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Positive ion chemistry of SiH_4/GeF_4 gaseous mixtures studied by ion trap mass spectrometry and *ab initio* calculations

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The positive ion chemistry occurring in SiH_4/GeF_4 gaseous mixtures was investigated by ion trap mass spectrometry and ab initio theoretical calculations. The GeF_3^+ cation, the only fragment obtained from ionised GeF_4, was unreactive towards SiH_4. All the primary ions SiH_n^+ ($n = 0–3$) react instead with GeF_4 to form SiF^+ or SiH_2F^+. The latter species reacts in turn with SiH_4 and GeF_4 to form SiH_3^+ and $SiHF_2^+$, respectively. The potential energy profiles conceivably involved in these reactions were investigated by *ab initio* calculations performed at the MP2 and coupled cluster [CCSD(T)] level of theory.

Keywords: gas-phase ion chemistry, germanium tetrafluoride, ion trap mass spectrometry, silane, theoretical calculations

Introduction

The gas-phase ion chemistry of SiH_4 and of various of its mixtures with other compounds is of both fundamental and applied interest. These systems are, in fact, employed to deposit electronic and opto-electronic materials by chemical vapour deposition techniques,[1] and it is of interest to investigate the conceivable role of ionic species in the early stages of the polymerisation. Thus, over the last four decades, numerous experimental and theoretical studies have been reported concerning the ion–molecule reactions occurring in ionised SiH_4,[2–12] and in mixtures of SiH_4 with hydrogen,[13] hydrocarbons,[14–22] inorganic oxides,[23,24] water[25] and ammonia.[26,27] In particular, to investigate the contribution of Si–C ion clusters and Si–C ionic species "doped" with N or P atoms in the formation of photovoltaic silicon carbides,[28–30] some of us extensively studied the ionic reactions occurring in binary[31–38] and ternary mixtures[39–44] containing SiH_4, saturated and unsaturated hydrocarbons and ammonia or phosphine. Ionised mixtures of SiH_4 and CH_3Cl, CH_2Cl_2, $CHCl_3$[45] and CF_4[46,47] have also been investigated. The primary SiH_n^+ ($n = 0–3$) showed a distinct tendency to attack the Cl or F atoms of the halocarbons to form neutral and/or ionic products with Si–Cl or Si–F bonds. The CF_x^+ ($x = 1–3$) also reacted with SiH_4 by both H^- abstraction and formation of products with extensive redistribution of F and H between carbon and silicon centres. Consistent with these findings, our recent study on the ion chemistry of SiH_4/NF_3 mixtures[48–50] revealed that the primary SiH_n^+ ($n = 0–3$) react efficiently with NF_3 to form the silicon–fluorine cations $SiHF_m^+$ ($m = 1, 2$), SiH_2F^+ and SiF_x^+ ($x = 1–3$). The fluorinated Si_2 clusters $Si_2H_2F^+$, $Si_2H_3F^+$ and $Si_2H_5F^+$ were also observed. The primary NF_x^+ ($x = 1–3$) react instead with SiH_4 mainly by charge transfer, even though additional products were observed which suggest the formation of intimate

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reaction complexes. As a continuation of this study, and stimulated also by our current interest for the gas-phase chemistry of germanium–fluorine compounds,[51–55] we decided to use ion trap mass spectrometry (ITMS) and a high level of theory *ab initio* calculations to investigate the positive ion–molecule reactions occurring in SiH_4/GeF_4 gaseous mixtures. These systems are also of applied interest when employed to deposit silicon–germanium thin films by plasma techniques.[56,57] Our results will be compared with those concerning the related SiH_4/CF_4 mixtures.[46,47]

Experimental and computational details

Silane (99.99% purity grade) and helium (99.9999%) were purchased from SIAD and germanium tetrafluoride (99.99% purity grade) was purchased from Sigma–Aldrich. All the gases were used without further purification.

The experiments were performed with a Finnigan ITMS instrument (Austin, TX, USA) maintained at 333 K. Reagent gases and buffer helium were introduced into the trap at typical pressures of about 1.3×10^{-4} to 1.3×10^{-3} (the SiH_4/GeF_4 ratio is about 1:1), and about 1.3×10^{-2} Pa, respectively, empirically set to maximise the abundance of the signals and measured by a Bayard Alpert ion gauge. The nominal values were corrected for different sensitivity toward different gases[58] and for a calibration factor which depends on the geometry of the instrument.[59] These pressure domains ensure appreciable signal-to-noise ratios but prevent too much high ion densities into the trap. This avoids space–charge effects which may compromise m/z ratio assignments or cause problems of mass discrimination. The q_z values of the reactant ions, determined by setting the low-mass cut-off value, were selected to ensure that the q_z value of any product ion (m/z ratio higher and lower than the precursor ion) falls well within the 0.15–0.908 range. This avoids ion loss due to ion ejection ($q_z > 0.908$) or to low trapping fields ($q_z < 0.15$).[60] Ion densities are also optimised with respect to ionisation times by an automatic gain control.[61] In addition, our investigated range of m/z ratios between 14 Th and 400 Th avoids the reduction of mass accuracy which occurs when resonance ejection is used to extend the standard highest limit of 650 Th of the commercial ion trap.[61] Therefore, even though we did not perform specific determinations of the dynamic range, we may reasonably assume that it is linear for all the experiments performed. In the ITMS, the ionising electron energy is a function of both the amplitude of the rf voltage applied to the ring electrode during ionisation and the phase of the rf as the electrons enter the trap. Therefore, no single electron energy can be assigned. However, simulations of the electron energy have shown[62] that for a low-mass cut-off value of 10 u (rf amplitude of 112 V_{0-p}), the average electron energy varies from 6 eV to 55 eV over one cycle of the rf. The low-mass cut-off value was selected in order to achieve an appreciable signal-to-noise ratio and, at the same time, to avoid formation of electronically excited ions following ionisation. The reaction sequences and the rate constants were determined by selective ion storage of the reactant ions performed by the apex method (superimposition of dc and rf voltages). This avoids the presence of interference ions and allows the detection of product ions with appreciable signal-to-noise ratios. The scan modes and the methods used for the data processing were described previously.[59] Assuming the usual uncertainties in measuring absolute pressures with the Bayard Alpert ion gauge, the phenomenological rate constants (average of al least two determinations) are expected to be accurate within ±30%. Unless otherwise stated, the experimental thermochemical values are based on the data compiled in the *NIST Chemistry Webbook*.[63] The enthalpies of formation of the cations, not explicitly quoted, were derived as the sum of the enthalpies of formation and the ionisation energies of the corresponding neutrals.

The *ab initio* calculations were performed with the Gaussian03 set of programs,[64] using the standard internal 6-311G(d,p) and 6-311++G(d,p) basis sets. The geometries were fully optimised at the Møller–Plesset level of theory[65] with inclusion of the inner electrons, MP2(full) and using the 6-311G(d,p) basis set. Any located critical point was characterised as an energy minimum or a transition structure (**TS**) by analytical frequency analysis at the same level and any **TS** was unambiguously related to its interconnected energy minima by intrinsic reaction coordinate (IRC) calculations.[66] The MP2(full)/6-311G(d,p) unscaled frequencies were also used to evaluate the zero-point corrections to total energies. The enthalpy changes at 298.15 K were evaluated by including the translational (3/2 *RT*), rotational (*RT* or 3/2 *RT*) and vibrational contributions to the thermal correction at this temperature. Accurate electronic energies were obtained by single-point calculations at the coupled cluster level of theory (full electrons), including the contribution from single and double substitutions and an estimate of connected triples, CCSD(T,full),[67] with the 6-311++G(d,p) basis set. The atomic charges were computed by natural bond orbital (NBO) analysis[68] of the MP2(full)/6-311G(d,p) wave function.

Results and discussion

Reactions in ionised SiH_4/GeF_4 mixtures

The electron ionisation (EI) mass spectrum of GeF_4 at 70 eV was so far measured by Harland *et al.*[69] No molecular ion was detected and the mass spectrum was dominated by the trifluorogermyl cation GeF_3^+. The intensity of this signal was indeed exceedingly large and the additionally observed fragments (Ge^+, F^+, GeF^+, GeF^{2+}, GeF_2^+ and GeF_2^{2+}) amounted to only 0.05–3% of the base peak. Consistent with these findings, irrespective of the average energy of the electron beam, the only ion detected under our ITMS conditions from ionised GeF_4 was GeF_3^+. This cation did not react with SiH_4. This finding resembles our recently ascertained inability of GeF_3^+ to activate the C–H bonds of CH_4.[55] On the other hand, all the primary ions SiH_n^+ ($n = 0$–3) from the electron ionisation

Table 1. Ion/molecule reactions in ionised SiH_4/GeF_4.

Reaction			k_{reaz}[a]	k_{cap}[b]	Efficiency[c]	ΔH[d]
$Si^+ + GeF_4$	→	$SiF^+ + GeF_3$	2.8	9.19	0.30	−93[e] −112[f] −605[g]
$SiH^+ + GeF_4$	→	$SiF^+ + GeHF_3$	2.6	9.06	0.29	−160[f]
$SiH_2^+ + GeF_4$	→	$SiH_2F^+ + GeF_3$	5.6	8.93	0.63	−68[f]
$SiH_3^+ + GeF_4$	→	$SiH_2F^+ + GeHF_3$	1.0	8.81	0.11	−57[f]
$SiH_2F^+ + SiH_4$	→	$SiH_3^+ + SiH_3F$	6.3	11.1	0.57	−21[f]
$SiH_2F^+ + GeF_4$	→	$SiHF_2^+ + GeHF_3$	0.38	7.35	0.05	−51[f]

[a] Rate constants are expressed as $10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$; experiments were run at 333 K; uncertainty is within ±30%

[b] Collisional rate constants ($10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$) calculated according to the parametrised trajectory theory,[73] taking the polarisability of SiH_4 and GeF_4 from Lide.[74]

[c] Calculated as the ratio k_{reaz}/k_{cap}.

[d] Reaction enthalpies expressed as $kJ\,mol^{-1}$.

[e] Experimental value based on thermochemical data quoted in Linstrom and Mallard.[63]

[f] Theoretical estimate at the CCSD(T)/6-311++G(d,p)//MP2/6-311G(d,p) level of theory and 298.15 K (present work).

[g] Experimental value assuming the formation of excited $Si^+(^4P)$.

of SiH_4[70] showed reactivity towards GeF_4. The secondary ion, SiH_2F^+, is also reactive towards both SiH_4 and GeF_4. The details of our observed processes are collated in Table 1.

The open-shell cations, Si^+ and SiH_2^+, react with GeF_4 and undergo the F-atom abstractions described by the reactions:

$$Si^+ + GeF_4 \rightarrow SiF^+ + GeF_3 \qquad (1)$$

$$SiH_2^+ + GeF_4 \rightarrow SiH_2F^+ + GeF_3 \qquad (2)$$

These processes are theoretically predicted to be exothermic by 112 kJ mol^{-1} and 68 kJ mol^{-1}, respectively, and these values reflect average Si–F bond energies which are in general larger than Ge–F (for example, 596 kJ mol^{-1} vs 470 kJ mol^{-1} passing from SiF_4 to GeF_4). The estimated enthalpy change of Reaction (1) differs in particular from the experimental value by nearly 20 kJ mol^{-1} and this deviation can be taken as an estimate of the accuracy of the presently employed CCSD(T)/MP2 level of theory. Both Reactions (1) and (2) conceivably occur by the attack of Si^+ or SiH_2^+ to a F atom of GeF_4, with formation of the Si–F bond and concomitant cleavage of the weaker Ge–F bond. The reaction between Si^+ and GeF_4 deserves an additional comment, however. The electron ionisation of SiH_4 in general produces both ground (^2P) and excited $Si^+(^4P)$. The latter is less stable by 5.3 eV, and amounts to about 38% of the ionic population.[13] The formation of electronically excited Si^+ is also expected under our ITMS conditions. Collisions with helium are, in fact, only partially effective in quenching excited electronic states. Consistent with this expectation, we noticed the contribution of excited Si^+ to the reaction between Si^+ and NF_3.[48] We observed the formation of both SiF^+ and NF_2 (definitely exothermic for both ground and excited Si^+), and of NF_2^+ and SiF, which is endothermic by 38 kJ mol^{-1} for ground state Si^+ but largely exothermic for excited Si^+. Likewise, it was observed[47] that the reaction of Si^+ with CF_4 at collision energies of 1 eV (laboratory frame) produces SiF^+ and CF_3 as well as CF_3^+ and SiF. The energy dependence of the cross sections suggested that both processes were exothermic. However, while the formation of SiF^+ is exothermic for both ground and excited Si^+, the formation of CF_3^+ is endothermic by nearly 50 kJ mol^{-1} for ground state Si^+ and exothermic only for excited Si^+. As for Reaction (1), the observed formation of SiF^+ and GeF_3 is exothermic for both ground and excited Si^+ (see Table 1). The time dependence of ln[Si^+] resulted in a straight line of constant slope over the entire time interval explored (0–40 ms), thus suggesting a single ionic population or two ionic populations which react at identical reaction rates. In addition, we did not observe any product firmly ascribable to excited Si^+. Therefore, at variance with the reaction of Si^+ with NF_3 and CF_4, we cannot distinguish the relative contribution of the ground and/or excited state to the fraction of the Si^+ ionic population which reacts with GeF_4 according to Reaction (1) (about 30%).

The closed-shell cations SiH^+ and SiH_3^+ react with GeF_4 and undergo the formal H/F exchange reactions described by the reactions:

$$SiH^+ + GeF_4 \rightarrow SiF^+ + GeHF_3 \qquad (3)$$

$$SiH_3^+ + GeF_4 \rightarrow SiH_2F^+ + GeHF_3 \qquad (4)$$

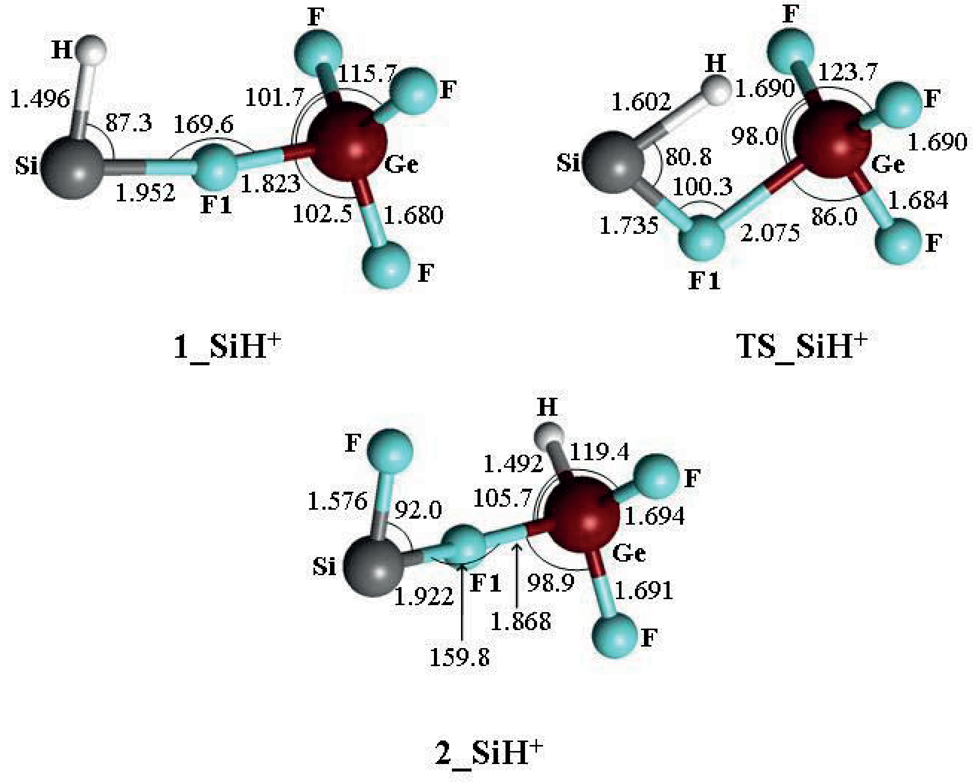
Both these processes are predicted to be exothermic and this essentially reflects the formation of the strong Si–F bonds of SiF^+ and SiH_2F^+. These products conceivably arise from the direct attack of SiH^+ and SiH_3^+ to a F atom of GeF_4, to form $HSi–F–GeF_3^+$ and $H_3Si–F–GeF_3^+$ intermediates, which undergo the eventual extrusion of $GeHF_3$. This process could occur directly, or pass through additional intermediates. To distinguish among the various conceivable paths, we performed *ab initio* calculations on the mechanisms of Reactions (3) and (4).

The obtained results are summarised in Figures 1–4, which show the optimised geometries and the relative energies at 0 K of the species involved in these processes.

Both Reactions (3) and (4) commence by the addition of the reactant ions SiH$^+$ or SiH$_3^+$ to GeF$_4$ so to form the fluorine-coordinated complex **1_SiH$^+$** (Figure 1) or **1_SiH$_3^+$** (Figure 3). Both these processes are exothermic (Figures 2 and 4), even though the complexation energy of SiH$_3^+$ is larger than SiH$^+$ by 40 kJ mol^{-1}. This higher Lewis acidity of SiH$_3^+$ also reflects in the optimised geometries of **1_SiH$^+$** and **1_SiH$_3^+$**. The former species features, in fact, a longer Si–F1 bond distance (1.952 Å vs 1.830 Å) and a shorter Ge–F1 bond distance (1.823 Å vs 1.843 Å). Consistently, the charge shift from GeF$_4$ to SiH$_3^+$ which accompanies the formation of **1_SiH$_3^+$**, computed as 0.180 *e*, is larger than the charge shift of 0.106 *e* which accompanies the formation of **1_SiH$^+$** from SiH$^+$ and GeF$_4$.

The subsequent fates of **1_SiH$^+$** and **1_SiH$_3^+$** and the detailed mechanisms of Reactions (3) and (4) are somewhat different. As shown in Figure 2, the former species passes through the four-centres transition structure **TS_SiH$^+$** (Figure 1) and undergoes the H/F exchange between the silicon and the germanium atom to form **2_SiH$^+$**, an ion–molecule complex arising from the coordination of the Si atom of SiF$^+$ to the F atom of GeHF$_3$. This reaction intermediate directly dissociates into its constituting moieties and this explains the observation of SiF$^+$ from Reaction (3). On the other hand, as shown in Figure 4, **1_SiH$_3^+$** passes through the four-centres transition structure **TS_SiH$_3^+$** (Figure 3), and undergoes the H/F exchange between the silicon and the germanium atom so to form the reaction intermediate **1′_SiH$_3^+$**. This species formally arises from the coordination of the silicon atom of SiH$_2$F$^+$ to the hydrogen atom of GeHF$_3$, and resides in a very flat region of the potential energy surface. Its dissociation into the constituting moieties is endothermic by only 10 kJ mol^{-1}, and this explains the experimental observation of SiH$_2$F$^+$ from Reaction 4. We explored also the conceivable role in Reaction (4) of isomer **2_SiH$_3^+$**, which is the corresponding analogue of **2_SiH$^+$**. We ascertained in particular that, passing through the four-centres transition structure **TS′_SiH$_3^+$** (Figure 3), isomer **1′_SiH$_3^+$** could actually collapse into the significantly more stable **2_SiH$_3^+$**. However, as shown in Figure 4, the transition structure **TS′_SiH$_3^+$** is less stable than the dissociation limit SiH$_2$F$^+$ + GeHF$_3$. Therefore, it is reasonable to suggest that isomer **1′_SiH$_3^+$** directly dissociates into its constituting fragments rather than isomerise into **1_SiH$_3^+$**, and that the latter intermediate is not involved in the mechanism of Reaction (4). Additional evidence, in this regard, comes from the theoretical prediction (see Figure 4) that the dissociation limit of lowest energy of **1_SiH$_3^+$** is GeHF$_2^+$ + SiH$_2$F$_2$ rather than SiH$_2$F$^+$ + GeHF$_3$. However, the GeHF$_2^+$ ionic product was not experimentally observed.

Isomer **2_SiH$_3^+$** is the corresponding analogue of **2_SiH$^+$** and arises from the coordination of the Si atom of SiH$_2$F$^+$ to the F



1_SiH$^+$

TS_SiH$^+$

2_SiH$^+$

Figure 1. MP2/6-311G(d,p) optimised geometries (distances in Å and angles in degrees) of the species involved in the reaction between SiH$^+$ and GeF$_4$.

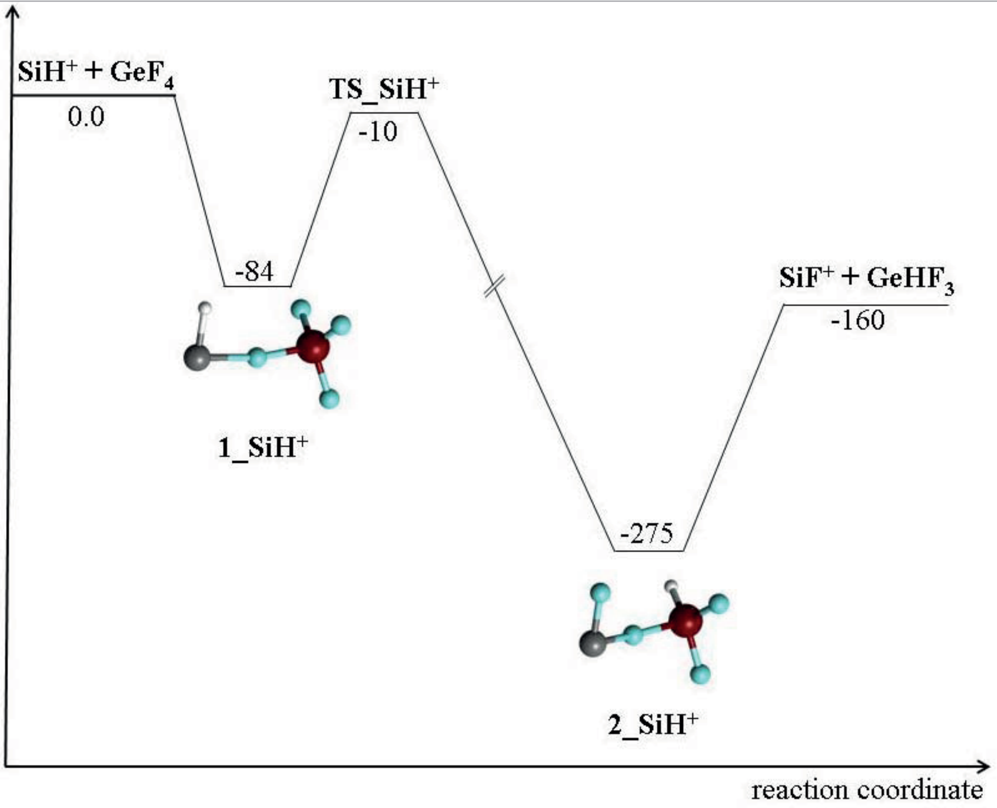


Figure 2. CCSD(T)/6-311++G(d,p)//MP2(full)/6-311G(d,p) relative energies at 0 K (kJ mol^{-1}) of the species involved in the reaction between SiH^+ and GeF_4.

atom of $GeHF_3$. Interestingly, the optimised geometries and charge distributions of **2_SiH$^+$** and **2_SiH$_3^+$** suggest that, likewise, SiH_3^+ is a Lewis acid stronger than SiH^+, and SiH_2F^+ is a Lewis acid stronger than SiF^+. We note, in particular, that the dissociation energy of **2_SiH$_3^+$** into SiH_2F^+ and $GeHF_3$ is larger by 80 kJ mol^{-1} than the dissociation energy of **2_SiH$^+$** into SiF^+ and $GeHF_3$. Consistently, the former species possesses a shorter Si–F1 bond distance (1.777 Å vs 1.922 Å) and a longer Ge–F1 bond distance (1.918 Å vs 1.868 Å) and the charge shift from $GeHF_3$ to SiH_2F^+, which accompanies the formation of **2_SiH$_3$$^+$**, computed as 0.206 *e*, is larger than the charge shift of 0.115 *e* which accompanies the formation of **2_SiH$^+$** from SiF^+ and $GeHF_3$.

As shown in Figures 2 and 4, the rate-determining step of Reactions (3) and (4) is the rearrangement of **1_SiH$^+$** or **1_SiH$_3^+$** into **2_SiH$^+$** or **1′_SiH$_3^+$**, respectively, passing through **TS_SiH$^+$** and **TS_SiH$_3^+$**. These transition structures are predicted to be more stable than the entrance channel SiH^+ or $SiH_3^+ + GeF_4$ by 10–14 kJ mol^{-1}. These values are indeed comparable with the estimated uncertainty of our calculations and the theoretical results essentially suggest that the transition structures involved in the rate-determining steps of Reactions (3) and (4) are comparably stable or only slightly more stable than the reactants. Therefore, in keeping with the experiments, their efficiencies are expected to be significantly less than unity.

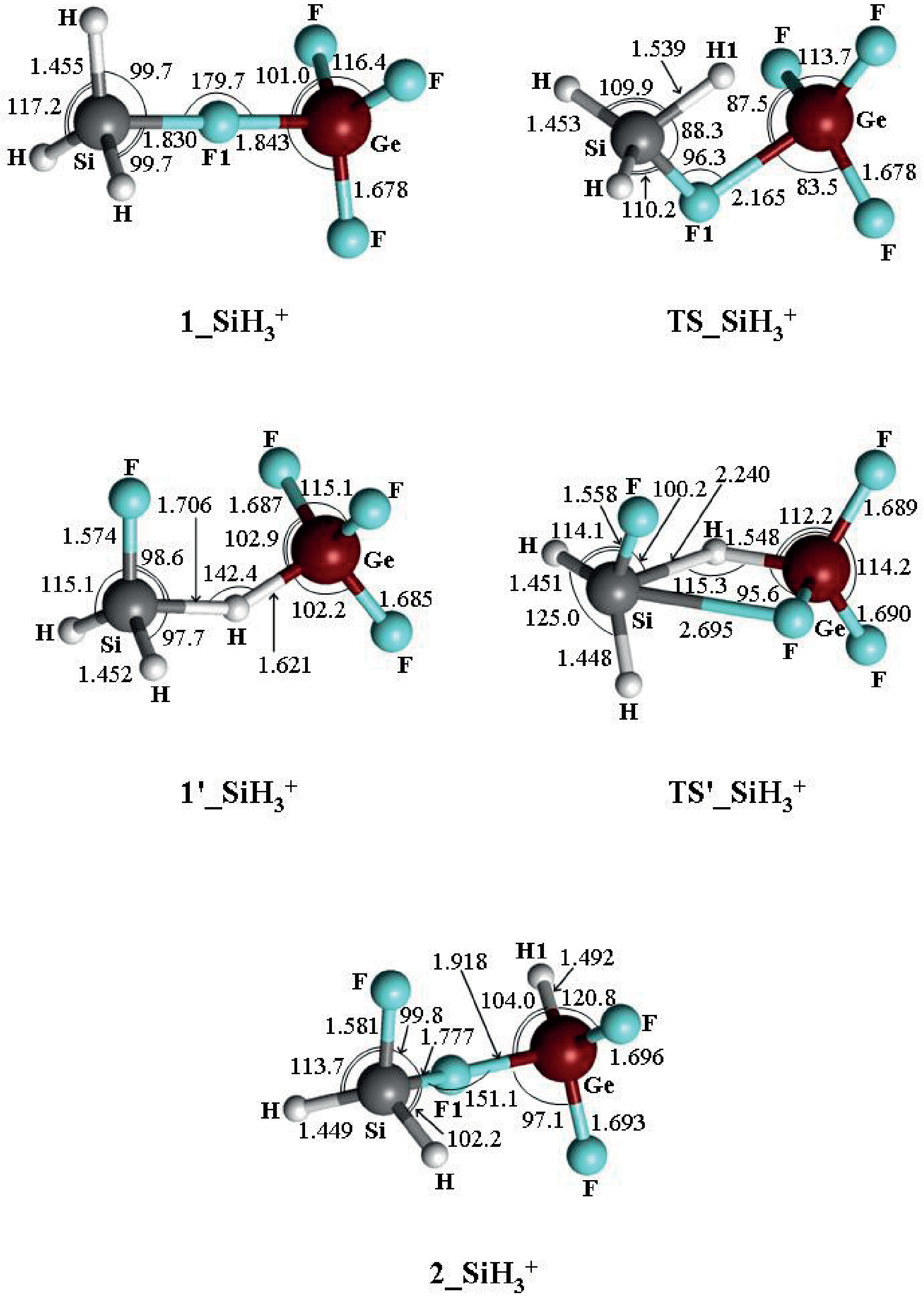
The SiH_2F^+ cation obtained from Reaction (4) reacts with SiH_4 by hydride transfer and, with GeF_4, undergoes the formal H/F atom exchange according to the reaction:

$$SiH_2F^+ + GeF_4 \rightarrow SiHF_2^+ + GeHF_3 \qquad (5)$$

The mechanism of this process is reasonably similar to those outlined for Reactions (3) and (4).

Comparison between ionised SiH_4/GeF_4 and SiH_4/CF_4

So far, the reactions of SiH_n^+ ions with CF_4 at collision energies of 1 eV (laboratory frame) have been investigated by tandem mass spectrometry.[46,47] Compared with GeF_4, the reactivity patterns include, in general, a larger number of products. The open-shell SiH_2^+ reacts with CF_4 predominantly by F atom abstraction. However, at variance with GeF_4, the product of the reaction between SiH_2^+ and CF_4 is CF_3^+ rather than SiH_2F^+. This suggests that the experimentally unknown ionisation energy of SiH_2F, so far theoretically estimated as 8.12 eV,[71] is indeed lower than GeF_3, ⩽ 10.3 ± 0.3 eV,[69] but higher than CF_3, 8.76 eV. The minor exothermic products SiF^+, $SiHF^+$, SiH_2F^+, CF_2^+ and CHF_2^+ were also observed. The reaction of SiH^+ with CF_4 produces comparable amounts of SiF^+ [by a reaction analogue to Reaction (3)] and CF_3^+, which is also by far the prevailing product from the reaction between SiH_3^+ and CF_4. The latter process also leads to minor SiH_2F^+ and CHF_2^+. Overall, while



$1\_SiH_3^+$ $TS\_SiH_3^+$

$1'\_SiH_3^+$ $TS'\_SiH_3^+$

$2\_SiH_3^+$

Figure 3. MP2/6-311G(d,p) optimised geometries (distances in Å and angles in degrees) of the species involved in the reaction between SiH_3^+ and GeF_4.

the major reaction of SiH_n^+ ($n = 1$–3) with GeF_4 is the F abstraction or H/F exchange reaction, the major reaction of positive silicon ions with CF_4 is the F^- abstraction.

It is also of interest to compare the reactivity toward SiH_4 of GeF_3^+ and CF_3^+.[46,47] Thus, at collision energies of 1 eV (laboratory frame), the latter cation forms SiH_3^+ (nearly 72% of the total cross section), CHF_2^+ (nearly 20%),and the minor CH_3^+ and CH_2F^+. The endothermic formation of SiH_2F^+ and $SiHF_2^+$ was also detected. Even though this rich reactivity pattern may at least partially reflect the translationally excited character of CF_3^+, the latter species is certainly more reactive toward SiH_4 than GeF_3^+. A factor which contributes to this observed difference is the weaker character of the Ge–H with respect to the C–H bond. For example, while the formation of CHF_3 from

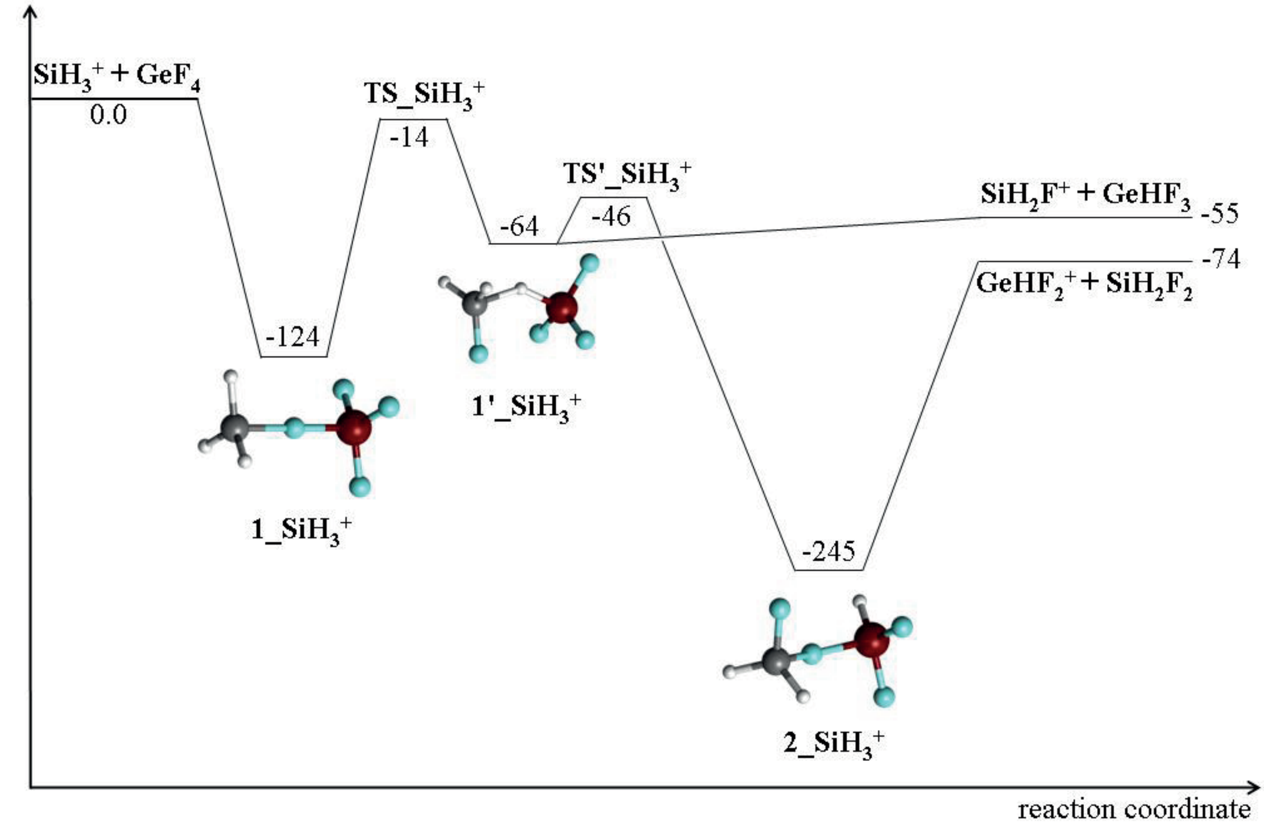


Figure 4. CCSD(T)/6-311++G(d,p)//MP2(full)/6-311G(d,p) relative energies at 0 K (kJ mol^{-1}) of the species involved in the reaction between SiH_3^+ and GeF_4.

CF_3^+ and SiH_4 is exothermic by 122 kJ mol^{-1}, the conceivable formation of $GeHF_3$ from GeF_3^+ and SiH_4 is estimated to be endothermic by 6 kJ mol^{-1} (this estimate is based on the experimental enthalpy of formation of GeF_3^+, quoted as 58 kJ mol^{-1} by Harland *et al.*,[69] and the theoretical enthalpy of formation of $GeHF_3$, derived as −888 kJ mol^{-1} from the G4 atomisation energy of 1715 kJ mol^{-1}.[72])

Conclusions

Our investigation of the positive ion chemistry occurring in mixtures of SiH_4 and GeF_4 did not reveal any formation of Si–Ge ionic species. This suggests that, when employed to deposit silicon–germanium thin films by plasma techniques,[56,57] the species involved in the early stages of the polymerisation are neutral rather than ionic. This information could contribute to optimising the running conditions during deposition processes.

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