

Gas Phase Formation of Methylgermylene (HGeCH₃)

Zhenghai Yang,^[a] Chao He,^[a] Srinivas Doddipatla,^[a] Vladislav S. Krasnoukhov,^[b]
Valeriy N. Azyazov,^[b, c] Alexander M. Mebel,^{*,[d]} and Ralf I. Kaiser^{*,[a]}

The methylgermylene species (HGeCH₃; X¹A') has been synthesized via the bimolecular gas phase reaction of ground state methylidyne radicals (CH) with germane (GeH₄) under single collision conditions in crossed molecular beams experiments. Augmented by electronic structure calculations, this elementary reaction was found to proceed through barrierless insertion of the methylidyne radical in one of the four germanium-hydrogen bonds on the doublet potential energy surface yielding the germylmethyl (CH₂GeH₃; X²A') collision complex. This insertion is followed by a hydrogen shift from germanium to carbon and unimolecular decomposition of the methylgermyl (GeH₂CH₃; X²A') intermediate by atomic hydrogen elimination leading to singlet methylgermylene (HGeCH₃; X¹A'). Our investigation provides a glimpse at the largely unknown reaction dynamics and isomerization processes of the carbon-germanium system, which are quite distinct from those of the isovalent carbon system thus providing insights into the intriguing chemical bonding of organo germanium species on the most fundamental, microscopic level.

Since the discovery of the main group element germanium (Ge) by Clemens Winkler in 1886,^[1] the chemistry of germanium has prompted extensive interest from the organometallic,^[2] physical chemistry,^[3] and theoretical chemistry^[4] communities predominantly due to the often exotic chemical bonding and molecular structures of organo germanium species compared to their isovalent hydrocarbon counterparts.^[5] Particular attention has been devoted to reactive intermediates connected to germyl free radicals (GeH₃),^[6] germylenes (GeH₂),^[7] and germynes (GeH).^[8] Although Langmuir's concept of isoelectronicity in which 'two molecular entities with the same number of valence electrons have similar chemistries'^[9] predicts that the chemical

bonding and molecular structures of ethylene (C₂H₄), disilene (Si₂H₄) and digermene (Ge₂H₄) should be alike, the geometries of these isovalent species differ strongly. The D_{2h} symmetric ethylene (C₂H₄; 1; X¹A_{1g}) is planar and represents the global minimum on the C₂H₄ potential energy surface (PES) with both carbon atoms sp² hybridized. For the heavier analogue of C₂H₄, a non-planar structure was first reported by Márquez et al.^[10] The thermodynamically most stable Si₂H₄ species – the trans-bent disilene (Si₂H₄; 3; X¹A_g) molecule – has a C_{2h} point group and carries two pyramidal silene moieties with each silicon atom being sp³ hybridized (Scheme 1).^[11] For the chemistries of digermene, the most stable Ge₂H₄ species – the trans-bent digermene (Ge₂H₄; 3; X¹A_g) molecule – also belongs to the C_{2h} point group and holds two germene moieties, in which each germanium atom is sp³ hybridized (Scheme 1).^[11] This finding initially proposed that germanium can hardly form germanium-germanium double bonds as a result of the covalent radius of the germanium atom which inhibits neighboring atomic 4p_z orbitals from approaching sufficiently close to form π molecular orbitals.^[12] The diverse electronic structures of these systems are exemplified when contemplating the C_s symmetric triplet methylcarbene (CH₃CH; 2; X³A''), singlet silylsilylene (SiH₃SiH) and singlet germylgermylene (GeH₃GeH; 4; X¹A') depicting triplet-singlet and singlet-triplet splittings of 16–25, 54–56 and 77–95 kJ mol⁻¹, respectively.^[7b,13] The peculiar molecular structures of germanium-based species are best reflected in terms of the non-classical mono-bridged H₂Ge(μ-H)GeH (5; X¹A), square di-bridged-trans-HGe(μ-H₂)GeH (6; X¹A_g), and square di-bridged-cis-HGe(μ-H₂)GeH (7; X¹A₁) species, whose isovalent carbon counterparts do not exist.^[14] This mirrors the stability of hydrogen-bridged dinuclear germanium-based species in the absence of carbon. Therefore, a replacement of isovalent carbon by germanium can lead to species, whose carbon-analogue structures do not exist.

Although substantial research has been devoted to an understanding of the chemical structures and bonding of the homonuclear systems (C₂H₄; Si₂H₄; Ge₂H₄), new attention need to be paid to the meticulous experimental characterization of the formation of free heteronuclear GeCH₄ species, which has been tentatively detected. Gas-phase kinetics of the reactions of germylenes have been studied^[15] and methylgermylene (HGeCH₃; 8; X¹A') was first tentatively characterized via laser flash photolysis of 1,3,4-trimethylgermacyclopent-3-ene; the UV spectrum and rate constants of its reactions with 10 different substrates were measured.^[16] In 2010, HGeCH₃ was inferred from matrix isolation studies^[17] via the ν₃ and ν₅ modes at 1803 and 1230 cm⁻¹. Electronic structure calculations predicted the existence of three structural isomers. Singlet methylgermylene (HGeCH₃; 8; X¹A') represents the thermodynamically most stable

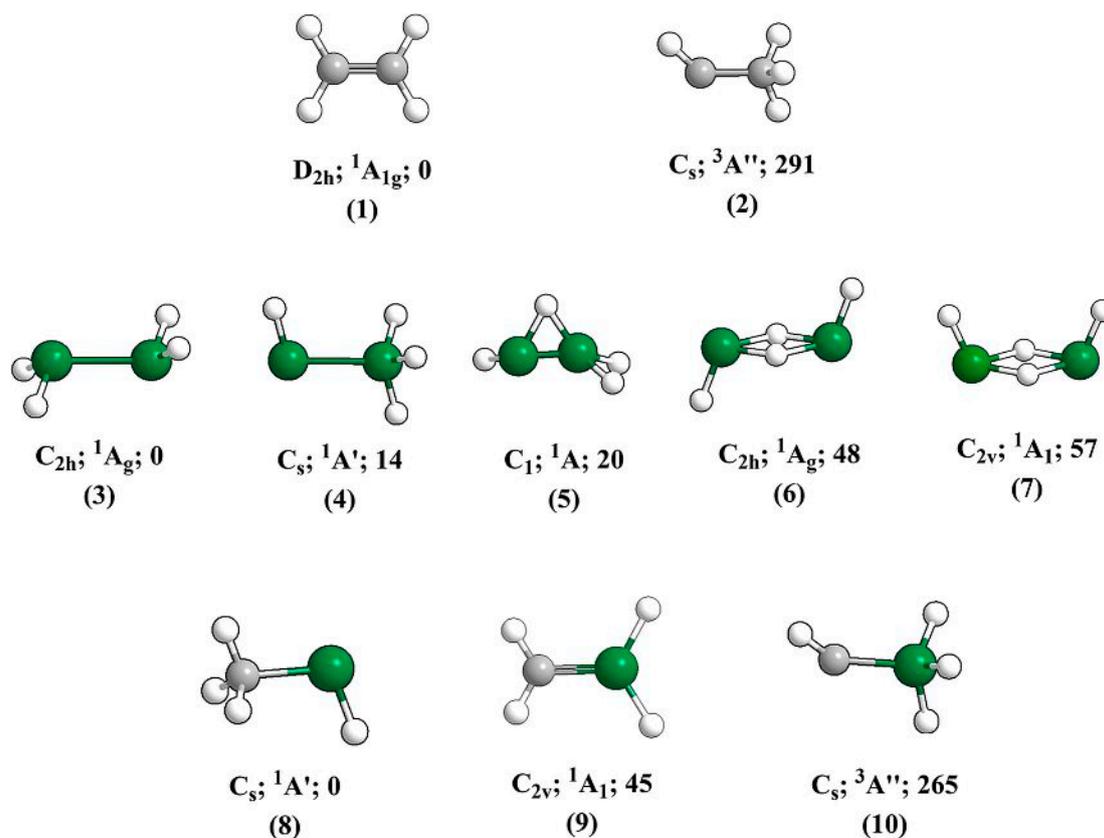
[a] Z. Yang, C. He, S. Doddipatla, Prof. R. I. Kaiser
Department of Chemistry
University of Hawai'i at Manoa
Honolulu, HI 96822, USA
E-mail: ralfk@hawaii.edu

[b] V. S. Krasnoukhov, Prof. V. N. Azyazov
Samara National Research University
Samara 443086, Russian Federation

[c] Prof. V. N. Azyazov
Lebedev Physical Institute
Samara 443011, Russian Federation

[d] Prof. A. M. Mebel
Department of Chemistry and Biochemistry
Florida International University
Miami, Florida 33199, USA
E-mail: mebela@fiu.edu

Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/cphc.202000392>



Scheme 1. Structures, point groups, electronic ground state wave functions, and relative energies (kJ mol^{-1}) of homo- and heteronuclear tetrahydrides of main group XIV elements involving carbon (gray) and germanium (green) with hydrogen atoms color coded in white.

structure with singlet germene (H_2GeCH_2 ; **9**; X^1A_1) and triplet germylmethylene (HCGeH_3 ; **10**; X^3A'') being less stable by 45 and 266 kJ mol^{-1} , respectively. The shortage of experimental data classifies the GeCH_4 system as a prototype target to provide fundamental perspectives on the chemical reactivity and synthesis of carbon- and germanium-bearing species together with information on their chemical bonding and electronic structure.

Here, we report on the experimental observation of the methylgermylene species (HGeCH_3 ; X^1A') under single collision conditions in the gas phase via the reaction of ground state methylidyne radicals (CH ; $X^2\Pi$) with germane (GeH_4 ; X^1A_1) exploiting the crossed molecular beam method and combining the experimental data with electronic structure calculations. This system explores the outcome of the elementary reaction of the simplest organic radical (methylidyne) with the prototype of a closed shell germanium bearing species (germane) to initiate a carbon-germanium bond coupling eventually forming the simplest representative of an organometallic alkylgermylene: methylgermylene. The chemical reaction dynamics are initiated on the doublet surface by a barrier-less insertion of the methylidyne radical with its carbon atom into a germanium – hydrogen bond followed by a hydrogen shift within the collision complex and unimolecular decomposition through atomic hydrogen loss leading to singlet methylgermylene (HGeCH_3 ; X^1A'). These findings reveal an exotic germanium

chemistry yielding methylgermylene, which strongly diverge from those of the isovalent methylidyne – methane system.^[18] By probing the formation of methylgermylene under single collision conditions in the gas phase, the nascent reaction products are ‘isolated’ and fly away undisturbed after the reactive collision between the methylidyne radical and germane. This prevents secondary collisions of the initial reaction products such as dimerization of methylgermylene thus providing a new synthetic route under controlled experimental conditions to the prototype of the organogermynes class. This enables us to synthesize a highly reactive molecule and to unravel its molecular structure and chemical reactivity at the most fundamental, microscopic level.

The reactive scattering experiments were carried out utilizing a crossed molecular beam apparatus at a collision energy of $20.6 \pm 0.3 \text{ kJ mol}^{-1}$ (Supporting Information; Table S1). The neutral reaction products were ionized at 80 eV by electron impact within a triply differentially pumped quadrupole mass spectrometric detector held at 6×10^{-12} Torr. The ions were then mass- and velocity-analyzed to record angular resolved time-of-flight (TOF) spectra. Considering the natural isotope abundances of carbon [^{12}C (98.9%), ^{13}C (1.1%)] and of germanium [^{70}Ge (20.4%), ^{72}Ge (27.3%), ^{73}Ge (7.7%), ^{74}Ge (36.7%), ^{76}Ge (7.8%)], the reactive scattering signal was probed from mass-to-charge (m/z) of $m/z=93$ ($^{76}\text{Ge}^{13}\text{CH}_4^+$) to $m/z=82$ ($^{70}\text{Ge}^{12}\text{C}^+$) with signal at $m/z=88$ ($^{76}\text{Ge}^{12}\text{C}^+ / ^{74}\text{Ge}^{12}\text{CH}_2^+$

$^{73}\text{Ge}^{13}\text{CH}_2^+ / ^{73}\text{Ge}^{12}\text{CH}_3^+ / ^{72}\text{Ge}^{13}\text{CH}_3^+ / ^{72}\text{Ge}^{12}\text{CH}_4^+$) depicting the best signal-to-noise ratio; the signals at $m/z=90$ ($^{76}\text{Ge}^{12}\text{CH}_2^+ / ^{76}\text{Ge}^{13}\text{CH}^+ / ^{74}\text{Ge}^{12}\text{CH}_4^+ / ^{74}\text{Ge}^{13}\text{CH}_3^+ / ^{73}\text{Ge}^{13}\text{CH}_4^+$) and $m/z=89$ ($^{76}\text{Ge}^{12}\text{CH}^+ / ^{76}\text{Ge}^{13}\text{C}^+ / ^{74}\text{Ge}^{12}\text{CH}_3^+ / ^{74}\text{Ge}^{13}\text{CH}_2^+ / ^{73}\text{Ge}^{12}\text{CH}_4^+ / ^{73}\text{Ge}^{13}\text{CH}_3^+ / ^{72}\text{Ge}^{13}\text{CH}_4^+$) were collected at levels of $22 \pm 2\%$ and $38 \pm 3\%$, respectively, compared to $m/z=88$. The TOF spectra recorded at distinct mass-to-charge ratios exhibit indistinguishable patterns and are superimposable after scaling proposing the existence of one reaction channel, i.e. the likely formation of $^{74}\text{Ge}^{12}\text{CH}_4$ isomer(s) along with atomic hydrogen. The angular resolved TOF spectra were collected at $m/z=88$ ($^{74}\text{Ge}^{12}\text{CH}_2^+$) revealing a laboratory angular distribution spread over at least 40° within the scattering plane spanned by the methylidyne and germane molecular beams (Figure 1). Ions at higher (93–89) and lower (87–82) mass-to-charge ratios are connected to isotopologues and/or isotopomers of $^{74}\text{Ge}^{12}\text{CH}_2^+$ ($m/z=88$) along with their fragment ions originating upon electron impact

ionization of the neutral product(s) in the electron impact ionizer.

Considering the natural abundances of carbon and germanium along with complex fragmentation patterns of neutral organo germanium species, it is crucial to transform the experimental data from the laboratory to the center-of-mass (CM) reference frame in an attempt to untangle the molecular formulae and the structural isomer(s) of the reaction product(s) along with the underlying chemical dynamics accompanying their formation.^[19] The laboratory data can be fit with a single channel defined by the mass combination of the products of 90 amu ($^{74}\text{Ge}^{12}\text{CH}_4$; hereafter: GeCH_4) and 1 amu (H) with ion counts at $m/z=89$ and 88 predominantly arising from dissociative electron impact ionization of the parent molecule in the ionizer. It should be stressed that no sensible fit could be achieved with a mass combination of 89 amu ($^{74}\text{Ge}^{12}\text{CH}_3$) plus 2 amu (H_2) with the simulated TOF spectra being too fast and

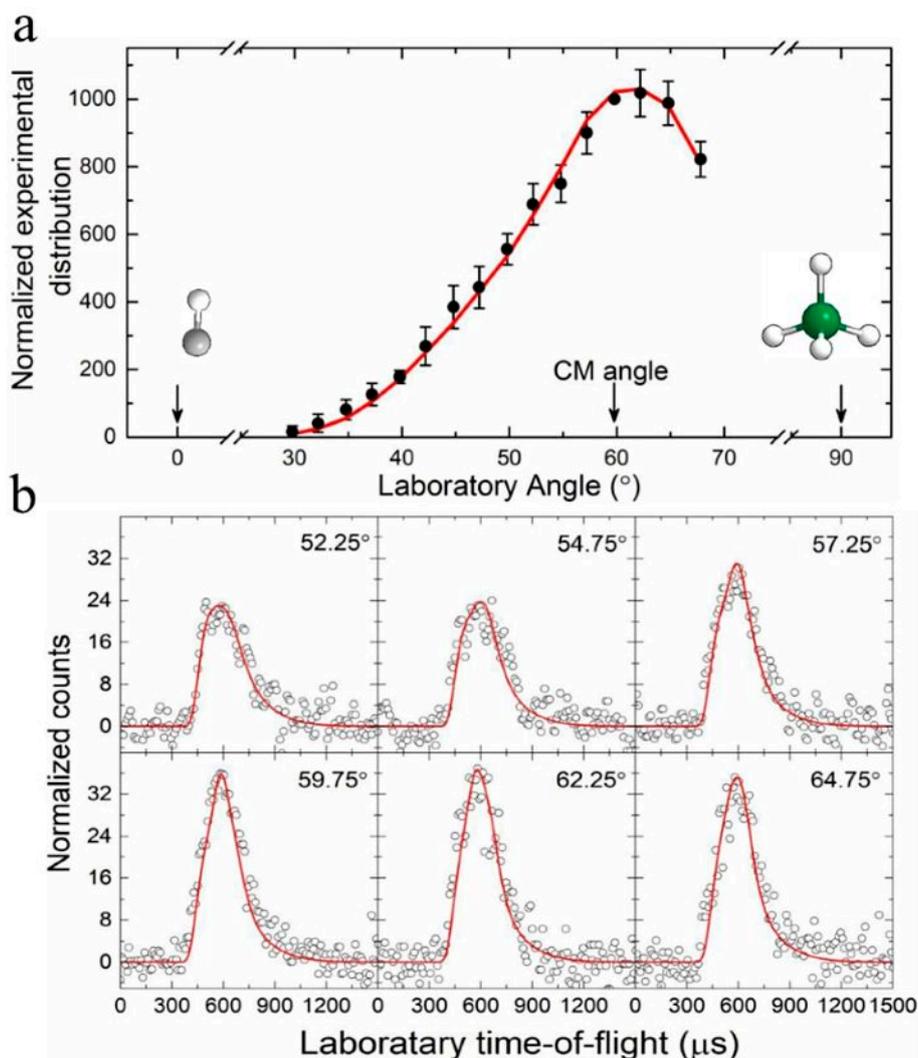


Figure 1. Laboratory angular distribution and the associated time-of-flight spectra. Laboratory angular distribution at mass-to-charge ratio (m/z) of $m/z=88$ recorded in the reaction of the methylidyne radical with germane (a) and the time-of-flight spectra recorded at distinct laboratory angles overlaid with the best fits (b). The solid circles with their error bars represent the normalized experimental distribution with $\pm 1\sigma$ uncertainty; the open circles indicate the experimental data points of the time-of-flight spectra. The red lines represent the best fits obtained from the optimized center-of-mass (CM) functions, as depicted in Figure 2. Carbon, germanium, and hydrogen are color coded in gray, green, and white, respectively.

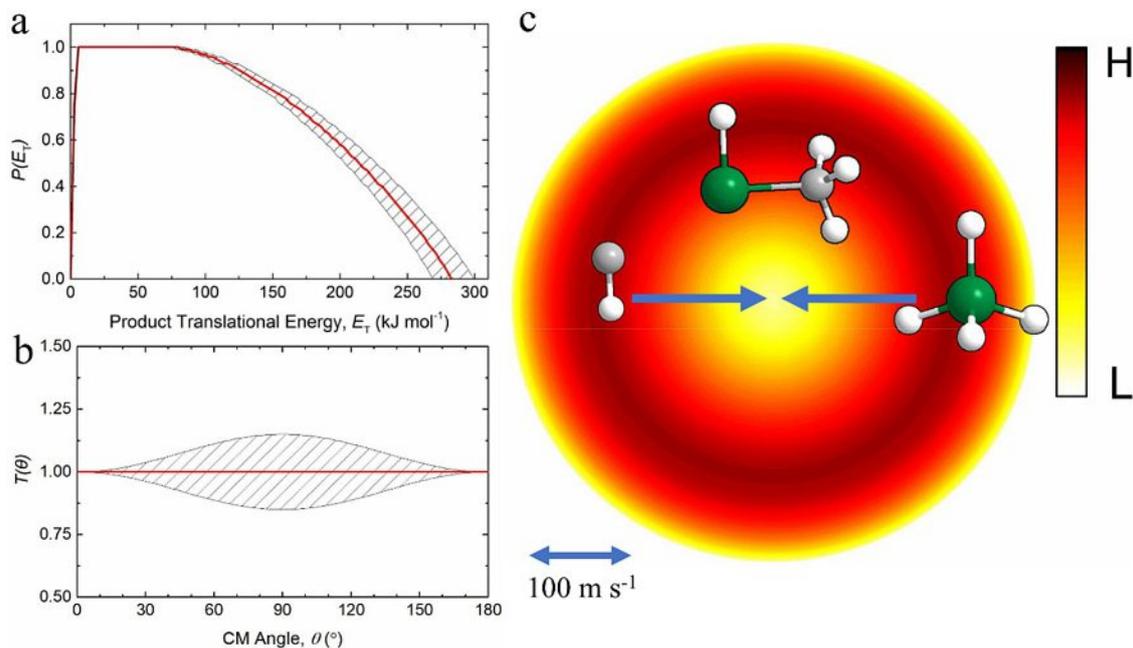


Figure 2. Center-of-Mass (CM) distributions and the associated flux contour map. CM translational energy flux distribution (a), CM angular flux distribution (b), and the top view of the flux contour map (c) leading to the formation of methylgermylene plus atomic hydrogen in the reaction of methylidyne with germane. Shaded areas indicate the error limits of the best fits accounting for the uncertainties of the laboratory angular distribution and TOF spectra; the red solid lines define the best-fit functions. The flux contour map represents the flux intensity of the reactive scattering products as a function of the CM scattering angle (θ) and product velocity (u). The color bar indicates the flux gradient from high (H) intensity to low (L) intensity. Carbon, germanium, and hydrogen are color coded in gray, green, and white, respectively.

laboratory angular distribution too broad. The best fit center-of-mass translational energy ($P(E_T)$) and angular distributions ($T(\theta)$) for the atomic hydrogen loss channel are depicted in Figure 2. A close inspection of the center-of-mass translational energy flux distribution, $P(E_T)$, assists in the identification of the GeCH_4 isomer formed. For molecules born without rovibrational excitation, the maximum translational energy, E_{max} , represents the sum of the reaction exoergicity plus the collision energy. Consequently, a subtraction of the collision energy ($20.6 \pm 0.3 \text{ kJ mol}^{-1}$) from the maximum translational energy ($284 \pm 15 \text{ kJ mol}^{-1}$) reveals that the formation of GeCH_4 along with atomic hydrogen is exoergic by $263 \pm 15 \text{ kJ mol}^{-1}$. A comparison of this data with the energetics obtained from electronic structure computations for distinct GeCH_4 isomers **p1** to **p3**, i.e. methylgermylene (HGeCH_3 ; **p1**; X^1A' ; $\Delta_r G = -255 \pm 4 \text{ kJ mol}^{-1}$), germene (H_2GeCH_2 ; **p2**; X^1A_1 ; $\Delta_r G = -210 \pm 4 \text{ kJ mol}^{-1}$), and germylmethylene (HCGeH_3 ; **p3**; X^3A'' ; $\Delta_r G = +10 \pm 4 \text{ kJ mol}^{-1}$) (Figure 3), suggests at least the formation of methylgermylene (HGeCH_3 ; **p1**) in its $^1A'$ electronic ground state. Contributions from the thermodynamically less stable germene (H_2GeCH_2 ; **p2**) and methylgermylene (HGeCH_3 ; **p3**) isomers cannot be excluded at the present stage since they might be masked in the low energy section of the center-of-mass translational energy distribution. Further, the distribution maximum of the $P(E_T)$ is relatively broad ($2\text{--}80 \text{ kJ mol}^{-1}$). This flat plateau suggests more than one exit transition state of which at least one is tight and a second one is loose.^[20] A single, loose exit transition state would be reflected in a $P(E_T)$ peaking very close to zero translational

energy, which is clearly not observed. Finally, the center-of-mass angular distributions ($T(\theta)$) depicts intensity over the

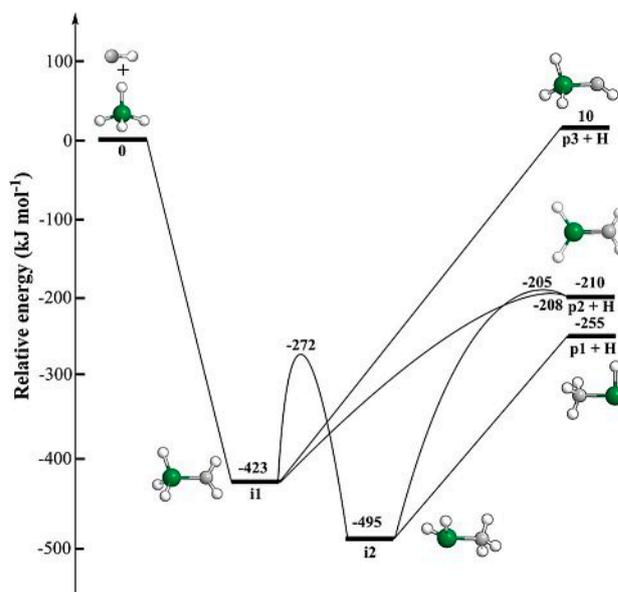


Figure 3. Potential energy surface for the reaction of the methylidyne radical with germane involving atomic hydrogen loss pathways. Optimized Cartesian coordinates of the atoms and vibrational frequencies are compiled in Table S2; a complete potential energy surface including the molecular hydrogen loss pathways is presented in Figure S1. Carbon, germanium, and hydrogen are color coded in gray, green, and white, respectively.

complete angular range from 0° to 180° (Figure 2) suggesting indirect scattering dynamics through the formation of GeCH₃ complex(es) having lifetimes longer than the(ir) rotational periods.^[21] The weak polarization, i.e. the flat T(θ) distribution, is the result of the inability of the light hydrogen atom to carry away significant angular momentum.^[19] In conclusion, our study reveals that at least the thermodynamically most stable methylgermylene isomer (HGeCH₃; **p1**) is formed via the reaction of the simplest organic radical (methylidyne) with the prototype of a closed shell germanium hydride (germane) under single collision conditions.

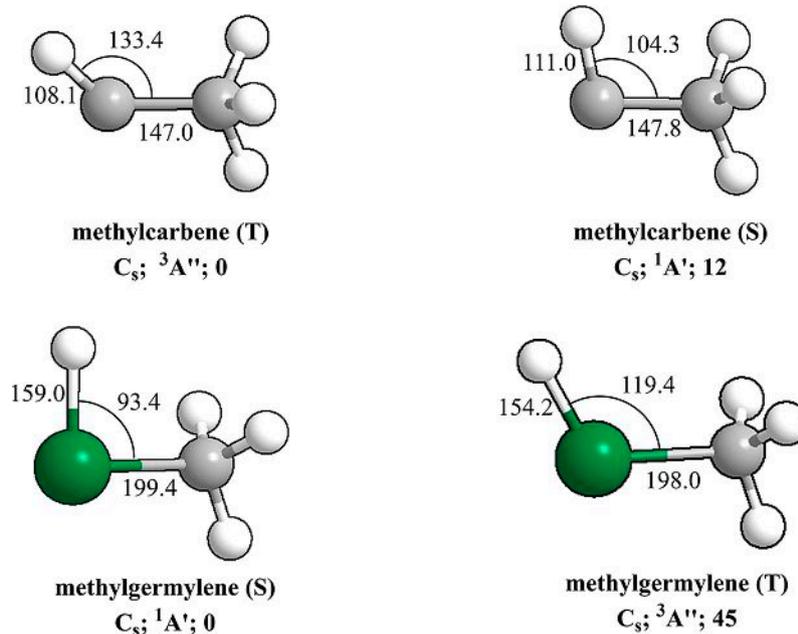
We are now merging the aforementioned experimental data with the computed potential energy surface (PES) to propose the underlying reaction mechanism(s) (Figure 3; Figure S1 in the Supporting Information). Supported by the calculated minimal potential energy profile for the entrance channel (Figure S4), the reaction of the methylidyne radical with germane is initiated on the doublet PES via a barrierless insertion of the methylidyne radical into one of the chemically equivalent germanium-hydrogen bonds leading to the germymethyl (CH₂GeH₃; X²A') collision complex **i1**. Interestingly, the potential energy does not change smoothly along the profile shown in Figure S4 because the reaction coordinate is more complex than the R(Ge–C) distance. Initially, at R > 3.8 Å, methylidyne simply approaches germane. Next, the germane molecule rotates to point one of its hydrogen atoms toward the carbon atom and this hydrogen atom transfers from germanium to carbon. The hydrogen shift completes between R = 3.2 and 3.1 Å resulting in a sharp potential energy decrease. Finally, the newly formed CH₂ group approaches the GeH₃ species thus finalizing the formation of the Ge–C bond. Intermediate **i1** can isomerize via a hydrogen shift from the germanium to the carbon atom yielding the methylgermyl (GeH₂CH₃; X²A') intermediate **i2** through a barrier of 151 kJ mol⁻¹. The methylgermyl radical represents the global minimum of the GeCH₃ PES. The energy difference between **i1** and **i2** of 72 kJ mol⁻¹ along with the barrier to isomerization of 151 kJ mol⁻¹ correlate nicely with earlier computational studies by Osamura et al. (60–69 kJ mol⁻¹)^[17] and Kudo and Nagase (151–160 kJ mol⁻¹).^[22] The methylgermyl radical (GeH₂CH₃; X²A'; **i2**) was found to undergo unimolecular decomposition via atomic hydrogen loss from the GeH₂ moiety via a loose exit transition state leading to the experimentally observed singlet methylgermylene (HGeCH₃; X¹A'; **p1**) product. The computations also identified two pathways leading to the thermodynamically less favorable germene isomer (H₂GeCH₂; **p2**) involving a unimolecular decomposition of **i1** and **i2** with exit transition states of the hydrogen atom loss located 2 and 5 kJ mol⁻¹, respectively, above the energy of the separated product. The energy difference between **p1** and **p2** of 45 kJ mol⁻¹ agrees well with Schaefer et al.'s results of 48 kJ mol⁻¹.^[23] Further, chemically activated germymethyl radicals (CH₂GeH₃; X²A'; **i1**) can decompose without an exit barrier to the least stable isomer: triplet germymethylene (HCGeH₃; **p3**).

To shed further light on the nature of the product isomers formed (**p1–p3**; Scheme 1; Figure 3) and on the elusive molecular hydrogen loss pathway (**p4–p7**; Figure S1), statistical rate

constants and branching ratios were computed via the Rice-Ramsperger-Kassel-Marcus (RRKM) theory (cf. the Supporting Information). These data suggest that within the limit of a complete intramolecular energy randomization under single collision conditions, the atomic hydrogen loss represents the nearly exclusive channel (99.981%) with only a minor contribution from molecular hydrogen elimination (0.019%). This is in full agreement with our experimental results and the failed detection of the molecular hydrogen loss. With respect to the atomic hydrogen channel, RRKM theory predicts a formation of methylgermylene (HGeCH₃; **p1**) and germene (H₂GeCH₂; **p2**) with nearly equal branching ratios of 48% and 52%; 36% and 16% of germene are formed via unimolecular decomposition of **i1** and **i2**, respectively. The thermodynamically least stable isomer germymethylene (HCGeH₃; **p3**) was predicted not to be formed.

To summarize, experiments and theory converge on the formation of the thermodynamically most stable methylgermylene isomer (HGeCH₃; **p1**; X¹A') via the elementary reaction of methylidyne with germane. Under single collision conditions, the reaction is initiated by the barrierless insertion of the methylidyne radical into the germanium-hydrogen bond forming the germymethyl (CH₂GeH₃; X²A') collision complex **i1**, which then isomerizes via hydrogen migration to the methylgermyl (GeH₂CH₃; X²A') intermediate **i2**. The latter ejects atomic hydrogen via loose exit transition state yielding methylgermylene (HGeCH₃; **p1**) in overall strongly exoergic reaction. RRKM calculations predict further that if the system undergoes a complete energy redistribution, germene (H₂GeCH₂; **p2**) may be also formed with a nearly equal fraction compared to methylgermylene (HGeCH₃; **p1**). Note that methylgermylene and germene can be interconverted through a barrier of 187 kJ mol⁻¹ with respect to methylgermylene (Figure S2). Hence, the transition state is located below the energy of the separated reactants. Therefore, in multicollision environments, methylgermylene formed with sufficient internal energy might not only overcome the barrier to isomerization to germene, but germene may also transfer part of the internal energy to a third body collider (bath molecule) thus stabilizing germene and making it available for spectroscopic detection.

The preference of the singlet multiplicity for methylgermylene (HGeCH₃; **p1**; X¹A'), but energetically favored triplet methylcarbene (CH₃CH; **2**; X³A'') can be rationalized exploiting valence bond theory (Scheme 2). Here, carbon has valence 2s and 2p orbitals, which are close in energy. Therefore, promotion of an electron from 2s to 2p and hybridization of 2s and 2p orbitals is rather favorable. Therefore, in carbenes, electrons of the carbon atom are sp²-hybridized; when one considers electrons available for bonding, there are 4 valence unpaired electrons, three of them on sp² hybrid orbitals and the last one on the p_z orbital of the carbon atom. Thus, for methylcarbene, two sp² electrons form bonds with hydrogen and the methyl group and the remaining two are still unpaired and according to Hund's rule should have parallel spins, hence the triplet ground state X³A''. This is corroborated quantitatively by the natural bond population analysis (NBO) showing that in triplet CHCH₃ the carbon atom of the methylidyne contributes to the



Scheme 2. Molecular structures, point groups, relative energies (kJ mol⁻¹), bond distances (pm), and selected bond angles (degrees) for triplet (T) and singlet (S) methylcarbene (CH₃CH) and methylgermylene (HGeCH₃). Carbon, germanium, and hydrogen are color coded in gray, green, and white, respectively.

C–C and C–H bonds its sp² hybrid orbitals (30% s and 70% p), whereas two unpaired electrons are localized one on the sp² hybrid (34% s and 66% p) and the other on the pure p orbital of the C atom. The sp² hybridization is also consistent with the HCC angle (133°, Scheme 2) in triplet CHCH₃. On the other hand, germanium is much less susceptible to promotion and hybridization due to the much larger energy gap between the 4s and 4p orbitals. Without promotion and hybridization, germanium has only two 4p electrons available for bonding, whereas two 4s electrons remain paired and hence are maintained as a lone pair. The p electrons form bonds with hydrogen and the methyl group with the bond angle close to 90°, i.e. 93.4° in singlet methylgermylene since the 4p orbitals are mutually perpendicular to each other. Hence, all electrons are paired leading to the singlet ground state X¹A'. Again, the NBO analysis supports this picture showing that in singlet GeHCH₃ the Ge atom contributes predominantly its p orbitals into the Ge–C and Ge–H bonds (respectively, 86% and 89%), while the lone pair on Ge mostly includes the contribution from its s orbital (78%) and only little mixing between Ge's s and p orbitals takes place. Energetically spoken, the orbital picture described above results in singlet-triplet gaps of 12 kJ mol⁻¹ for methylcarbene in favor of triplet and of 45 kJ mol⁻¹ for methylgermylene in favor of singlet.

In conclusion, our combined experimental and computational investigation of the elementary gas phase reaction of ground state methylidyne radicals with germane expose a barrierless and overall exoergic route to eventually synthesize the singlet methylgermylene (HGeCH₃; X¹A'; **p1**) under single collision conditions. The chemical dynamics are initiated by insertion of methylidyne into a germanium-hydrogen bond followed by isomerization of the germylmethyl collision com-

plex (CH₂GeH₃; X²A'; **i1**) via hydrogen shift to the methylgermyl intermediate (GeH₂CH₃; X²A'; **i2**) and subsequent ejection of a hydrogen atom to form methylgermylene (HGeCH₃; X¹A'; **p1**). These dynamics are distinctive from the isoivalent methylidyne-methane reaction (Figure S3).^[18] The initial barrierless insertion of methylidyne into a carbon-hydrogen bond of methane leads to an ethyl collision complex which then emits atomic hydrogen to yield the ethylene molecule (C₂H₄; **1**; X¹A_{1g}) via a tight exit transition state rather than the thermodynamically less stable triplet methylcarbene (CH₃CH; **2**; X³A''). The energy difference of 291 kJ mol⁻¹ for ethylene versus triplet methylcarbene and 45 kJ mol⁻¹ for singlet methylgermylene (HGeCH₃; **p1**; X¹A') versus germene (H₂GeCH₂; **p2**; X¹A₁) along with the dissimilar dynamics can be understood in terms of the double bond rule stating that elements of the third period should not form multiple bonds with themselves or with other elements. For singlet methylgermylene (HGeCH₃; **p1**; X¹A'), the charge distributions calculated exploiting natural bond population analysis conclude that the germanium atom is positively (+0.76 e) and carbon negatively (–1.09 e) charged thus revealing the ylide character of singlet methylgermylene (Supplementary Information; Table S3). All together, the isovalency of germanium and carbon supplies a deceptive prediction of reactivity in this system. This effects how we rationalize chemical bonding, molecular structure, and the underlying reaction mechanisms of isoivalent systems. The results of the methylidyne-germane system lead to a better understanding and planning of a directed synthesis of small organo germanium species compared to recent preparations via, e.g., thermal decomposition of bicyclic molecules and photolysis or air sensitive precursors.^[5a] Considering that the hydrogen atom(s) in germane can be replaced by side groups, the elementary reaction

of methylidyne with germane reflects the prototype reaction leading to alkylgermylenes which may be difficult to make by other means. Thus, this system can serve as a test bed toward an intimate understanding of the formation of organo germanium species on the molecular level.

Acknowledgements

The experimental work was supported by the U.S. National Science Foundation (NSF) for support under Award CHE-1853541 (Z.Y., C.H., S.D., R.I.K.). V.K.S. thanks the Ministry of Higher Education and Science of the Russian Federation for his Presidential Scholarship and Science of the Florida International University (FIU) in the Spring Semester 2020.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbon-germanium bond · gas-phase reactions · germanium · methylgermylene · reaction dynamics

- [1] C. Winkler, *J. Prakt. Chem.* **1887**, *36*, 177–209.
- [2] a) L. Gusef'nikov, N. Nametkin, *Chem. Rev.* **1979**, *79*, 529–577; b) J. Satge, *Pure Appl. Chem.* **1984**, *56*, 137–150.
- [3] Y.-H. Kuo, Y. K. Lee, Y. Ge, S. Ren, J. E. Roth, T. I. Kamins, D. A. Miller, J. S. Harris, *Nature* **2005**, *437*, 1334–1336.
- [4] a) T. Kudo, S. Nagase, *Chem. Phys. Lett.* **1981**, *84*, 375–379; b) H. F. Schaefer III, *Acc. Chem. Res.* **1982**, *15*, 283–290; c) J.-F. Gal, M. Decouzon, P.-C. Maria, A. I. González, O. Mó, M. Yáñez, S. E. Chaouch, J.-C. Guillemin, *J. Am. Chem. Soc.* **2001**, *123*, 6353–6359; d) J.-C. Guillemin, S. El Chaouch, J.-F. Gal, P.-C. Maria, O. Mo, M. Yáñez, *Main Group Met. Chem.* **2002**, *25*, 85–92.
- [5] a) J. Barrau, J. Escudie, J. Satge, *Chem. Rev.* **1990**, *90*, 283–319; b) K. N. Kudin, J. L. Margrave, V. N. Khabashesku, *J. Phys. Chem. A* **1998**, *102*, 744–753; c) A. Ariafard, Z. Lin, *Organometallics* **2005**, *24*, 6283–6286; d) W. Zierkiewicz, M. Michalczyk, S. Scheiner, *Molecules* **2018**, *23*, 1416; e) G. Trinquier, J. C. Barthelat, J. Satge, *J. Am. Chem. Soc.* **1982**, *104*, 5931–5936; f) C. Liang, L. C. Allen, *J. Am. Chem. Soc.* **1990**, *112*, 1039–1041; g) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479–3511.
- [6] a) P. Hou, F. Tian, D. Li, Z. Zhao, D. Duan, H. Zhang, X. Sha, B. Liu, T. Cui, *RSC Adv.* **2015**, *5*, 19432–19438; b) J. Espinosa-García, C. Rangel, J. Corchado, *Phys. Chem. Chem. Phys.* **2016**, *18*, 16941–16949.
- [7] a) M.-D. Su, S.-Y. Chu, *J. Am. Chem. Soc.* **1999**, *121*, 4229–4237; b) A. Bundhun, P. Ramasami, H. F. Schaefer III, *J. Phys. Chem. A* **2009**, *113*, 8080–8090.
- [8] a) M. Vinodkumar, C. Limbachiya, K. Korot, K. Joshipura, N. Mason, *Int. J. Mass Spectrom.* **2008**, *273*, 145–150; b) N. Liu, G. Bo, Y. Liu, X. Xu, Y. Du, S. X. Dou, *Small* **2019**, *15*, 1805147; c) L. T. Xu, J. V. Thompson, T. H. Dunning Jr, *J. Phys. Chem. A* **2019**, *123*, 2401–2419.
- [9] a) I. Langmuir, *J. Am. Chem. Soc.* **1919**, *41*, 1543–1559; b) I. Langmuir, *J. Am. Chem. Soc.* **1919**, *41*, 868–934.
- [10] A. Márquez, G. G. González, J. F. Sanz, *Chem. Phys.* **1989**, *138*, 99–104.
- [11] a) G. Trinquier, *J. Am. Chem. Soc.* **1990**, *112*, 2130–2137; b) D. Nori-Shargh, S. N. Mousavi, J. E. Boggs, *J. Phys. Chem. A* **2013**, *117*, 1621–1631.
- [12] P. Jutzi, *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 232–245.
- [13] a) M. M. Gallo, H. F. Schaefer III, *J. Phys. Chem.* **1992**, *96*, 1515–1517; b) J. Kalcher, A. F. Sax, *J. Mol. Struct.* **1992**, *253*, 287–302.
- [14] W. Carrier, W. Zheng, Y. Osamura, R. I. Kaiser, *Chem. Phys.* **2006**, *330*, 275–286.
- [15] S. Bogdanov, M. Egorov, V. Faustov, I. Krylov, O. Nefedov, R. Becerra, R. Walsh, *Russ. Chem. Bull.* **2005**, *54*, 483–511.
- [16] a) R. Becerra, C. R. Harrington, W. J. Leigh, L. A. Kefala, R. Walsh, *Organometallics* **2006**, *25*, 4439–4443; b) R. Becerra, R. Walsh, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2817–2835.
- [17] R. I. Kaiser, W. Carrier, Y. Osamura, R. M. Mahfouz, *Chem. Phys. Lett.* **2010**, *492*, 226–234.
- [18] a) P. Fleurat-Lessard, J.-C. Rayez, A. Bergeat, J.-C. Loison, *Chem. Phys.* **2002**, *279*, 87–99; b) J. M. Ribeiro, A. M. Mebel, *Mol. Phys.* **2015**, *113*, 1865–1872.
- [19] R. D. Levine, *Molecular reaction dynamics*, Cambridge University Press, Cambridge, UK, **2009**.
- [20] A. M. Mebel, R. I. Kaiser, *Int. Rev. Phys. Chem.* **2015**, *34*, 461–514.
- [21] W. Miller, S. Safron, D. Herschbach, *Discuss. Faraday Soc.* **1967**, *44*, 108–122.
- [22] S. Nagase, T. Kudo, *Organometallics* **1984**, *3*, 324–325.
- [23] R. S. Grev, H. F. Schaefer III, *Organometallics* **1992**, *11*, 3489–3492.

Manuscript received: May 8, 2020

Revised manuscript received: June 14, 2020

Accepted manuscript online: June 28, 2020

Version of record online: August 11, 2020