.¹⁴ The exotic chemical bonding and unusual molecular structures of silicon and germanium are demonstrated by spectroscopic detection of the nonclassical, hydrogen-bridged Si(μ -H₂)Si (13)¹⁵-HSi(μ -H)Si (14)¹⁶ and $Ge(\mu-H_2)Ge(17)-HGe(\mu-H)Ge(18)$ isomer pairs,¹⁷ whose carbon-analogue structures do not exist as equilibrium structures. The hydrogen-bridged geometries are energetically favorable compared to their carbene $[H_2Si=Si (15), H_2Ge=$ Ge (19)], and trans-acetylenic-type isomers [HSiSiH (16), HGeGeH (20)] (Figure 2).^{12,18,19}

However, although substantial research has been conducted in understanding of the chemical bonding and structures of the

homonuclear $[C_2H_2, Si_2H_2, Ge_2H_2]$ and heteronuclear systems [SiCH₂, GeCH₂], a detailed experimental characterization of the formation of free heteronuclear GeSiH₂ molecules has remained elusive, with only substituted forms of the silagermenylidene (Ge=SiH₂) isomer being observed in the laboratory thus far.^{20,21} Electronic structure calculations predict the existence of six structural isomers in their singlet electronic ground states, with the exotic $Si(\mu-H_2)Ge$ butterfly molecule being the thermodynamically most stable structure.¹² This reflects the preferential stability of hydrogen-bridged dinuclear molecules in the absence of carbon, which in contrast favors acetylenic or carbene-type structures. Therefore, replacement of both carbon atoms in acetylene by silicon and germanium is expected to lead to novel molecules, whose isovalent carbon counterparts do not exist, thus classifying the GeSiH₂ system as a prototype target to provide fundamental perspectives on chemical reactivity of silicon- and germaniumbearing species along with their chemical bonding.

Here, we report on the very first observation of the hitherto elusive germaniumsilylene butterfly molecule $(Ge(\mu-H_2)Si)$ under single-collision conditions in the gas phase by reacting ground-state germanium atoms $(Ge({}^{3}P_{i}))$ with silane $(SiH_{4};$ X¹A₁), exploiting the crossed molecular beam method and combining the experimental data with electronic structure calculations. This system represents a benchmark to explore the consequence of a single-collision event with the simplest germanium-bearing open-shell species (atomic germanium) with the prototype closed-shell silicon-carrying molecule (silane). The chemical reaction proceeds via a van der Waals complex in the entrance channel followed by isomerization and insertion of germanium into the silicon-hydrogen bond, nonadiabatic dynamics through intersystem crossing (ISC) from the triplet to the singlet surface, hydrogen migrations, and eventually unimolecular decomposition by molecular hydrogen elimination via a tight exit transition state, leading to the dibridged $Ge(\mu-H_2)Si$ isomer. These findings act as a benchmark to shed light on an unusual germanium-silicon chemistry and strongly diverge from those of isovalent carbonbased systems.

The reactive scattering experiments were performed using a crossed molecular beam apparatus (Methods). Accounting for the natural isotope abundances of silicon [³⁰Si (3.1%), ²⁹Si (4.67%), ²⁸Si (92.23%)] and of germanium [⁷⁰Ge (20.4%), ⁷²Ge (27.3%), ⁷³Ge (7.7%), ⁷⁴Ge (36.7%), and ⁷⁶Ge (7.8%)], reactive scattering signal was explored from mass-to-charge (m/z) of m/z = 110 (⁷⁶Ge³⁰SiH₄⁺) to m/z = 98 (⁷⁰Ge²⁸Si⁺), with the signal at m/z = 104 (⁷⁴Ge ²⁸SiH₂⁺) depicting the best signal-to-noise. It is important to note that after scaling the TOF spectra recorded at different mass-to-charge ratios reveal identical patterns suggesting the existence of a single channel; no signal of any GeSiH₄ adduct could be observed. On the basis of these considerations, the angular-resolved TOF spectra were taken at m/z = 104 (⁷⁴Ge ²⁸SiH₂⁺) with the laboratory angular distribution spread over 28° within the scattering plane, as defined by atomic germanium and silane reactant beams (Figures 3 and 4). The nearly forward-backward symmetry with respect to the center-of-mass (CM) of 23.2 \pm 0.2° suggests that the reaction of ground-state germanium atoms with silane involves indirect reaction dynamics through the formation of ⁷⁴Ge²⁸SiH₄ complex(es). The unimolecular decomposition of the intermediate(s) forms a molecule with the formula ⁷⁴Ge²⁸SiH₂ (hereafter GeSiH₂) via molecular hydrogen loss. Note that ions at higher (109-105) and lower



Figure 3. Time-of-flight spectra recorded at distinct laboratory angles at $m/z = 104 (^{74}\text{GeSiH}_2^+)$ for the reaction of ground-state germanium ($^{74}\text{Ge}(^{3}\text{P}_j)$) atoms with silane (SiH₄; X¹A₁). The open circles indicate the experimentally measured data and red lines the best fits.

(103–98) mass-to-charge ratios are linked to isotopologues and/or isotopomers of $^{74}\text{Ge}~^{28}\text{SiH}_2^+$ and their fragment ions generated upon electron impact ionization of the neutral $^{74}\text{Ge}~^{28}\text{SiH}_2$ product in the electron impact ionizer.

Our objective extends beyond establishing the chemical formula of the reaction product to rationalizing its structure and the underlying reaction mechanism governing its formation. This requires transformation of the laboratory experimental data obtained at m/z = 104 (GeSiH₂⁺) into the



Figure 5. CM translational energy (a) and angular (b) flux distributions of $^{74}\text{GeSiH}_2$ produced from the reactive scattering of germanium $(^{74}\text{Ge}(^3\text{P}_j))$ with silane (SiH_4; X¹A_1). Shaded areas indicate the acceptable upper and lower error limits of the fits accounting for the uncertainties of the laboratory angular distribution and time-of-flight spectra, with the red solid lines defining the best-fit functions.

CM reference frame. Figure 5a shows the resulting best fit CM translational energy $P(E_T)$ and angular flux $T(\theta)$ distributions along with the error limits. Importantly, the laboratory data were fit with a single product channel of a mass combination of 104 amu (GeSiH₂) and 2 amu (H₂); it is critical to stress that the formation of any GeSiH₃ isomer via atomic hydrogen loss is highly endoergic by at least 120 kJ mol⁻¹²² and hence is closed under our experimental conditions. It is critical to stress that fits of the experimental data could only be achieved by



Figure 4. Laboratory angular distribution and Newton diagram with associated GeSiH_2 flux contour map. (a) Laboratory angular distribution of ion signal obtained at mass-to-charge ratio 104 (⁷⁴GeSiH₂⁺) for the reaction of ground-state germanium (⁷⁴Ge(³P_j)) atoms with silane (SiH₄; X¹A₁). The incident germanium and silane beams are indicated at 0 and 90°, respectively. The black dots indicate the experimental data with $\pm 1\sigma$ uncertainty, and the red line indicates the best fit. (b) Corresponding Newton diagram of the germanium–silane system; the red circle holds a radius equivalent to the maximum CM velocity of the thermodynamically most stable ⁷⁴GeSiH₂ isomer with the flux contour map inset.

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Figure 6. Section of the relevant PES of the reaction of ground-state atomic germanium $(Ge ({}^{3}P_{0}))$ with silane $(SiH_{4}; X^{1}A_{1})$. The minimal-energy crossing point (MSX) is shown for ISC from the triplet surface (black) to the singlet surface (red).

incorporating a reaction threshold of 14–16 kJ mol⁻¹ into the fitting routine, i.e., a threshold energy of the colliding germanium atom and silane molecules must have to form at least one of the GeSiH₂ species. Inspecting the CM translational energy flux distribution, $P(E_T)$, the maximum translational energy $(E_{\text{max}} = 71 \pm 14 \text{ kJ mol}^{-1})$ of the products helps to identify the nature of the GeSiH₂ isomer. For molecules born without rovibrational excitation, E_{max} characterizes the sum of the reaction exothermicity and the collision energy. Therefore, subtraction of the collision energy (16 kJ mol⁻¹) suggests that the formation of GeSiH₂ plus molecular hydrogen is exothermic by 55 \pm 14 kJ mol⁻¹. The GeSiH₂ isomer formed can be assigned by comparing the experimentally determined reaction exothermicity with the energetics obtained from electronic structure computations for distinct GeSiH₂ isomers (Figure S1). The experimental reaction energy agrees exceptionally well with the computed energy of -55 ± 4 kJ mol⁻¹ to form the thermodynamically most stable $Ge(\mu-H_2)Si(^1p1)$ molecule in its $^1A'$ electronic ground state. The cis-monobridged $Ge(\mu-H)SiH$ (¹p2) and Ge=SiH₂ (¹p3) isomers are less stable by 25 and 28 kJ mol⁻¹; this would result in reaction energies of -30 ± 4 and -27 ± 4 kJ mol⁻¹, respectively. Therefore, ¹p2 and ¹p3 along with higher-energy isomers ${}^{1}p3 - {}^{1}p6$ might be formed as well and might be masked in the low-energy part of the CM translational energy distribution. We note that these energies are given for germanium atoms formed in their ³P₀ electronic ground state. The j = 1 and 2 states are higher in energy by 6.7 and 16.9 kJ mol⁻¹. For $Ge(\mu-H)SiH$ (¹p2) and $Ge=SiH_2$ (¹p3), this would yield reaction energies of 37 ± 14 kJ mol⁻¹ (*j* = 1) and 47 ± 14 kJ mol⁻¹ (j = 2) for ¹p2 and 34 ± 14 kJ mol^{-1} (j = 1) and 44 ± 14 kJ mol⁻¹ (j = 2) for ¹p2. Hence,

thermodynamically most stable $Ge(\mu-H_2)Si$ (¹p1) isomer is formed from reaction of germanium in its ³P₀ ground state with higher-energy isomers possibly masked in the low-energy part of the CM translational energy distribution. Among potential triplet products, even the energetically most favorable isomer ${}^{3}p3$ (+14 ± 4 kJ mol⁻¹) does not correlate with the experimentally derived reaction energy of $-55 \pm 14 \text{ kJ mol}^{-1}$. Therefore, we conclude that because the reaction of groundstate atomic germanium with silane starts on the triplet surface but the energetically feasible product(s) hold singlet ground states, at least one channel of the reaction involves ISC and hence nonadiabatic reaction dynamics. Finally, the CM angular distribution, $T(\theta)$, has intensity over the complete angular range from 0 to 180° (Figure 5b). This finding implies indirect scattering dynamics through the formation of GeSiH₄ complex(es) holding lifetimes longer than their rotational periods.²³ Note that best fits were achieved with a distribution maximum at 80°, implying geometrical constraints of the exit transition state(s) with the hydrogen molecule emitted perpendicularly to the plane of the decomposing complex almost parallel to the total angular momentum vector. In conclusion, at least the thermodynamically most stable germaniumsilylene molecule (Ge(μ -H₂)Si) (¹p1) is formed from reaction of germanium in its ³P₀ ground state with silane involving nonadiabatic reaction dynamics and ISC from the triplet to the singlet surface.

within the error limits, we believe that at least the

We are now combining the aforementioned discussion with the computational results to unravel the underlying reaction mechanism(s) (Figures 6 and S1–S6). Because the energetically accessible product isomers $(^{1}p1-^{1}p6)$ plus molecular hydrogen have singlet ground states but the bimolecular

collision is initiated on the triplet surface, potential molecular hydrogen loss channels are explored on both triplet and singlet GeSiH₄ potential energy surfaces (PESs) together with ISC. The formation of any GeSiH₃ isomer via atomic hydrogen loss is highly endoergic by at least 120 kJ mol⁻¹,²² and hence closed at the experimental collision energy of 16 kJ mol⁻¹. The complete PES is very complex (Figure S2), containing 10 intermediates and 18 transition states. The complexity of this surface requires a simplification. Considering the experimental collision energy of 16 kJ mol⁻¹, all transition states and products above this energy-accounting for the accuracy of the calculations-cannot be overcome in our crossed beam study. The removal of these transition states and energetically inaccessible products results in a simplified PES that contains only four intermediates, four transition states, and three possible product channels (Figure 6).

Our calculations expose that the reaction is initiated on the triplet surface via defacto insertion of the germanium atom into the silicon-hydrogen bond of silane. Once the germanium atom approaches the silane molecule, the PES is attractive and results in a van der Waals complex ³i0 that is stabilized by 29 kJ mol⁻¹ with respect to the separated reactants. This complex can rearrange through insertion of the germanium atom into the silicon-hydrogen bond of silane involving a barrier of 33 kJ mol⁻¹. This leads to the covalently bound reaction intermediate ³il silvlgermylene (H₃SiGeH). The transition state connecting the van der Waals complex ³i0 and intermediate ³i1 is only slightly higher in energy by 4 kJ mol⁻¹ than the separated reactants and can be passed easily considering the collision energy of 16 kJ mol⁻¹. We also located a transition state connecting intermediate ³i1 to the thermodynamically most stable triplet product (3p3) that lies 86 kJ mol⁻¹ above the energy of the separated reactants. Therefore, at a collision energy of 16 kJ mol⁻¹, the pathway even to the energetically most stable triplet isomer is closed (Figure S2), confirming our earlier conclusion that under our experimental conditions, triplet GeSiH₂ isomers are not formed in the bimolecular reaction of ground-state germanium atoms with silane.

The computations predict that ³i1 undergoes ISC to intermediate ¹i1, which resides in a deep potential energy well of 151 kJ mol⁻¹ with respect to the separated reactants. The seam of crossing (MSX) between the triplet structure ³i1 and ¹il located a crossing point between the lowest triplet and singlet electronic states of intermediate ¹i1 close to ³i1. The seam of crossing is 79 kJ mol⁻¹ in energy below the separated reactants, slightly above ³[i1]. What is the fate of ¹i1? Our calculations reveal that H₃SiGeH can undergo unimolecular decomposition to $Ge(\mu-H_2)Si(^1p1)$ via a tight transition state located 22 \pm 4 kJ mol⁻¹ above the separated reactants (Figure S3). Recall that the experimental data could only be replicated by incorporating a reaction threshold of 14-20 kJ mol⁻¹ into the fitting routine, which agrees nicely with the computed barrier. Regarding the exit transition state connecting H₃SiGeH (¹i1) to Ge(μ -H₂)Si (¹p1), our electronic structure calculations suggest that molecular hydrogen departs the dissociating complex at angles with respect to the principal axes A, B, and C of 81.5, 11.1, and 82.9°, respectively (Figure S4). Close inspection of the principal moments of inertia reveal that the ⁷⁴Ge²⁸SiH₄ decomposing structure is a near-prolate complex with I_a (2.00 × 10⁻⁴⁶ kg m²) < I_b (2.17 × 10⁻⁴⁵ kg m²) $\approx I_c$ (2.28 × 10⁻⁴⁵ kg m²), and in the prolate limit, molecular hydrogen emission perpendicular to the symmetric

axis (81.5°) results in sideways scattering.²⁴ The geometry of the dissociating complex to form ¹p1 therefore agrees well with the $T(\theta)$ distribution maximum at 80° (Figure 5b) derived from experiment. Considering the inherent barriers to isomerization of the reaction intermediates, H₃SiGeH (¹i1) is also expected to eliminate molecular hydrogen via a fourcenter elimination, leading to the van der Waals complex ¹i3. The decay of this complex yields either silagermenylidene (Ge=SiH₂; ¹p3) via barrierless dissociation (Figure S5) or $Ge(\mu-H)SiH$ (¹p2) via a relatively loose transition state (Figure S6). It should be noted that intermediates ¹i2 and ${}^{1}i4 - {}^{1}i7$ are also energetically accessible at our collision energy via isomerization of ¹il (Figure S2). However, unimolecular decomposition of these structures via molecular hydrogen loss leads to GeSiH₂ isomers whose energetics do not account for the experimentally derived reaction energy of -55 ± 14 kJ mol^{-1} .

In summary, the experimental data and computations propose that at least the thermodynamically most stable $Ge(\mu-H_2)Si$ (¹p1) molecule is formed via nonadiabatic reaction dynamics in the reaction of ground-state germanium atoms plus silane. Considering the inherent barriers to isomerization of the reaction intermediates, the $Ge(\mu-H)Si$ (¹p2) and $Ge=SiH_2$ (¹p3) isomers likely contribute the reactive scattering signal as well, but a quantification represents a tricky problem and is beyond the scope of the present study as this investigation would require the consideration of spin-orbit coupling and the exact branching ratios of the ³P₀, ³P₁, and ³P₂ states for the atomic germanium reactant. Despite these open questions, single-collision conditions provide an ideal tool to form novel molecules such as dibridged germaniumsilylene ($Ge(\mu-H_2)Si$) (¹p1).

Our combined experimental and theoretical investigation of the bimolecular reaction of ground-state germanium atoms with silane exposes overall exothermic channels to the previously elusive germanium silvlene molecule ($Ge(\mu-H_2)Si$) (¹**p1**) under single-collision conditions in the gas phase. This reaction begins on the triplet surface via formation of a van der Waals complex followed by isomerization through insertion of the germanium atom into a silicon-hydrogen bond of the silane molecule, yielding the silylgermylene (H_3SiGeH) intermediate. This intermediate is predicted to undergo ISC to singlet H₃SiGeH, which undergoes unimolecular decomposition via molecular hydrogen loss to $Ge(\mu-H_2)Si$ (¹p1) involving a tight exit transition state in an overall exoergic reaction. It is critical to recall that a fit of the laboratory data could *only* be obtained through the incorporation of a reaction threshold of 14–20 kJ mol⁻¹ into the fitting routine. This energy correlates closely with the computed energy of the transition state connecting ¹i1 and ¹p1 plus molecular hydrogen of 22 \pm 4 kJ mol⁻¹; however, our experimental data and, in particular, the relevant PES (Figure 6) do not exclude the potential formation of ${}^{1}p2$ and/or ${}^{1}p3$ as well. Carrying a 0.61 D dipole moment (Table S8), the C_s symmetric Ge(μ -H₂)Si (¹p1) is stabilized by one σ -bond and two donor-acceptor bonds that form two three-center/twoelectron hydrogen bridges; it has no π -bonds.²⁵ The hydrogen atoms and heavy nuclei occupy separate planes, and the 104.5° dihedral between them is geometrically reminiscent of a perched butterfly. It is worth noting that silicon and germanium are metalloids and that the geometry and bonding of $Ge(\mu-H_2)Si$ are strikingly consistent with those of the isoelectronic diborane[4] $(HB(\mu-H_2)BH)$,²⁶ which is also

stabilized by one σ -bond and two three-center/two-electron hydrogen bridges and adopts a butterfly configuration.

Despite sharing the same period, the differences in the equilibrium geometries of the dicarbon hydrides and the silicon-germanium hydrides are tremendous, as documented in numerous detailed computational reports over the last decades. More recently, theory and experiment have come together in an effort to connect exotic molecules like $Ge(\mu-H_2)$ Si to bimolecular gas-phase reactants, as was done in this study, to understand exactly how these molecules form by evaluating the reactivity of group XIV atoms with their tetrahydrides. In the simplest case, the reaction of the ground-state carbon $(C(^{3}P))$ atom with methane (CH_{4}) is initially attractive due to a weakly bound van der Waals complex, but the pathways leading to triplet C_2H_2 isomers are inhibited by a 51 kJ mol⁻¹ (0 K) barrier²⁷ and hence closed under identical experimental conditions in crossed molecular beam experiments. Compared to the carbon-methane system, replacing $C(^{3}P)$ with a silicon (Si(³P)) atom results in low-energy pathways to triplet and singlet SiCH₂ isomers whose features lie below the energy of the separated Si(³P) and CH₄ reactants, enabling the reaction to proceed spontaneously,²⁸ and when both carbon atoms are replaced with silicon atoms, both the spontaneity and exotic structures familiar to the present study are open to the reactants.¹⁸ Si(³P) insertion at silane (SiH₄) is mitigated by a low-lying van der Waals interaction, and the resulting Si₂H₄ complex eliminates molecular hydrogen to form singlet disilavinylidene (H₂SiSi(¹A₁)),¹⁸ which, as illustrated in Figure 2, is not the thermodynamically favored Si₂H₂ isomer. Importantly, as uncovered in the present study, substituting $Si(^{3}P)$ with $Ge(^{3}P)$ further alters the reaction dynamics such that the minimum-energy isomer, here the dibridged germaniumsilylene (¹p1) molecule, is selected as the nascent reaction product following insertion of Ge(³P) into SiH₄.

The reaction dynamics of the germanium-silane system are clearly distinct as compared to those of isovalent systems comprising a carbon or silicon atom that reacts with methane or silane. Further, the incredibly varied differences uncovered by the systematic substitution of carbon atoms in the $C(^{3}P)$ + CH₄ reaction with silicon and/or germanium reveal that the data accrued in deceptively analogous reaction systems differ so strongly that insight from one reaction system is not readily leveraged toward interpreting another. That chemical intuition is not sufficient for predicting the reactivity of heavy group XIV atoms in what are seemingly similar and simple (six atoms) isovalent reaction systems affects how we think about the reaction dynamics of isovalent systems and the chemical bonding of germanium- and silicon-bearing molecules. The germanium-silane system therefore serves as a critical benchmark toward an intimate understanding of the formation of hitherto elusive silicon- and germanium-bearing molecules, thus influencing the conception of chemical structure and exotic chemical bonding in the future.

METHODS

Experimental Methods. The reaction between ground-state atomic germanium $(Ge({}^{3}P_{j}))$ and silane $(SiH_{4}; X^{1}A_{1})$ was carried out in the gas phase at the molecular level under single-collision conditions exploiting a crossed molecular beam machine²⁹ coupled with a laser ablation source.³⁰ Briefly, a pulsed supersonic beam of ground-state germanium atoms was prepared in situ by laser ablation³⁰ of an optical-grade germanium rod (Alfa Aesar) at 266 nm (30 Hz; 3.3 mJ

pulse⁻¹) and subsequently seeding the ablated germanium atoms in neon (Ne, 99.9999%, Matheson) gas, which was released by a pulsed valve operated at 60 Hz and a backing pressure of 3040 Torr. No higher germanium clusters were observed under these experimental conditions. The germanium atom beam was collimated by a skimmer, velocity-selected (peak velocity $v_p = 851 \pm 2 \text{ m s}^{-1}$; speed ratio $S = 7.8 \pm 0.1$) and then perpendicularly crossed with a pulsed supersonic beam of pure silane (SiH₄, 99.999%, Voltaix, 550 Torr) with a peak velocity of $841 \pm 10 \text{ ms}^{-1}$ and a speed ratio of 10.2 ± 0.3 in the scattering chamber at a collision energy of 16.0 ± 0.2 kJ mol^{-1} . The reaction products were monitored by a rotatable quadrupole mass spectrometer after electron impact ionization of the neutral products at 80 eV in an ultrahigh-vacuum chamber. The velocity distributions of the products were recorded through the angular-resolved time-of-flight (TOF) technique by recording the arrival time of the ions at welldefined mass-to-charge ratios (m/z) of the ionized products at different scattering angles. The TOF spectra at each angle were then integrated to obtain the laboratory angular distribution. To allow a "laser-on" minus "laser-off" background subtraction, both valves were triggered at 60 Hz, but the laser was operated at half of the frequency at 30 Hz. To extract information on the chemical dynamics and hence the reaction mechanism from the experimental data, a forward convolution fitting technique was applied. This approach simulates the laboratory data (TOF spectra, laboratory angular distribution) of the reactively scattered products and yields two "best-fit" functions: the CM translational energy flux distribution $P(E_{\rm T})$ and the angular flux distribution $T(\theta)$.^{31,32} Finally, we note that in its ³P electronic ground state, three *j* levels (0, 1, 2) can be populated, with *j* = 1 and 2 lying 6.7 and 16.9 kJ mol⁻¹ higher in energy than j = $0.^{33}$ Therefore, we characterized the *j*-level distribution of the germanium atoms in their ground electronic states (³P) employing laser-induced fluorescence (LIF). These data suggest the presence of atomic germanium in the ${}^{3}P_{0}$, ${}^{3}P_{1}$, and ³P₂ states.

Computational Methods. The reaction of ground-state atomic germanium (Ge(³P)) with silane (SiH₄; X^1A_1) is also explored theoretically. The geometries of possible triplet and singlet $GeSiH_2$ and $GeSiH_4$ isomers are optimized via coupled cluster³⁴⁻³⁷ CCSD/cc-pVTZ calculations. The complete basis set limits,³⁸ CCSD(T)/CBS energies, are obtained by extrapolating the CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ energies, with CCSD/cc-pVTZ zeropoint energy corrections. The accuracy of these CCSD(T)/CBS energies are expected to be within 4 kJ mol^{-1.39} The minimum-energy crossing point between ³i1 and ¹i1 was located with the CPMCSCF⁴⁰/TZVPP method with energy refined via CCSD(T)/CBS. GAUSSIAN09 programs⁴¹ were used in density functional and coupled cluster calculations, and MOLPRO⁴⁰ was exploited for the surface-crossing computations. To verify the overall energetics of the reactions and the relative stabilities of the triplet and singlet GeSiH₂ isomers, a modified HEAT-345(Q) approach (designated hereafter as mHEAT-345(Q)), which was previously applied to mediumsized molecules, was exploited.^{42,43}

$$E_{\text{mHEAT}} = E_{\text{SCF}}^{\infty} + \Delta E_{\text{CCSD}(\text{T})}^{\infty} + \Delta E_{\text{T}-(\text{T})} + \Delta E_{(\text{Q})-\text{T}} + \Delta E_{\text{ZPE}} + \Delta E_{\text{DBOC}} + \Delta E_{\text{Scalar}}$$
(1)

The composite method mHEAT-345(Q) is defined as follows: (i) It uses a molecular structure, which is fully

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optimized with the frozen-core (FC) CCSD(T)/ANO1 level of theory; (ii) Hartree-Fock energy is extrapolated to a complete basis set using Dunning's basis sets,^{38,44} specifically cc-pVTZ, cc-pVQZ, and cc-pV5Z; (iii) an electron-correlation energy with the CCSD(T) method is obtained by an extrapolation based on the cc-pVQZ and cc-pV5Z basis sets (in these calculations, all core electrons are frozen); (iv) highlevel correction (HLC) is calculated as a sum of two contributions, i.e., a full triple correction and a quadruple excitation correction from perturbation theory; the former is calculated as a difference in energy between FC-CCSDT/ccpVTZ and FC-CCSD(T)/cc-pVTZ, while the latter is obtained from the difference between FC-CCSDT(Q)/ccpVDZ and FC-CCSDT/cc-pVDZ; (v) the anharmonic zeropoint vibrational energy (ZPE) is calculated using FC-CCSD(T) and the atomic natural basis set⁴⁵⁻⁴⁷ based on second-order vibration perturbation theory (VPT2).48,49 Like the HEAT protocol, other small corrections such as scalar relativity effects and diagonal Born-Oppenheimer correction (DBOC) are also included. It is expected that mHEAT calculations give an accuracy of about $4 kJ mol^{-1}$ for relative energies. All calculations are done using the CFOUR quantum chemistry package.⁵⁰

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.9b00284.

Details on the triplet and singlet $GeSiH_4$ potential energy surfaces including energies, vibrational frequencies, Cartesian coordinates, rotational constants, and dipole moments of intermediates, transition states, and reaction products (PDF)

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A.M.T, B.B.D., T.Y., G.Y., and R.I.K. carried out the experimental measurements and data analysis. B.-J.S., S.-Y.C., A.H.H.C., T.L.N., J.F.S., and A.M.M. performed the theoretical calculations. All authors discussed the results and contributed to the manuscript.

Notes

The authors declare no competing financial interest.

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