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Cationic germanium fluorides
2. An experimental and theoretical investigation on the reaction between GeF^+ and H_2O [1]

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Abstract

The reaction between singlet ground state GeF^+ ($^1\Sigma^+$) and H_2O, with formation of Ge–OH^+ and HF, was investigated by ion trap mass spectrometry (ITMS) and ab initio calculations at the MP2 and CCSD(T) level of theory. The process involves the initial formation of the addition product FGe^+–OH_2 (**1**), its interconversion into $HOGe^+$–FH (**2**), and the eventual barrier-free dissociation into Ge–OH^+ and HF. The activation barrier of the **1** → **2** isomerization is comparable with the exothermicity (exoergicity) of the formation of **1**, and this explains the relatively low efficiency of the process, experimentally evaluated as 0.14 from the ratio of the absolute rate constant, 3.2×10^{-10} cm^3 molecule^{-1} s^{-1}, and the collisional rate constant. The mechanism of the reaction between GeF^+ and H_2O is strictly analogue to that of the reaction between SiF^+ and H_2O, investigated so far by selected-ion flow tube (SIFT) mass spectrometry and ab initio calculations. From a general point of view, the conceivable occurrence of additional similarities between the still essentially unexplored reactivity of $GeF_n{}^+$ (n = 1–3) and the rich and variegated chemistry of $SiF_n{}^+$ suggests novel attractive opportunities in the gas-phase positive ion chemistry of germanium.

Keywords: Ab initio calculations; Germanium–fluorine cations; Ion trap mass spectrometry; Silicon–fluorine cations; Structure and reactivity

1. Introduction

Neutral and ionic germanium fluorides $GeF_n{}^{+/0/-}$ (n = 1–5) are of considerable interest not only for fundamental reasons but also for their role in the fine processing of semiconductors [2–4]. With particular regard to the charged species, the structure, stability, and thermochemistry of $GeF_n{}^-$ (n = 1–5) have been systematically investigated by density functional methods [5], and discussed in connection with previous related experimental and theoretical data [6–19]. As for cationic germanium fluorides, experimental and theoretical studies [8,20] indicate that, in the ground state, $GeF_4{}^+$ is unstable and prone to dissociate into $GeF_3{}^+$ and atomic fluorine. On the other hand, all the other ground state $GeF_n{}^+$ (n = 1–3) are quite stable in the gas phase and abundantly detected, for example, from the electron impact fragmentation of GeF_4 [8]. The GeF^+ and $GeF_2{}^+$ ions have been also investigated by spectroscopic methods [21–23], and various calculations, at different levels of theory, have been performed to investigate the properties of $GeF_n{}^+$ (n = 1–3) [9,24–28]. Quite recently, as part of our continuing interest in the chemistry of fluorinated inorganic ions [29–33], we have reported [1] a comparative theoretical study, at an uniform and accurate level of theory, on the structure, stability, and thermochemistry of $GeF_n{}^+$ (n = 1–3) and of their neutral counterparts GeF_n. The reactivity of gaseous $GeF_n{}^+$ is instead still essentially unexplored, and we report here a first contribution to this subject discussing the reaction between GeF^+ and H_2O. Similar to $SiF_n{}^+$ (n = 1–3) [34–36] and to other fluorinated cations such as $NF_2{}^+$ [37] and $PF_2{}^+$ [38], GeF^+ activates the robust H_2O according to a reaction path strictly analogue to that involved in the reaction between SiF^+ and H_2O [36]. From a general point of view, the conceivable occurrence of additional similarities between the

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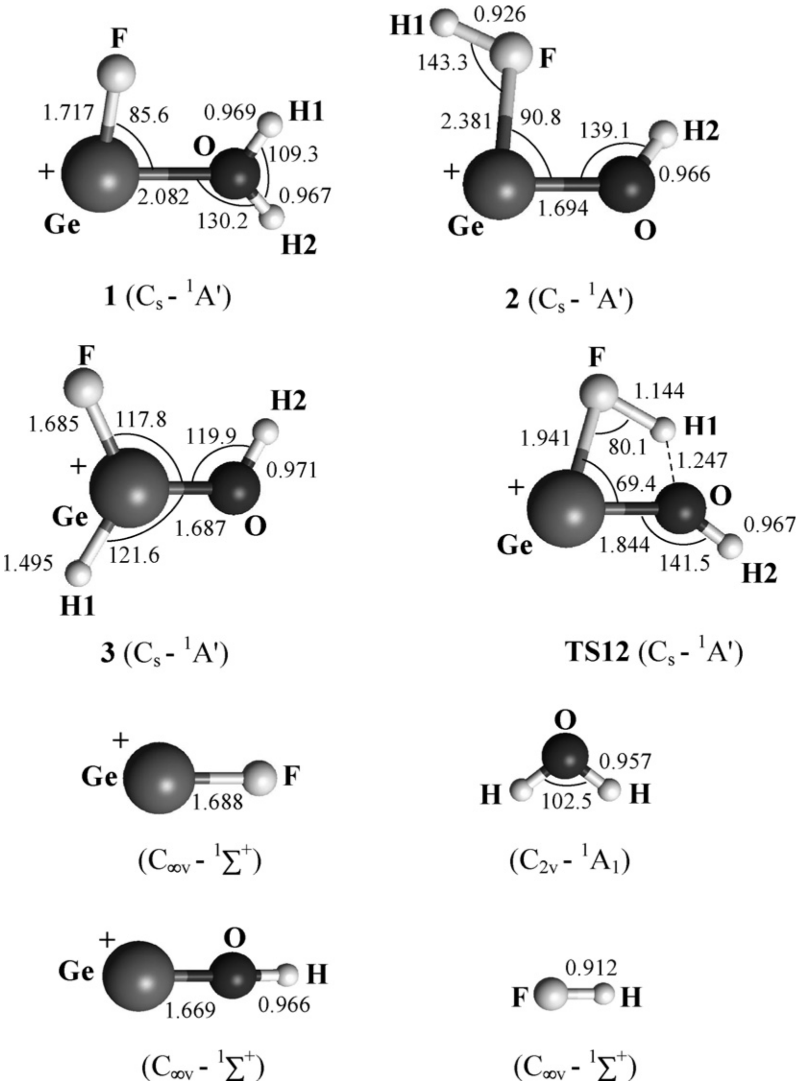

1 (C_s - $^1A'$)

2 (C_s - $^1A'$)

3 (C_s - $^1A'$)

TS12 (C_s - $^1A'$)

($C_{\infty v}$ - $^1\Sigma^+$)

(C_{2v} - $^1A_1$)

($C_{\infty v}$ - $^1\Sigma^+$)

($C_{\infty v}$ - $^1\Sigma^+$)

Fig. 1. MP2(full)/6-311G(d,p) optimised geometries (Å and °) of the species involved in the reaction between GeF^+ and H_2O.

reactivity of $GeF_n{}^+$ and the rich and variegated chemistry of $SiF_n{}^+$ [34–36,39–46] suggests novel attractive opportunities in the gas-phase positive ion chemistry of germanium.

2. Experimental and computational details

The mass spectrometric experiments have been performed using a Finnigan ITMS instrument maintained at 333 K. Reagent gases and buffer helium were introduced into the trap at typical pressures of ca. 6.0×10^{-7} and ca. 1.0×10^{-4} Torr (1 Torr = 133 Pa), respectively, empirically set so to maximize the abundance of the signals and measured by a Bayard Alpert ion gauge. The nominal values of the pressure were corrected for different sensitivity toward different gases,[1] and for a calibration factor which depends on the geometry of the instrument [47]. Electron ionisation was achieved by an electron beam of 35 eV (average energy), and the isolation of selected ions was performed by the apex method (superimposition of dc and rf voltages). The scan modes used to determine the reaction sequencies and the rate constants, as well as the corresponding methods of data processing, have been already described in detail [47] and will not be repeated here. Although the reactions are carried out in the presence of He as a buffer, it is always difficult to estimate how truly thermal they are in an ion trap. Assuming the usual uncertainties in measuring absolute pressures with the Bayard Alpert ion gauge, the presently measured rate constant, which is the average of two estimates, is expected to be accurate within ±20%. In all the experiments, the ions detection range was set between 10 and 300Th.

High-purity NF_3 (Rivoira) and GeH_4, prepared as described in the literature [48,49], were dried by sodium sulfate before using, while extra-high purity He (SIAD) was used without further purification.

The ab initio calculations were performed using the GAUSSIAN98 [50] set of programs installed on an AlphaServer 1200 and a DS20E Compaq machine. The geometries of the various intermediates, transition structures, and products involved

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[1] M. Decouzon, J.F. Gal, P.C. Maria, A.S. Tchinianga, private communication.

in the reaction between singlet XF^+ and H_2O (X = Si and Ge) were fully optimised, using the 6-311G(d,p) basis set [51], at the Møller–Plesset level of theory [52], with inclusion of the inner electrons, (MP2(full)), and the located structures unambiguously characterized by calculating their analytical harmonic vibrational frequencies. For the transition structures, intrinsic reaction coordinate (IRC) calculations [53] were also performed to confirm their interconnected energy minima. The MP2(full)/6-311G(d,p) unscaled frequencies were also used to calculate the zero-point vibrational energies (ZPE) and the vibrational contribution to the thermal correction (TC), obtained at 298.15 K by standard statistical mechanics formulas [54]. The overall TC term was finally obtained by adding the translational (3/2 RT) and rotational (RT or 3/2 RT) contributions at this temperature. Accurate total energies of the investigated species were finally 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) [55,56], with the 6-311++G(d,p) basis set [51]. The basis set superposition error was computed according to the procedure by Boys and Bernardi [57].

3. Results

3.1. Mass spectrometric experiments

The GeF^+ cations, produced from the ionization of GeH_4/NF_3 mixtures [58] and allowed to react with water, undergo the exclusive formation of $GeOH^+$ according to the reaction shown

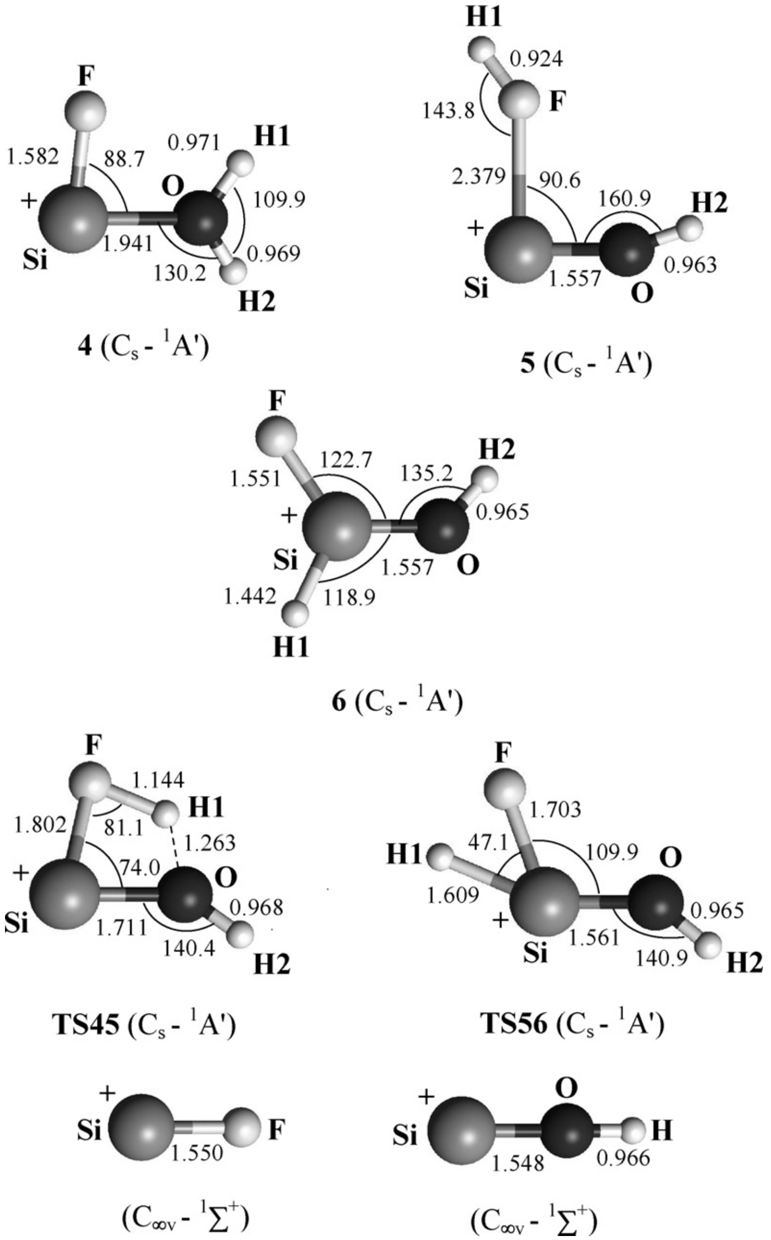


Fig. 2. MP2(full)/6-311G(d,p) optimised geometries (Å and °) of the species involved in the reaction between SiF^+ and H_2O.

in Eq. (1):

$$GeF^+ + H_2O \rightarrow GeOH^+ + HF \qquad (1)$$

No further reaction between $GeOH^+$ and H_2O was observed. The rate constant of (1), measured as 3.2×10^{-10} cm^3 molecule^{-1} s^{-1}, is approximately one-tenth (0.14) of the collisional rate constant, calculated as 2.2×10^{-9} cm^3 molecule^{-1} s^{-1} from the average dipole orientation (ADO) theory [59]. The analogue reaction involving SiF^+, shown in Eq. (2):

$$SiF^+ + H_2O \rightarrow SiOH^+ + HF \qquad (2)$$

was so far investigated by Bohme and co-workers [36] using selected-ion flow tube (SIFT) mass spectrometry and ab initio calculations. The absolute rate constant was measured as 7.6×10^{-11} cm^3 molecule^{-1} s^{-1}, and the efficiency evaluated as 0.03 from the ratio with the ADO collisional constant of 2.5×10^{-9} cm^3 molecule^{-1} s^{-1}. Therefore, although SiF^+ and GeF^+ react with water by an identical reaction path, the process involving GeF^+ appears more efficient by approximately five times.

3.2. Ab initio calculations

The MP2(full)/6-311G(d,p) optimised geometries of the relevant intermediates, transition structures, reactants, and products involved in reactions (1) and (2) are shown in Figs. 1 and 2. Their harmonic frequencies are listed in Tables 1 and 2, and their absolute and relative energies and free energies are reported in Tables 3 and 4.

Isomers **1** and **4** are complexes between singlet ground state ($^1\Sigma^+$) XF^+ [1,60] (X = Si and Ge) and H_2O. The X–O bond lengths range around 2.0 Å and are appreciably longer than typical Si–O and Ge–O covalent bonds (e.g., 1.613 Å in F_3SiOH and 1.732 Å in F_3GeOH), and the corresponding harmonic frequencies occur at low values of 342 and 417 cm^{-1}, respectively. Consistently, the interaction energies between XF^+ and H_2O are

Table 1
MP2(full)/6-311G(d,p) harmonic frequencies (cm^{-1}) of the intermediates involved in the reaction between GeF^+ and H_2O (for connectivities and labelling of the atoms, see Fig. 1)

Species	State	ν	Symmetry	Assignment
1 (C_s)	$^1A'$	200.2 (12.9)	A′	F–Ge–O scissoring
		292.1 (197.2)	A″	H–O–H wagging
		342.0 (57.3)	A′	Ge–O stretching
		368.8 (158.2)	A″	H–O–H twisting
		598.4 (26.5)	A′	H–O–H rocking
		748.0 (101.9)	A′	Ge–F stretching
		1636.0 (83.3)	A′	H–O–H scissoring
		3772.5 (234.3)	A′	H–O stretching
		3885.3 (270.9)	A′	H–O stretching
2 (C_s)	$^1A'$	118.7 (7.4)	A′	F–Ge–O scissoring
		183.9 (24.4)	A′	Ge–F stretching
		206.5 (165.4)	A″	Ge–F–H1 wagging
		330.3 (297.9)	A″	Ge–O–H2 wagging
		340.9 (196.4)	A′	Ge–F–H1 scissoring
		453.8 (202.3)	A′	Ge–O–H2 scissoring
		852.0 (67.8)	A′	Ge–O stretching
		3856.4 (425.1)	A′	H2–O stretching
		4060.5 (407.5)	A′	H1–F stretching
3 (C_s)	^1A	226.7 (40.7)	A′	F–Ge–O scissoring
		424.1 (158.0)	A″	Ge–O–H2 wagging
		595.4 (31.3)	A″	H1–Ge–O wagging
		663.5 (2.7)	A′	H1–Ge–O scissoring
		786.1 (22.9)	A′	Ge–F stretching
		841.1 (195.4)	A′	Ge–O stretching
		930.1 (28.0)	A′	Ge–O–H2 scissoring
		2348.8 (25.5)	A′	Ge–H1 stretching
		3782.4 (361.5)	A′	H2–O stretching
GeF^+ ($C_{\infty v}$)	$^1\Sigma^+$	798.0 (78.8)	σ	Ge–F stretching
$GeOH^+$ ($C_{\infty v}$)	$^1\Sigma^+$	164.9 (286.5)	π	Bending
		892.3 (80.0)	σ	Ge–O stretching
		3856.7 (664.0)	σ	H–O stretching
H_2O (C_{2v})	$^1A_1$	1667.9 (51.5)	A_1	Bending
		3908.7 (6.3)	A_1	H–O stretching
		4016.1 (34.0)	B_2	H–O stretching
HF ($C_{\infty v}$)	$^1\Sigma^+$	4254.6 (106.4)	σ	H–F stretching

IR intensities (km mol^{-1}) are given in parenthesis.

Table 2
MP2(full)/6-311G(d,p) harmonic frequencies (cm^{-1}) of the intermediates involved in the reaction between SiF^+ and H_2O (for connectivities and labelling of the atoms, see Fig. 2)

Species	State	ν	Symmetry	Assignment
4 (C_s)	$^1A'$	264.3 (9.3)	A'	F–Si–O scissoring
		364.8 (41.3)	A''	H–O–H twisting
		399.1 (327.7)	A''	H–O–H wagging
		417.3 (133.5)	A'	Si–O stretching
		687.1 (35.9)	A'	H–O–H rocking
		965.7 (155.5)	A'	Si–F stretching
		1658.4 (117.6)	A'	H–O–H scissoring
		3739.9 (239.2)	A'	H–O stretching
		3850.4 (300.6)	A'	H–O stretching
5 (C_s)	$^1A'$	136.6 (21.7)	A'	F–Si–O scissoring
		179.8 (29.6)	A'	Si–F stretching
		210.5 (184.0)	A''	Hl–F–Si wagging
		339.9 (187.4)	A'	Hl–F–Si scissoring
		380.6 (320.6)	A''	Si–O–H2 wagging
		389.3 (318.8)	A'	Si–O–H2 scissoring
		1125.8 (126.6)	A'	Si–O stretching
		3907.0 (552.7)	A'	H2–O stretching
		4080.0 (369.8)	A'	Hl–F stretching
6 (C_s)	$^1A'$	318.3 (69.8)	A'	F–Si–O scissoring
		483.1 (309.7)	A''	Si–O–H2 wagging
		625.7 (215.7)	A'	Si–O–H2 scissoring
		631.2 (0.5)	A''	H1–Si–O wagging
		829.3 (25.1)	A'	H1–Si–O scissoring
		983.6 (132.4)	A'	Si–F stretching
		1202.0 (156.5)	A'	Si–O stretching
		2491.4 (6.4)	A'	Si–Hl stretching
		3865.7 (477.1)	A'	H2–O stretching
SiF^+ ($C_{\infty v}$)	$^1\Sigma^+$	1043.7 (134.7)	σ	Si–F stretching
$SiOH^+$ ($C_{\infty v}$)	$^1\Sigma^+$	343.0 (286.2)	π	Bending
		1146.5 (117.4)	σ	Si–O stretching
		3874.4 (657.7)	σ	H–O stretching

IR intensities (km mol^{-1}) are given in parenthesis.

by far lower than typical Si–O and Ge–O covalent bond energies and amount, at the CCSD(T,full)/6-311++G(d,p)//MP2(full)/6-311G(d,p) level of theory and 0 K, to 36.5 kcal mol^{-1} for X = Si (32.7 kcal mol^{-1} once corrected for the BSSE) and to 34.9 kcal mol^{-1} for X = Ge (30.9 kcal mol^{-1} once corrected for the BSSE). Thus, SiF^+ and GeF^+ appear Lewis acids of comparable strength.

Isomers **2** and **5** are loosely bound complexes between singlet ground state $X–OH^+$ [61,62] (X = Si and Ge) and HF. We note in particular the low interaction energies between

Table 3
Total energies (a.u.), zero-point energies (ZPE, a.u.), thermal corrections (TC, a.u.), and total entropies (S, cal mol^{-1} K^{-1}) of the species involved in the reaction between GeF^+ and H_2O (see Fig. 1)

Species	CCSD(T,full)/6-311++G(d,p)[a]	ZPE[b]	TC (298.15 K)[b]	S (298.15 K)[c]	ΔE (0 K)[d]	ΔG (298.15 K)[d]
1	−2251.55893	0.02698	0.00479	71.0	−34.9	−27.4
2	−2251.53892	0.02370	0.00575	75.7	−24.4	−17.7
3	−2251.49769	0.02415	0.00403	67.7	+1.7	+9.8
TS12	−2251.51397	0.02263	0.00387	67.4	−9.5	−1.4
GeF^+	−2175.19409	0.00182	0.00244	54.2	0.0	0.0
H_2O	−76.30587	0.02185	0.00284	45.1		
$GeOH^+$	−2151.21257	0.01157	0.00365	59.0	−12.1	−11.9
HF	−100.30421	0.00969	0.00236	41.4		

[a] At the MP2(full)/6-311G(d,p) optimised geometries.
[b] Based on MP2(full)/6-311G(d,p) harmonic frequencies.
[c] Based on MP2(full)/6-311G(d,p) harmonic frequencies and moments of inertia.
[d] At the CCSD(T,full)/6-311++G(d,p)//MP2(full)/6-311G(d,p) level of theory (kcal mol^{-1}).

Table 4
Total energies (a.u.), zero-point energies (ZPE, a.u.), thermal corrections (TC, a.u.), and total entropies (S, cal mol^{-1} K^{-1}) of the species involved in the reaction between SiF^+ and H_2O (see Fig. 2)

Species	CCSD(T,full)/6-311++G(d,p)[a]	ZPE[b]	TC (298.15 K)[b]	S (298.15 K)[c]	ΔE (0 K)[d]	ΔG (298.15 K)[d]
4	−464.93148	0.02813	0.00441	66.8	−36.5	−28.8
5	−464.90941	0.02449	0.00568	73.0	−24.9	−18.2
6	−464.92671	0.02604	0.00388	64.3	−34.8	−26.7
TS45	−464.87723	0.02352	0.00361	63.8	−5.4	+2.7
TS46	−464.82590	0.02076	0.00462	70.7	+25.1	+31.8
TS56	−464.81293	0.02082	0.00435	66.2	+33.3	+41.2
SiF^+	−388.56354	0.00238	0.00239	51.1	0.0	0.0
H_2O	−76.30587	0.02185	0.00284	45.1		
$SiOH^+$	−364.58741	0.01300	0.00312	53.4	−14.9	−14.3
HF	−100.30421	0.00969	0.00236	41.4		

[a] At the MP2(full)/6-311G(d,p) optimised geometries.

[b] Based on MP2(full)/6-311G(d,p) harmonic frequencies.

[c] Based on MP2(full)/6-311G(d,p) harmonic frequencies and moments of inertia.

[d] At the CCSD(T,full)/6-311++G(d,p)//MP2(full)/6-311G(d,p) level of theory (kcal mol^{-1}).

the constituting fragments, computed, at the CCSD(T,full)/6-311++G(d,p)//MP2(full)/6-311G(d,p) level of theory and 0 K, as 10.0 kcal mol^{-1} for X = Si (8.5 kcal mol^{-1} once corrected for the BSSE) and 12.3 kcal mol^{-1} for X = Ge (10.3 kcal mol^{-1} once corrected for the BSSE), and the consistently long Si–F (2.379 Å) and Ge–F (2.253 Å) bond distances. The corresponding low vibrational modes around 200 cm^{-1} are also typical of non-covalent structures. From Tables 3 and 4, at 0 K isomers **2** and **5** of HOX^+–FH connectivity are less stable than the corresponding isomers **1** and **4** of FX^+–OH_2 connectivity by 11.6 kcal mol^{-1} for X = Si and by 11.7 kcal mol^{-1} for X = Ge.

The interconversion between isomers **1** and **2** and isomers **4** and **5** occurs through the four-centres transition structures **TS12** and **TS45**. Their single imaginary frequencies of 1273.3i and 1322.5i cm^{-1}, respectively, refer to the in-plane motion of the hydrogen atom (H1), which shifts from oxygen to fluorine. Compared with their interconnected minima, the geometries of these transition structures are significantly different, and, consistently, the activation barriers at 0 K are computed as large as 31.1 kcal mol^{-1} for the silicon-containing ions and 25.4 kcal mol^{-1} for the germanium-containing ions.

On the $(X,O,F,H_2)^+$ potential energy surfaces (X = Si and Ge) we have also located the isomers **3** and **6** of FX–(H)–OH^+ connectivity, unambiguously identified as covalent structures by their geometries and harmonic frequencies. As for their stability, at the CCSD(T,full)/6-311++G(d,p)//MP2(full)/6-311G(d,p) level of theory and 0 K, the silicon-containing isomer **6** is less stable than the FSi^+–OH_2 complex **4** by only 1.7 kcal mol^{-1} but more stable than the $HOSi^+$–FH complex **5** by approximately 10 kcal mol^{-1}. On the other hand, the germanium-containing isomer **3** is less stable than the FGe^+–OH_2 complex **1** by 36.6 kcal mol^{-1}, and quite close in energy to the separated GeF^+ and H_2O. This extremely large stability difference between intermediates **3** and **6** reflects the increased tendency, down group XIV, to lower oxidation numbers [63] and is in particular consistent with our recent theoretical evidence [64] for the larger stability of ion-molecule complexes such as FGe^+–(H_2) and FGe^+–(HF) with respect to their corresponding covalent structures F–GeH_2^+ and H–GeF_2^+.

To aid the discussion of the detailed mechanism of reaction (2) (*vide infra*), we have also located the transition structure **TS56** which connects the silicon-containing isomers **5** and **6**. This isomerization occurs through the in-plane motion of the H atom (imaginary frequency: 1533.5i cm^{-1}), and the high activation barrier of 68.1 kcal mol^{-1} with respect to isomer **6** reflects the appreciable structural differences between the minimum and the transition structure.

4. Discussion

The thermochemistry and the mechanistic details of reactions (1) and (2) can be adequately discussed and compared in terms of the potential energy and free energy profiles depicted in Figs. 3 and 4.

As for the ionic product of reaction (1), assuming that the GeF^+ reactant ions, thermalized by unreactive collisions with helium, are in their singlet ground state $^1\Sigma^+$ [1], the process only becomes exothermic through formation of the Ge–OH^+ isomer. On the other hand, assuming the formation of the alternative H–GeO^+ isomer, invariably predicted by various ab initio calculations [62,65–67] to be less stable than Ge–OH^+ by several tens of kilocalories for mole, reaction (1) would result highly endothermic (e.g., by 58.1 kcal mol^{-1} at the CCSD(T,full)/6-311++G(d,p)//MP2(full)/6-311G(d,p) level of theory and 0 K). A similar conclusion holds true for reaction (2), which was so far suggested [36] to occur exclusively by the exothermic formation of the Si–OH^+ isomer.

As to the mechanism of reactions (1) and (2), they could in principle occur by the alternative or concurrent paths reported in Scheme 1.

However, the energy and free energy data reported in Tables 3 and 4 and schematised in Figs. 3 and 4 in practice discard any kinetic role of the FX–(H)–OH^+ intermediates (X = Si

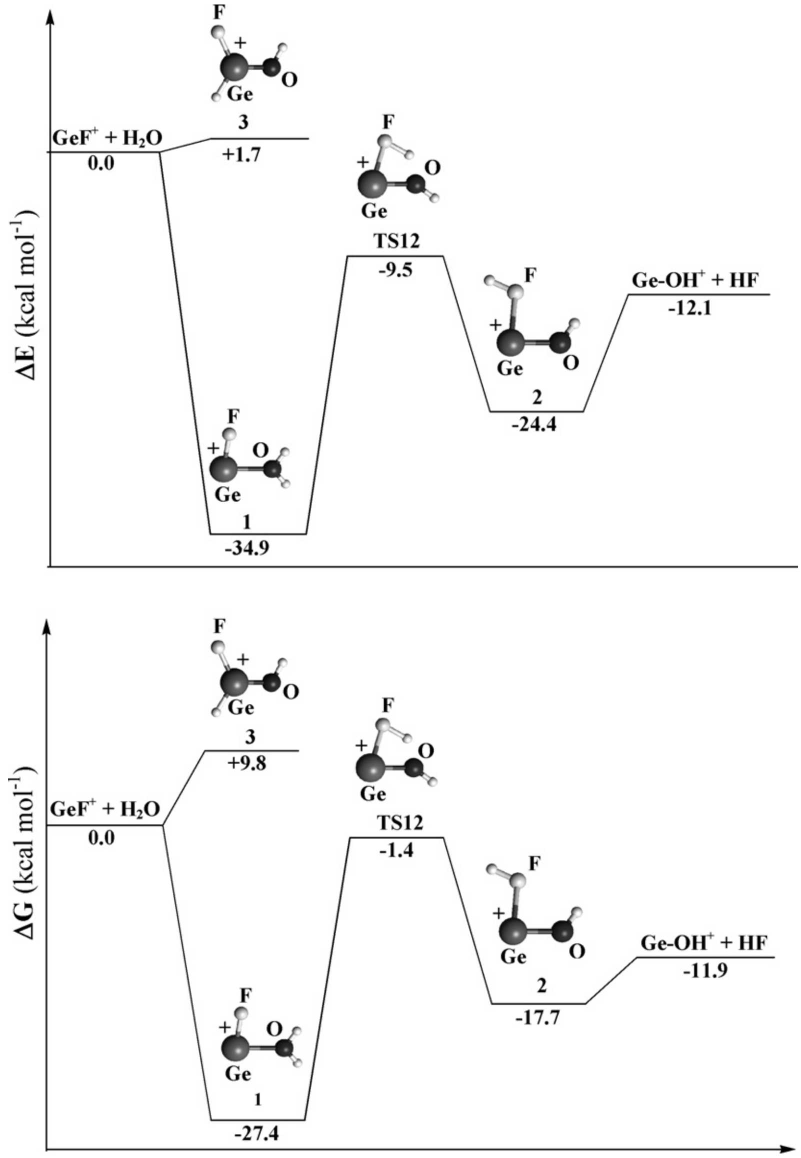


Fig. 3. CCSD(T)/6-311++G(d,p)//MP2(full)/6-311G(d,p) relative energies at 0 K (ΔE) and relative free energies at 298.15 K (ΔG) of the species involved in the reaction between GeF^+ and H_2O.

and Ge) and point to the sequence (**I**) → (**I**′) of Scheme 1 as the exclusive path of both reactions (1) and (2). In fact, for SiF^+, the formation of the FSi–(H)–OH^+ isomer **6** from SiF^+ and H_2O (ascertained to be barrier-free) is exothermic by ca. 35 kcal mol^{-1} and exoergic by ca. 27 kcal mol^{-1}, and the ion results comparably stable with the addition product FSi^+–OH_2. However, the activation barrier for the isomerization **4** → **6** (via **TS46**, see Fig. 4 and Table 4) is computed as 61.6 kcal mol^{-1} at the CCSD(T,full)/6-311++G(d,p)//MP2(full)/6-311G(d,p) level of theory and 0 K and is significantly higher than the $SiF^+ + H_2O$ entrance channel. This rules out the mechanistic path (**I**) → (**I**″) of Scheme 1. In addition, from Fig. 4, the activation barrier for the 1,1-HF elimination from **6**, computed as 68.1 kcal mol^{-1} at the CCSD(T,full)/6-311++G(d,p)//MP2(full)/6-311G(d,p) level of theory and 0 K, is so high that **TS56** protrudes the $SiF^+ + H_2O$ entrance channel by more than 30 kcal for mole and rules out the conceivable occurrence of path (**II**) of Scheme 1. For GeF^+, the FGe–(H)–OH^+ isomer **3** lies ca. 2 kcal mol^{-1} above the GeF^+ and H_2O reactants, and the barrier for the HF extrusion from this intermediate is therefore expected to be significantly higher than the $GeF^+ + H_2O$ entrance channel. Therefore, the first general conclusion from our calculations is that the formation of X–OH^+ from the reaction between singlet ground state XF^+ and H_2O (X = Si and Ge) follows the mechanistic path already suggested for SiF^+ [36] and schematized in the sequence (**I**) → (**I**′) of Scheme 1, namely the exothermic and exoergic formation of the addition product XF^+–OH_2, its isomerization into HOX^+–FH, and the eventual dissociation into HOX^+ and FH (ascertained to be barrier-free). As for the efficiency of these processes, according to the double-well potential model [68], it is qualitatively expected to be a balance of two factors, namely the energy (free energy) gained in the formation of FX^+–OH_2 and the height of the activation barrier for its interconversion into HOX^+–FH. From Figs. 3 and 4, for both SiF^+ and GeF^+, these two ener-

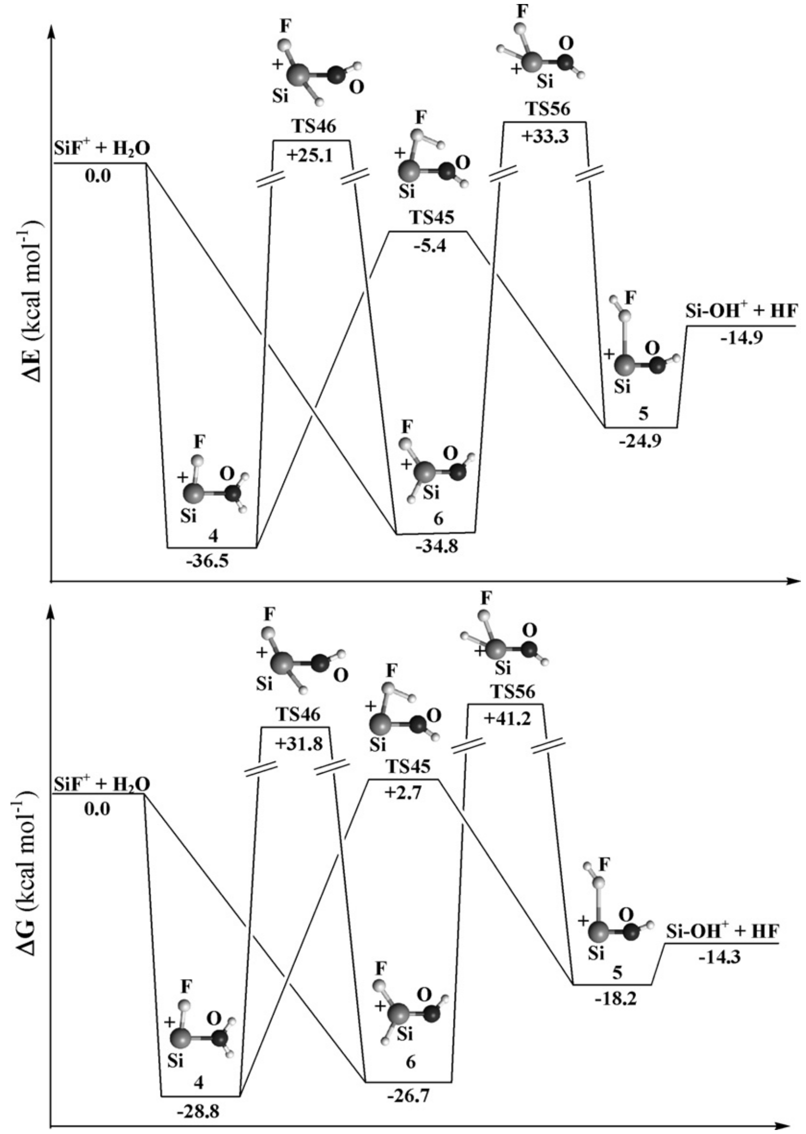
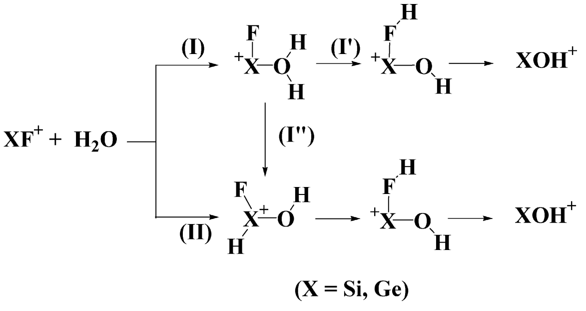


Fig. 4. CCSD(T)/6-311++G(d,p)//MP2(full)/6-311G(d,p) relative energies at 0 K (ΔE) and relative free energies at 298.15 K (ΔG) of the species involved in the reaction between SiF^+ and H_2O.

gies (free energies) are comparably high and, consistent with the ITMS and SIFT experiments, point to ionic processes of relatively low efficiency. From the quantitative point of view, the mass spectrometric measurements suggest also that the rate constant of reaction (1) is approximately five times higher than reaction (2). Whereas this difference may partially reflect the difference in the employed mass spectrometric techniques, and although it is well known that the absolute rate constants of processes occurring by double-well potentials are not simply related to the involved energy differences [68], the theoretical results reinforce the expectation of a higher rate constant for reaction (1). In fact, from Figs. 3 and 4, while the activation energy (free energy) of the **1** → **2** isomerization is lower than the energy (free energy) gained in the formation of **1** from GeF^+ and H_2O by ca. 9 (ca. 1) kcal mol^{-1}, the exothermicity of the formation of **4** from SiF^+ and H_2O is only 5 kcal mol^{-1} higher than the activation energy of the isomerization **4** → **5**, and the exoergicity is even slightly lower than the corresponding free energy barrier.



Scheme 1.

5. Concluding remarks

Our experimental and theoretical investigation on the reaction between GeF^+ and H_2O provides the first insight into the still essentially unexplored reactivity of cationic germanium fluorides. Similar to the previously investigated reaction between SiF^+ and H_2O [36], this process occurs by a typical double-well potential and involves the initial formation of the $FGe^+–OH_2$ intermediate, its isomerization to $HOGe^+–FH$, and the eventual dissociation into $Ge–OH^+$ and HF. Compared with SiF^+, the reaction between GeF^+ and H_2O is apparently more efficient. From a general point of view, this suggests that the $GeF_n{}^+$ cations ($n = 1–3$) could undergo ion-molecule reactions similar to the rich and variegated processes already ascertained for the cationic silicon fluorides [34–36,39–46]. This suggests novel opportunities in the positive ion chemistry of germanium.

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