Combined Quantum Chemical and Mass Spectrometry Study of $[Ge,C,H]^+$ and Its Neutral Counterpart

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Dedicated to Professor Hans Bock on the occasion of his 70th birthday

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The cation $[Ge,C,H]^+$ has been generated by the electron ionisation of trichloromethylgermane. Collisional activation experiments were used to establish a Ge–C–H connectivity in this species, for which a significant fraction of the ion population was found to survive neutralisation-reionisation mass spectrometry (NRMS) experiments. Thus, the neutral counterpart $[Ge,C,H]^0$ is stable on a microsecond timescale. Becke's 3 parameter hybrid density functional (B3LYP) was used to map the ion and neutral potential-energy surfaces, in conjunction with double-zeta and triple-zeta basis sets. The computational results obtained using the triple-zeta basis sets suggest that, for the cation, the global minimum is the high spin $^3\Sigma$ $GeCH^+$, with the first Ge–C–H excited state, $^1\Sigma$ $GeCH^+$, approximately 39 kcal mol^{-1} less stable. The lowest energy ion structure with H–Ge–C connectivity is bent ($^3A''HGeC^+$, $\angle$H–Ge–C = 126.3) and 69 kcal mol^{-1} less stable than the global minimum. For the neutral, a doublet ($^2\pi$) with Ge–C–H connectivity is predicted to be the global minimum. The classical barrier for the neutral 1,2-hydrogen shift reaction on the doublet surface is negligible (0.1 kcal mol^{-1}), while the smallest barrier for the cation is 13.0 kcal mol^{-1}, corresponding to ($^3A''$) $HGeC^+ \rightarrow$ ($^3\Sigma$) $GeCH^+$. Natural bond order analysis has been used to establish the order of the metal–carbon bond for selected states of both the neutral and the ion. Neutral and cationic isomers with Ge–C triple bonds were found to be high-energy excited states, with the metal–carbon bonds in the cation and neutral ground states of order 2.0 and 2.5, respectively. The instability of Ge–C triple bonded species is attributed to the energy required for electronic promotion in the metal in order to achieve a hybrid configuration suitable for the formation of such a bond.

Introduction

In 1991, neutral [Si,C,H] was detected by means of neutralisation-reionisation mass spectrometry (NRMS).[1] Collisional activation (CA) experiments established the connectivity in the cation precursor as Si−C−H, for which a subsequent NR recovery signal was detected. Thus, the CA and NRMS results together vindicated the predictions of ab initio calculations, which suggested that the radical $SiCH^\bullet$ was 2.6 eV more stable than the $CSiH^\bullet$ isomer, and that $SiCH^+$ is more stable than $HSiC^+$ by at least 3.0 eV.[2] In the years since 1991, a plethora of molecules whose existence has only been proposed by spectroscopists or theoreticians have been detected using this technique.[3]

Whereas the number of challenges remaining in the area of silicon chemistry are now few,[4] the chemistry of germanium is still largely unexplored. This is perhaps due to a low terrestrial abundance[5] and broad similarities in the chemistry of main-group elements as one progresses from the third to fifth rows, which enable predictions based on the behaviour of lighter or heavier congeners. It is interesting to note that there has been recent interest in the electronic structure and gas-phase chemistry of homonuclear germanium clusters.[6] Several small germanium-hydrocarbon molecules have been previously generated in the gas phase, but still very little is known of their structures. Operti et al. were able to generate $GeCH_n^+$ (n = 1−5) and some digermanium-organo cations from ion-molecule reactions between germane and methylgermane in a high pressure source,[7] although studies towards structural characterisation were not undertaken. Willett and coworkers[6c] were able to generate $GeC_2H_3^+$, $GeC_3H_5^+$, and $Ge_nCH_2^+$ (n = 1,2) via the reactions of laser ablated Ge^+, Ge_2^+ with cyclopropane. While $Ge_2CH_2^+$ was the only reaction product observed for Ge_2^+, branching for Ge^+ yielded $GeCH_2^+$ as the major product, followed by $GeC_2H_3^+$ and $GeC_3H_5^+$. Density functional theory (BLYP/6-31G*) investigations of $[Ge_2,C,H_2]^+$ suggests that the disubstituted methane isomer Ge−CH_2−Ge is more stable than the isomer with Ge−Ge−CH_2 connectivity by approximately 15 kcal mol^{-1}.[6c] Although it was established that both structures were minima on the PES, and the disubstituted methane structure is probably the ground state, it must be noted that no structures with Ge−H bonds were investigated.[8]

Concerning other small germanium molecules and ions, $[Ge,O,H]^{0/+}$ have been studied using double- and triple-zeta basis sets in conjunction with the coupled cluster theory.[9] The most stable isomer for the ion was linear and possessed Ge−O−H connectivity, whereas a bent structure, with analogous connectivity, was found to be the ground state of the neutral. Results from a kinetic study of the neutral-neutral reaction between germylene (GeH_2) and germane

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(GeH_4) have appeared recently,[10] and the experimental evidence suggests the rate of the association reaction leading to Ge_2H_6 depends on collisional cooling by a third body. The structures of the triatomic halogermylenes HGeX (X = Cl, Br) have been proposed on the basis of high level ab initio calculations[11] and rovibrational bands observed in laser-induced fluorescence experiments.[12] In the last year, this technique has been employed to characterise HGeI.[13]

This paper is divided into two sections: in the first, experimental results for $[Ge,C,H]^{0/+}$ are presented. In the second section, the results of density functional calculations are discussed in relation to the ground states of $GeCH^{0/+}$ and the possible existence of $HGeC^{0/+}$ isomers. The 1,2 hydrogen shift barrier, and results from Ge−C bond order analyses of selected ion and neutral isomers are then examined. The nature of multiple bonds involving heavier main-group elements are the focus of current interest and speculation.[3e,14] According to criteria proposed by Goubeau in 1957,[15] double bonds stable towards polymerisation are achievable if the sum of the electronegativities of the bonding partners exceeds the approximate value of 5. Using the literature values for the Mulliken electronegativities[16] of Ge ($4sp^3$), 2.50, and C (2sp), 3.29,[17] the sum obviously exceeds this value, suggesting there is a good chance of forming a Ge−CH bond of order 2 or greater.

Results and Discussion

Mass Spectrometry

The CA-mass spectrum of $GeCH^+$ is presented in Figure 1. Loss of $CH^\bullet$ is the major fragmentation observed under single collision conditions (66% fragment ion current), suggesting a Ge−C−H connectivity in the ion. It is interesting to note that there is also a minor signal corresponding to GeH^+ at *m/z* 71 (5% fragment ion current), indicating that there may be small amounts of an isomer with H−Ge−C connectivity, or that post-collisional isomerisation precedes fragmentation. If the barrier for the associated 1,2-shift lies above the GeC^+ + H and GeH^+ + C dissociation asymptotes, then the CA spectrum unequivocally confirms the existence of $HGeC^+$ (see below). In contrast, there was an additional source of uncertainty regarding the assignment of the fragment at *m/z* 29 in the CA spectrum of the silicon congener,[1] due to the small but non-negligible abundance of the ^{29}Si isotope.

The NR-mass spectrum of $[Ge,C,H]^+$ yields a distinct recovery signal for the parent ion (Figure 2), thus demonstrating that [Ge,C,H] is a stable molecule on the microsecond timescale. The most intense fragment ion that results from the reduction and subsequent oxidation of $[Ge,C,H]^+$ is Ge^+, which suggests that the Ge−C bond length in the neutral is displaced from the bond length in the ion, resulting in vertical transitions to high vibrational levels. Although it appears that there is a peak of low intensity at *m/z* 71 corresponding to loss of C, the uncertainty due to the higher signal to noise ratio suggests that only a tentative assignment can be made in this instance. In summary, the precursor structure as well as the CA and the NR spectra of $[Ge,C,H]^+$ are in accord with a Ge−C−H connectivity.

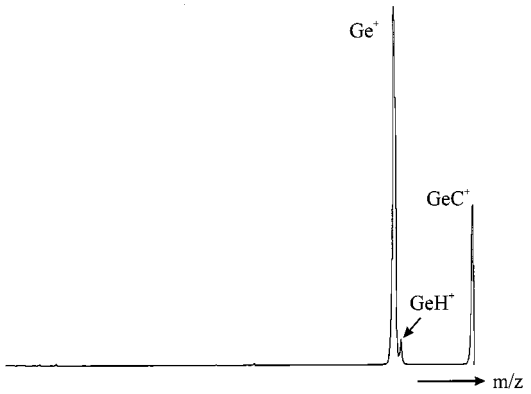

Figure 1. CA-mass spectrum of B(1)/E(1) mass-selected $^{70}GeCH^+$ generated by electron ionisation of methyltrichlorogermane

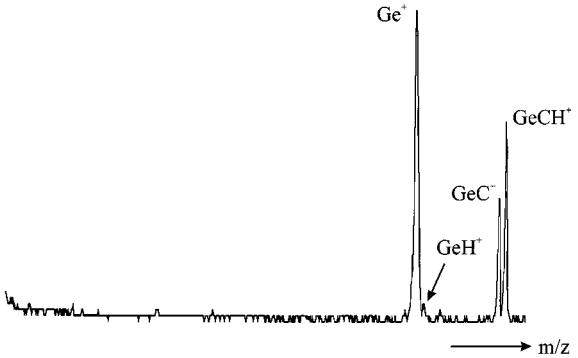

Figure 2. NR-mass spectrum of B(1)/E(1) mass-selected $^{70}GeCH^+$ generated by electron ionisation of methyltrichlorogermane

Theoretical Calculations

In order to map the potential-energy surfaces (PES) of neutral and cationic $[Ge,C,H]^{0/+}$, the relative energies were investigated for various spin isomers in linear and bent geometries for the connectivities Ge−C−H and H−Ge−C. Although the various cation and neutral minima were investigated using both BS-I and BS-II, only the results obtained using BS-II are presented here. The corresponding BS-I results can be provided on request.

(i) $[Ge,C,H]^+$ Potential Energy Surface: A schematic of the cation PES is presented in Figure 3. For the sake of clarity, we have omitted high-lying excited states. In Table 2, we present the bond energies of any associated diatomics and the zero-point corrected energies required to effect various ion dissociations. Only the lowest energy asymptotes corresponding to each particular dissociation are shown.

The global minimum on the $[Ge,C,H]^+$ PES corresponds to linear $^3\Sigma$ $GeCH^+$. This state lies approximately 110 kcal mol^{-1} below the lowest energy Ge^+ + CH dissociation asymptote, and almost 82 kcal mol^{-1} below the transition structure ^{3}TS for the associated 1,2 H-shift. The lowest energy cation isomer with H−Ge−C connectivity is $^3A''$

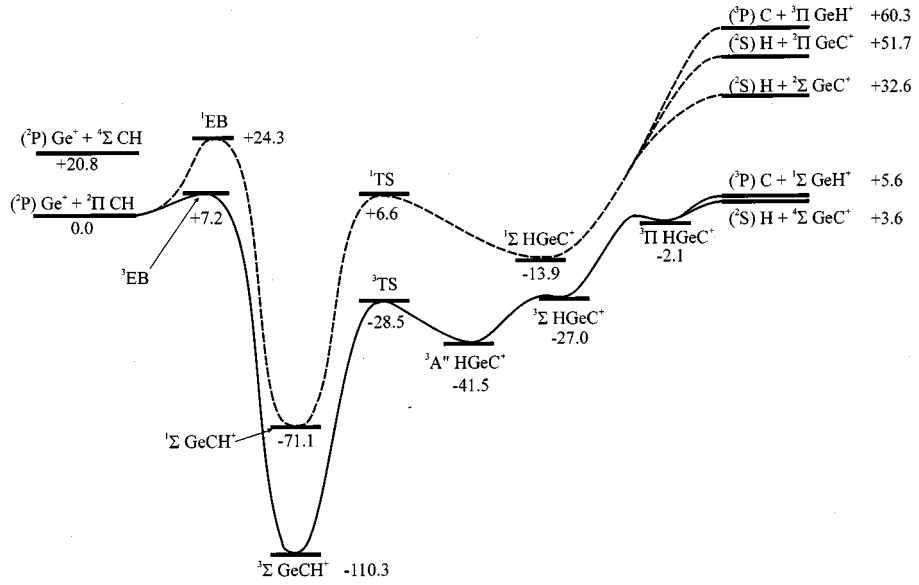

Figure 3. PES for $[Ge,C,H]^+$ from B3LYP/6-311++G(d,p) calculations; refer to Table 1 for details of particular structures, and Table 2 for details regarding asymptotes

Table 1. Total energies (E_{SCF}, Ha), bond lengths (r_e, in Å), bond angles (α, in degrees), and absolute relative energies (E_{rel}, in kcal mol^{-1}) of stationary points for electronic states of $[Ge,C,H]^+$ at B3LYP/6-311++G(d,p) level of theory

Structure	State	E_{SCF}	r_e(Ge−C)	r_e (C−H)	r_e (Ge−H)	α	E_{rel}
$GeCH^+$	$^3\Sigma$	−2115.2903912	1.894	1.090			0.0
	$^1\Sigma$	−2115.2284407	1.914	1.092			39.2
	$^3\Pi$	−2115.2042964	1.739	1.092			54.5
	$^3\Sigma$	−2115.1892111	1.725	1.091			64.0
	$^1\Sigma$	−2115.0613128	1.636	1.113			145.0
^{1}EB [a]	$^1\Sigma$	−2115.0777673	6.219	1.122			134.6
^{1}EB [a]	$^3\Sigma$	−2115.1048022	6.084	1.122			117.5
^{3}TS	$^3A''$	−2115.1611256	1.925		1.579	90.8	81.8
^{1}TS	$^1A'$	−2115.1058258	1.801		1.582	88.0	116.8
$HGeC^+$	$^3A''$	−2115.1631782	1.899		1.548	126.3	68.8
	$^3\Sigma$	−2115.1588284	1.906		1.549		83.3
	$^3\Pi$	−2115.1193585	1.714		1.510		108.2
	$^1\Sigma$	−2115.1380349	1.918		1.548		96.4
	$^1\Sigma$	−2115.0098613	1.629		1.511		177.5

$D^0(Ge^+-CH)$[b] = 107.7 kcal mol^{-1}
$D^0(GeC^+-H)$[c] = 104.9 kcal mol^{-1}

[a] These structures correspond to the entrance channel barriers depicted in Figure 3. − [b] Evaluated using zero point energies derived from BS-I vibrational frequencies for $^3\Sigma$ $GeCH^+$ and $^2\Pi$ CH, calculated at the BS-I optimised geometries: $^3\Sigma$ $GeCH^+$, r_e(Ge−C) = 1.919 Å; r_e(C−H) = 1.094 Å, ZPE = 9.9 kcal mol^{-1}. $^2\Pi$ CH, r_e(C−H) = 1.151 Å, ZPE = 3.9 kcal mol^{-1}. − [c] Evaluated using zero point energies derived from BS-I vibrational frequencies for $^3\Sigma$ $GeCH^+$ (see footnote 2) and $^4\Sigma$ GeC^+, calculated at the BS-I-optimised geometries: $^4\Sigma$ GeC^+, r_e(Ge−C) = 1.973 Å, ZPE = 0.9 kcal mol^{-1}.

$HGeC^+$. According to B3LYP/BS-II, the classical barrier for the 1,2 H-shift reaction on the triplet surface is 13.0 kcal mol^{-1}, which may suffice for the detection of $HGeC^+$ from suitable precursors.

Although several linear isomers of $HGeC^+$ were found as minima on the triplet surface at the B3LYP/BS-I level, all are less stable than the bent structure. Moreover, transition state searching failed to locate a barrier linking the linear and bent isomers, suggesting the linear species reside in shallow minima and should convert into bent structures with minimal activation.

From Figure 3, it is apparent that there is only one curve crossing between the singlet and triplet surfaces, and this is near the Ge^+ + CH dissociation limit. A distinctive feature of the singlet PES is the large energy required to couple the ground states of Ge^+ ($^2\Pi$) and CH ($^2\Pi$) to form $^1\Sigma$ $GeCH^+$. Although pure DFT methods are largely considered unsuitable for the calculation of van der Waals and charge-exchange complexes,[18] hybrid DFT often performs better in this regard, and because this barrier is much larger than typical rotational barriers (of the order of a few kcal mol^{-1}), it must be associated with an electron promotion

Table 2. States, total energies (E_{SCF}, Ha), bond lengths (r_e, in Å), calculated ionization energies (IE, in eV), and bond dissociation energies (D^0, in kcal mol^{-1}) of various atomic and diatomic fragments used in the calculations of bond energies and dissociation asymptotes at B3LYP/6-311++G(d,p) level of theory. Tabulated dissociation energies include zero point energy corrections calculated using the frequencies obtained with BS-I.[a]

	State	E_{SCF} (ha)	r_e	IE	D^0(X−Y)
H	^{2}S	− 0.50225698			
C	^{3}P	−37.85726708			
Ge	^{3}P	−2076.90984966		7.83	
Ge^+	^{2}P	−2076.62207107			
CH	$^2\Pi$	−38.49410314	1.126		81.3
CH	$^4\Sigma$	−38.46117836	1.096		59.9
GeH	$^2\Pi$	−2077.52295375	1.598	7.30	67.5
GeH	$^4\Sigma$	−2077.44569581	1.578		18.8
GeH^+	$^1\Sigma$	−2077.25460678	1.592		79.6
GeH^+	$^3\Pi$	−2077.16815521	1.695		25.9
GeC	$^1\Sigma$	−2114.86335882	1.715		59.7
GeC	$^3\Pi$	−2114.92334025	1.806	8.58	99.9[b]
GeC	$^3\Sigma$	−2114.89668382	1.900		82.7
GeC^+	$^2\Pi$	−2114.52648018	1.812		30.8
GeC^+	$^2\Sigma$	−2114.55672709	1.962		49.8
GeC^+	$^4\Sigma$	−2114.60816155	1.928		80.6

[a] Geometries and harmonic frequencies calculated using BS-I: $^2\Pi$ CH, r_e = 1.151 Å, ω_e = 2671 cm^{-1}. $^4\Sigma$ CH, r_e = 1.103 Å, ω_e = 3046 cm^{-1}. $^2\Pi$ GeH, r_e = 1.630 Å, ω_e = 1812 cm^{-1}. $^4\Sigma$ GeH, r_e = 1.588 Å, ω_e = 1709 cm^{-1}. $^1\Sigma$ GeH^+, r_e = 1.607 Å, ω_e = 1944 cm^{-1}. $^3\Pi$ GeH^+, r_e = 1.673 Å, ω_e = 1267 cm^{-1}. $^1\Sigma$ GeC, r_e = 1.744 Å, ω_e = 864 cm^{-1}. $^3\Pi$ GeC, r_e = 1.844 Å, ω_e = 742 cm^{-1}. $^3\Sigma$ GeC, r_e = 1.981 Å, ω_e = 479 cm^{-1}. $^2\Pi$ GeC^+, r_e = 1.856 Å, ω_e = 641 cm^{-1}. $^2\Sigma$ GeC^+, r_e = 1.992 Å, ω_e = 545 cm^{-1}. $^4\Sigma$ GeC^+, r_e = 1.973 Å, ω_e = 617 cm^{-1}. − [b] Experimental value: D^0(GeC) = 109.8 kcal mol^{-1}, from ref.[19].

Table 3. Total energies (E_{SCF}, Ha), bond lengths (r_e, in Å), bond angles (α, in degrees), and absolute relative energies (E_{rel}, in kcal mol^{-1}) of stationary points for electronic states of [Ge,C,H] at B3LYP/6−311++G(d,p) level of theory

Structure	State	E_{SCF}	r_e(Ge−C)	r_e(C−H)	r_e(Ge−H)	α	E_{rel}
GeCH	$^2\Pi$	−2115.5843426	1.774	1.082			0.0
	$^2\Sigma$	−2115.5286932	1.667	1.078			35.2[a]
	$^4\Sigma$	−2115.4093521	1.813	1.078			110.7
	$^2\Pi$	−2115.2723698	1.710	1.090			197.4
	^{4}A′′	−2115.5165009	2.001	1.099		131.2	42.9
^{4}TSa	$^4\Pi$	−2115.5101950	2.011	1.087			46.9
^{4}TSb	^{4}A′′	−2115.4414048	2.032		1.662	50.0	90.5
^{4}TSc	$^4\Pi$	−2115.4167485	2.055		1.548		106.0
HGeC	^{4}A′′	−2115.4770732	1.960		1.597	97.1	67.9
	^{4}A′	−2115.4207679	2.051		1.547	128.8	103.5
	^{2}A′[b]	−2115.5026479	1.789		1.554	117.2	51.7
^{2}TSa	^{2}A′	−2115.5025132	1.797		1.567	101.1	51.8
^{2}TSb	$^2\Pi$	−2115.4812352	1.791		1.539		65.2
	$^2\Sigma$	−2115.4488889	1.659		1.492		85.7
	$^4\Sigma$	−2115.3429078	1.801		1.492		152.8

D^0(Ge−CH) [c] = 110.8 kcal mol^{-1}
D^0(GeC−H) [c] = 94.3 kcal mol^{-1}
IE_{ad} (GeCH) = 8.00 eV

[a] A second $^2\Sigma$ GeCH minimum was located using Gaussian 94, lying 44.4 kcal mol^{-1} above the global minimum with a slightly shorter r_e(Ge−C) = 1.664 Å, than the lowest energy $^2\Sigma$ state. Analysis of the molecular orbitals and populations revealed this minimum to be an artefact (identical to the lowest $^2\Sigma$ GeCH). − [b] A second ^{2}A′ HGeC minimum was located using Gaussian 94, lying 61.1 kcal mol^{-1} above the global minimum with bond lengths r_e(Ge−C) = 1.780 Å, r_e(Ge−H) = 1.544 Å and ∠H−Ge−C = 121.3°. Analysis of the molecular orbitals and populations revealed this minimum to be an artefact (identical to the lowest ^{2}A′ HGeC). − [c] Evaluated using zero point energies derived from BS-I vibrational frequencies for $^2\Pi$ GeCH, $^2\Pi$ CH or $^3\Pi$ GeC, calculated at the BS-I-optimised geometries: $^2\Pi$ GeCH, r_e(Ge−C) = 1.798 Å; r_e(C−H) = 1.086 Å, ZPE = 7.3 kcal mol^{-1}. $^2\Pi$ CH, r_e(C−H) = 1.151 Å, ZPE = 3.9 kcal mol^{-1}. $^3\Pi$ GeC, r_e(Ge−C) = 1.844, ZPE = 1.1 kcal mol^{-1}.

in the diatomic fragment. Even though the coupling energy required is close to the calculated B3LYP first excitation energy of CH ($^4\Sigma \leftarrow {}^2\Pi$, 20.8 kcal mol^{-1}: B3LYP/BS-II), this state does not correlate with the singlet surface. Rather, it must correspond to either an $a^2\Pi$ or $^2\Sigma$ excitation.

The lowest energy minimum on the singlet surface is $^1\Sigma$ $GeCH^+$, which is ca. 71 kcal mol^{-1} below the ground state Ge^+ + CH dissociation asymptote, and almost 78 kcal mol^{-1} below ^{1}TS. No bent minima could be located, so ^{1}TS effectively connects two linear isomers. This was verified by following the reaction coordinate downhill from the saddle-point. The classical barrier to the 1,2 H-shift on the singlet surface is 20.5 kcal mol^{-1}, which is larger than the triplet barrier. In summary, we conclude that $^3\Sigma$ $GeCH^+$ is by far

the most stable $[Ge,C,H]^+$ species, whereas all other conceivable states and/or structures are much more energy demanding. These results support our assignment of a Ge−C−H ion structure derived from the fragmentation patterns in the CA and NR experiments (see above).

(ii) $[Ge,C,H]^0$ Potential Energy Surface: The neutral PES is presented in Figure 4. For further information regarding the various minima depicted or higher excited states not shown in this figure, consult Table 3. In contrast to the cation PES, the global minimum of the neutral corresponds to a *low* spin Ge−C−H isomer, $^2\Pi$ GeCH. This state lies more than 114 kcal mol^{-1} below the lowest energy $^3\Pi$ Ge + $^2\Pi$ CH dissociation asymptote, almost 43 kcal mol^{-1} below the most stable bent quadruplet state $^4A''$ GeCH, and more than 61 kcal mol^{-1} below the lowest energy structure with H−Ge−C connectivity, $^2A'$ HGeC. It is important to note that all linear structures having H−Ge−C connectivity were characterised as transition structures using BS-I. In order to unambiguously establish the instability of linear HGeC isomers towards rearrangement, vibrational analysis of $^2\Pi$ HGeC using BS-II was undertaken, which revealed this species is indeed a transition structure. It should also be noted that the PES in the vicinity of the $^2A'$ HGeC minimum is very flat, and ^{2}TSa, which links $^2\Pi$ GeCH and $^2A'$ HGeC (1,2 H-shift barrier), lies only 0.1 kcal mol^{-1} above the bent minimum. For the quadruplet PES, the classical barrier for the 1,2 H-shift reaction is 22.6 kcal mol^{-1}, and is of a similar magnitude to the singlet barrier on the cation PES. No barrier was encountered for the coupling of Ge and CH on the doublet PES.

(iii) Natural Bond Order (NBO) Analyses: A qualitative MO diagram for the linear Ge−C−H ground states of both $[Ge,C,H]^{0/+}$ is presented in Figure 5. For the $^3\Sigma$ ground state of the cation, the uncoupled electrons reside in π-bonding MOs with 18% Ge and 82% C character. Note that the next MO lower in energy than the π-bonding MOs is a σ-nonbonding MO, which is occupied by both 4s electrons of Ge. This implies that the CH unit, or more precisely C, is the source of the two π-electrons, as the remaining Ge electron is involved in formation of the Ge−C σ-bond. Thus, we deduce that the electronic configuration of Ge^+ in $^3\Sigma$ $GeCH^+$ is $4s^24p^1$, which also corresponds to the electron configuration of the $^2\Pi$ Ge^+ ground state. The NBO evaluation of the natural electron configuration of the constituent atoms yields $Ge(4s^{1.89}4p^{0.83})$ $C(2s^{1.54}2p^{2.90})$ $H(1s^{0.80})$, in agreement with empirical deductions. Moreover, the C atom is sp^3 hybridised, and the Ge^+−C σ-bond contribution from the metal is $4s^{0.08}4p^{0.92}$. The order of the Ge^+−C bond was evaluated by (i) summing the orbital populations of the σ- and π-*bonding* MOs, and subtracting from this, (ii) the sum of the populations of the Ge^+−C σ- and π-*antibonding* MOs. This result is then divided by two to yield a value of 1.99 for the Ge^+−C bond in $^3\Sigma$ $GeCH^+$. It should be noted that the derived bond order of 1.99, does

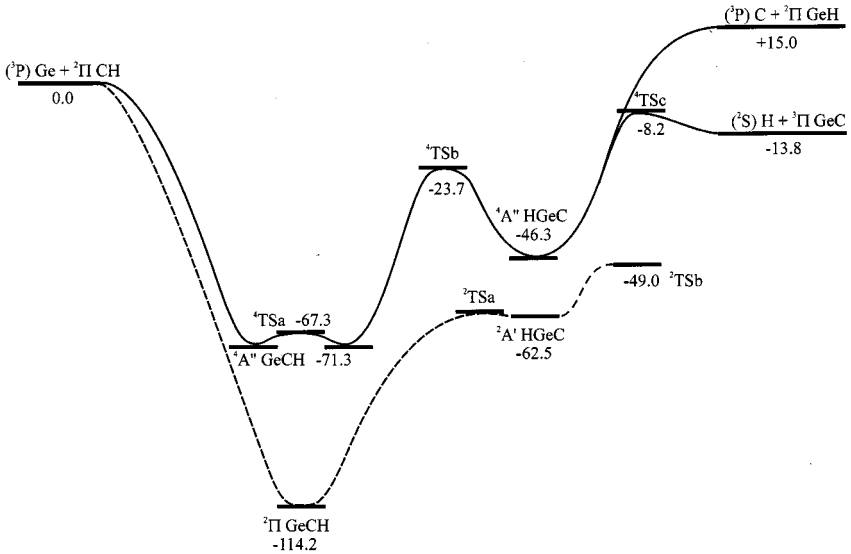

Figure 4. PES for $[Ge,C,H]^0$ from B3LYP/6-311++G(d,p) calculations; refer to Table 3 for details of particular structures, and Table 2 for details regarding asymptotes

The (quadruplet) 1,2 H-shift barrier height suggests that $HGeC^+$ isomers may be detectable in matrix isolation or other spectroscopic experiments. Unfortunately, the barrier for the bent to linear conversion of the neutral is negligible, and given the finite possibility for spin inversion, generation of long-lived HGeC appears unlikely.[3d] Finally, the isomerisation barriers on the singlet and triplet surfaces of the cation, are either lower than, or close in energy to, the lowest energy exit channels. Thus the CA results regarding the formation of H−Ge−C isomers are inconclusive, as the keV ion-neutral collisions excite the ions to dissociative vibrational levels well above the barriers associated with interconversion between GeCH and HGeC.

not imply the presence of formally paired π-electrons on both the germanium and carbon centres. The addition of an electron to one of the π-bonding MOs of $^3\Sigma$ $GeCH^+$ leads to some minor electronic and geometrical adjustments in the transition to the neutral ground state. The minor increase in Ge−C bond strength for the ground state neutral (Tables 1 and 3) is expected; however, the large decrease

in the C−H bond strength could be considered unusual. Comparison of the MO energies reveals the C−H σ-bonding MO in $^2\Pi$ GeCH is inverted with respect to the Ge−C σ-bonding MO in $^3\Sigma$ $GeCH^+$, and the population of the C−H σ-antibonding MO is much higher in $^2\Pi$ GeCH than $^3\Sigma$ $GeCH^+$. The second order energy of interaction between the σ-nonbonding MO, localised on the metal, and the C−H σ-antibonding MO in the neutral is 13.5 kcal mol^{-1} (alpha + beta sum), while the Ge 3s/C−H σ-antibonding MO interaction energy amounts to 7.7 kcal mol^{-1}. It is evident that core polarisation effects, in particular electron donation to the C−H σ-antibonding MO, has a pronounced effect on the C−H bond *strength* in the neutral, but the expected effect on the bond length is not dramatic. In fact, a slight bond contraction is observed, which is ascribed to enhanced Coulombic attraction between the C and H atoms of the neutral. The atomic charges in the neutral and cation ground states verify this point i.e. $C^{-0.85e}H^{+0.18e}$ for $^2\Pi$ GeCH, and $C^{-0.45e}H^{+0.20e}$ for $^3\Sigma$ $GeCH^+$.

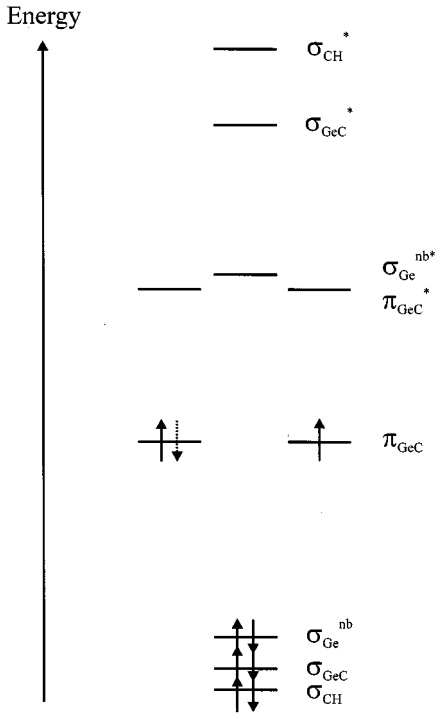

Figure 5. Qualitative MO diagram for the linear ground states of $[Ge,C,H]^{0/+}$; the dashed electron signifies the neutralisation of the cation to form the ground state configuration of the neutral

The Ge−C bond contraction upon formation of the ground state neutral (bond order 1.99) corresponds to 0.12 Å, which is significant considering the new Ge−C bond order is only 2.49, compared with 1.99 for the ground state cation. It is not surprising then that a significant signal for Ge^+ is detected in the NRMS spectrum of $GeCH^+$. For comparison, the typical bond length contraction for reduction of an alkane to an alkene is approximately 0.20 Å, and from an alkene to alkyne is 0.14 Å.[20]

The other noteworthy features of the NBO analysis of $^2\Pi$ GeCH are the extent to which the carbon atom is reduced, and the energy difference between the closed and half filled π-bonding MOs. To discuss the reduction of the carbon atom, first consider the natural electron configurations of the constituent atoms in $^2\Pi$ GeCH: $Ge(4s^{1.79}4p^{1.51})$ $C(2s^{1.44}2p^{3.41})$ $H(1s^{0.83})$. Comparison with the cation values presented above reveals the carbon atom to be sufficiently electronegative in the neutral to have gained $0.85e^-$, most of which comes from the metal. Even in the cation, the carbon atom has managed to extract 0.24 e^- from Ge. The origin of the energy splitting of the π MOs is more difficult to explain, but is probably due to closed-shell core-valence repulsions.

We have also performed NBO analyses for some of the neutral and cation excited states, and interesting aspects of the bonding and electronic features of these isomers is discussed in the following paragraphs. The first excited neutral state, $^2\Sigma$ GeCH, r_{GeC} = 1.667 Å, has a bond order of 2.99, and probably represents the best possibility of generating and observing a Lewis-type triple bond between Ge and C. Destabilisation of this isomer with respect to the ground state is due to excitation of a metal 4s electron from the σ-nonbonding orbital to the nearest π-bonding orbitals. This excitation costs 35.2 kcal mol^{-1}, ignoring additional molecular stabilisation gained by bond adjustments. The electronic configurations of the constituent atoms of this isomer are: $Ge(4s^{1.25}4p^{1.89})$ $C(2s^{1.30}2p^{3.77})$ $H(1s^{0.76})$. This suggests the electron promotion gives rise to a highly polar bonding arrangement in which a metal 4s electron is virtually transferred to the carbon atom, as confirmed by the calculated atomic charges: $Ge^{+0.85e}C^{-1.08e}H^{+0.24e}$. The first cation excited state is formed by the spin inversion of one of the two parallel-spin π-bonding electrons of the ground state isomer. Most of the inherent bonding features of this isomer are described in the NBO analysis of ground state $^3\Sigma$ $GeCH^+$, and no further discussion is warranted.

Before continuing with the relative structures of high energy excited states, it is acknowledged that at the full-CI level of theory, the particular cation configurations examined in the following paragraphs could correspond to transition structures on the potential energy hypersurface. For an understanding of the origins of Ge−C triple bond instability, a discussion of these structures cannot be overlooked.

The species with the shortest Ge−C bond lengths, and highest Ge−C bond orders, are the high energy excited states $^1\Sigma$ $GeCH^+$, r_{GeC} = 1.636 Å, and $^1\Sigma$ $HGeC^+$, r_{GeC} = 1.629 Å (see Table 2). The electronic configurations of the various constituent atoms in each isomer are: $Ge(4s^{0.94}4p^{1.50})$ $C(2s^{1.35}2p^{3.60})$ $H(1s^{0.61})$ and $H(1s^{0.83})$ $Ge(4s^{1.07}4p^{1.94})$ $C(2s^{1.30}2p^{2.87})$. It is immediately apparent that the electronic configuration of Ge in these high energy structures is approximately $4s^14p^2$, which corresponds to the excited cation state ^4P Ge^+. According to B3LYP/BS-II, the promotion energy required for hybridisation of Ge^+, in the absence of electric fields, is 6.5 eV ($^2\Pi$ $Ge^+ \rightarrow$ $^4\Pi$ Ge^+). The corresponding neutral value is 5.5 eV, whereas the promotion energy for CH (see Table 1), which for simplicity can be extracted from the $^2\Pi$ CH → $^4\Sigma$ CH excitation energy, amounts to 0.85 eV. It is clear that little, if

any, of this energy is recovered by GeC triple-bond stabilisation. Thus, it appears that the energy required to hybridise heavy group 14 congeners for triple-bond formation accounts for any relative destabilisation. The other characteristic feature of the excited states with short Ge−C bonds is the nature of the Ge−C σ bonding orbital. In the cation and neutral ground states, this orbital is a Ge($4p_z$) C($2sp_z$) hybrid, whereas the hybridisation for the excited cationic states is Ge(4s) C($2sp_z$). Moreover, this orbital has 47% Ge character in $^1\Sigma$ $GeCH^+$, 32% Ge character in $^1\Sigma$ $HGeC^+$ but only 18% Ge character in the cation ground state $^3\Sigma$ $GeCH^+$. This suggests the greater the carbon character of the Ge−C σ-bond, the greater the stability of the isomer.

Finally, it is interesting to compare the relative atomic charges of $^1\Sigma$ $GeCH^+$ and $^1\Sigma$ $HGeC^+$, which are: $Ge^{+1.58e}C^{-0.96e}H^{+0.38e}$ and $H^{+0.17e}Ge^{+1.01e}C^{-0.18e}$. On the basis of these values, it is expected that the $^1\Sigma$ $GeCH^+$ excited state would be more reactive than the $^1\Sigma$ $HGeC^+$ state, due to the much higher polarity of the Ge−C bond. Electronic reorganisation of $^1\Sigma$ $GeCH^+$ to a more stable open shell configuration would be favourable on the grounds of simple entropy arguments.

Experimental Section

For a detailed description of the experiment and the instrument used, the reader is advised to consult the recent review by Schalley et al.[21] In brief, the experiments were performed using a four-sector modified HF-ZAB AMD 604 mass spectrometer with BEBE configuration, where B and E represent magnetic and electric sectors respectively. $^{70}GeCH^+$ was generated by the 100 eV electron ionisation of trichloromethylgermane (Gelest Inc., PA, USA). The isotopomer $^{70}GeCH^+$ was selected for analysis as there are no isobaric interferences at *m*/*z* 83 due to other possibilities such as $GeCH_n$ (n = 0−3). Typical electron ionisation source conditions are as follows: source temperature 200°C; trap current 100 μA; repeller voltage 15 V; ion extraction voltage 8 kV; $m/\Delta m \geq 1500$. Collisional activation of B(1)/E(1)-mass selected $GeCH^+$ was effected in collision cells, positioned between E(1) and B(2), using He as a target gas. The collision cell pressure was maintained such that 80% of the parent ion beam was recovered after passing through this cell. This corresponds to an average of 1.1−1.2 collisions per ion.[22] CA products were recorded by scanning the second magnetic sector B(2).

NRMS experiments were performed for B(1)/E(1)-mass selected $GeCH^+$, utilising the dual collision cells between sectors E(1) and B(2). Cation neutralisation was achieved by collision with Xe at 80% transmittance, while reionisation was achieved by collision of the neutrals with O_2, again at 80% transmittance. Any ions remaining after the first collision event were deflected from the primary neutral beam using an electrode maintained at a high voltage (2 kV) positioned before the second collision cell. In order to detect a reionisation signal, the neutral species must be stable for approximately one microsecond. NRMS spectra were averaged over 100 acquisitions in order to obtain a sufficient S/N ratios, while CA spectra were averaged over 20−50 acquisitions.

The B3LYP calculations were performed using the Gaussian 94 software[23] on IBM RS/6000 computers running AIX 4.2.1. The structures of $[Ge,C,H]^+$ were investigated as follows: first, geometry optimisations were performed using the 3-parameter hybrid density functional method of Becke (B3LYP)[24] in conjunction with valence basis sets of double-zeta quality, and an effective core potential (ECP) replacing the $1s^2-3d^{10}$ electrons of Ge.[25] These basis sets are collectively referred to hereafter as BS-I. The nature of each stationary point located at this level of theory was then established via subsequent frequency analysis.

The optimised structures obtained using BS-I were then re-optimised using the all-electron 6-311G basis set of Krishnan and coworkers for C and H,[26] and the basis set of McGrath, Curtiss and coworkers for Ge.[27] The respective all-electron basis sets were supplemented with single p and d functions for Ge, one p and one d function for C, and one s and one p function for H. These basis sets are referred to as BS-II. The natural bond orbital analyses were performed at the re-optimised BS-II geometries using version 3.0 of the NBO code of Weinhold and coworkers.[28] In some instances, frequency analyses were repeated using BS-II at the optimised BS-II geometry to unambiguously establish the nature of low energy stationary points.

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