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Fluoromethyl Cations and Group XIV Congeners $AH_nF_{3-n}^+$ (A = Si, Ge, Sn, Pb; n = 0–2): From Covalent Structures to Ion-Molecule Complexes

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Ab initio calculations at the MP2 and CCSD(T) level of theory (triple-zeta quality basis sets for Si and Ge and effective core potentials plus DZ valence basis sets for tin and lead) have been performed to investigate the geometries, harmonic frequencies and relative stabilities of the $(Si,H,F)^+$, $(Ge,H,F)^+$, $(Si,F_3)^+$, $(Ge,F_3)^+$ and $(A,H_n,F_{3-n})^+$ (A = Si, Ge, Sn, Pb; n = 1 and 2) isomeric ions. While the $H–Si–F^+$, $F–SiH_2^+$, $H–SiF_2^+$ and SiF_3^+ covalent structures are invariably predicted as the most stable isomers, the $Ge^+–(HF)$, $FA^+–(H_2)$ and $FA^+–(HF)$ complexes (A = Ge, Sn, Pb) are the global minima on the potential energy surfaces, more stable than the corresponding covalent structures by up to some tens of kilocalories per mole. For tin and lead, the $HA^+–(HF)$ isomeric ions are also significantly more stable than $F–AH_2^+$ (A = Sn and Pb). Compared with the parent group XIV hydrides $(A,H_3)^+$, investigated so far by Schleyer and co-workers (*J. Am. Chem. Soc.* **1996**, *118*, 12154–12158) and found to possess, for A = Sn and Pb, energetically favoured $HA^+–(H_2)$ connectivities, the structural switch from covalent structures to ion-dipole complexes occurs, therefore, even earlier. This suggests that the "regular" covalent connectivity of even the simplest AH_2X^+ or AHX_2^+ cations of group XIV cannot be taken for granted, and, especially for germanium, tin and lead, the role of ion-molecule complexes must be carefully investigated.
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Introduction

In 1996, Schleyer and co-workers performed a benchmark theoretical study[1] on the structure and stability of the heavier group XIV congeners of the methyl cation. Before that investigation, the D_{3h} geometries of all the AH_3^+ ions (X = C, Si, Ge, Sn, Pb) had been taken for granted, as such species are expected to obey the Walsh rules for six valence electron compounds.[2] As a matter of fact, for CH_3^+ the D_{3h} structure is the only energy minimum located at the highest levels of theory.[3] However, for the heaviest, Sn and Pb, the calculations show[1] that the $HSn^+–(H_2)$ and $HPb^+–(H_2)$ ion-molecule complexes are more stable than the SnH_3^+ and PbH_3^+ D_{3h} covalent structures by about 5 and 23 kcal mol^{-1}, respectively. In addition, although SiH_3^+ and GeH_3^+ are more stable than $HSi^+–(H_2)$ and $HGe^+–(H_2)$, the energy difference between the covalent structure and the ion-molecule complex substantially reduces from about 28 to about 10 kcal mol^{-1} passing from silicon to germanium.[1] The order of stability of the GeH_3^+ and $HGe^+–(H_2)$ isomers has been more recently confirmed by Schwarz and co-workers,[4] who have also found that the $Ge^+–(H_2)$ complex is nearly degenerate with the $H–Ge–H^+$ covalent structure (C_{2v} symmetry) and plays an active role in the gas-phase ion chemistry of GeH_2^+. The order of stability of $Si^+–(H_2)$ and $H–Si–H^+$ is, however, opposite, and the latter species is more stable by about 12 kcal mol^{-1}.[5] From a general point of view, these theoretical and experimental findings are in line with the increased tendency, down group XIV, toward lower oxidation numbers, clearly evident, for example, in the thermodynamic instability of various Pb(IV) compounds.[6,7] Concerning the structure of cations such as AHX^+, AX_2^+, AH_2X^+, AHX_2^+ and AX_3^+ (A = C, Si, Ge, Sn, Pb; X = monovalent group), they are usually assumed to be "regular" covalent structures and the conceivable role of ion-molecule complexes such as $A^+–(HX)$, $AH^+–(HX)$ or $AX^+–(H_2)$ is still essentially unexplored. As a first step in this direction, stimulated by our continuing interest in the chemistry of fluorinated cations,[8] we report here an ab initio study on the heavier congeners of the fluoromethyl cations CH_2F^+, CHF_2^+ and CF_3^+, which are known to possess covalent structures of C_{2v} or D_{3h} symmetry,[9–12] as well as on the additional exemplary species $SiHF^+$ and $GeHF^+$. While the $(Si,H,F)^+$ and $(Si,H_n,F_{3-n})^+$ (n = 0–3) isomeric ions are structurally similar to their carbon congeners, the global minima on the $(Ge,H,F)^+$,

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$(A,H_2,F)^+$ and $(A,H,F_2)^+$ potential energy surfaces (A = Ge, Sn, Pb) are invariably ion-molecule complexes such as $Ge^+–(HF)$, $HA^+–(HF)$ or $FA^+–(H_2)$. Therefore, our calculations provide additional examples of only "seemingly familiar"[1] compounds of group XIV and confirm the crucial role of noncovalent isomers in the gas-phase ion chemistry of the heaviest elements: germanium, tin and lead.

Results and Discussion

All the $(Si,H,F)^+$, $(Ge,H,F)^+$, $(Si,F_3)^+$, $(Ge,F_3)^+$ and $(A,H_n,F_{3-n})^+$ (A = Si, Ge, Sn, Pb; n = 1 and 2) isomeric ions shown in Figure 1, Figure 2, Figure 3 and Figure 4 have been characterised as minimum points on the MP2(full)/6-311G(d,p) (Si and Ge) or MP2(full)/6-311G(d,p)/LANL2DZ (Sn and Pb) potential energy surfaces. Their harmonic frequencies are listed in Tables 1S–4S of the supporting information. The geometries of the silicon- and germanium-containing ions were also refined at the CCSD(T,full)/cc-pVTZ level of theory, finding however only minor differences with the MP2(full)/6-311G(d,p) bond lengths and bond angles. The CCSD(T,full)/cc-pVTZ-optimised structures were finally used to perform CCSD(T,full)/aug-cc-pVTZ single-point calculations, so as to obtain accurate estimates of the relative stability of the various isomers and to evaluate the accuracy of the corresponding values obtained by MP2 calculations. The obtained data, reported in Table 1 and Table 2, reveal that the MP2(full)/6-311G(d,p) level of theory invariably predicts the correct order of stability of the various isomers but in general overestimates the stability of the ion-molecule com-

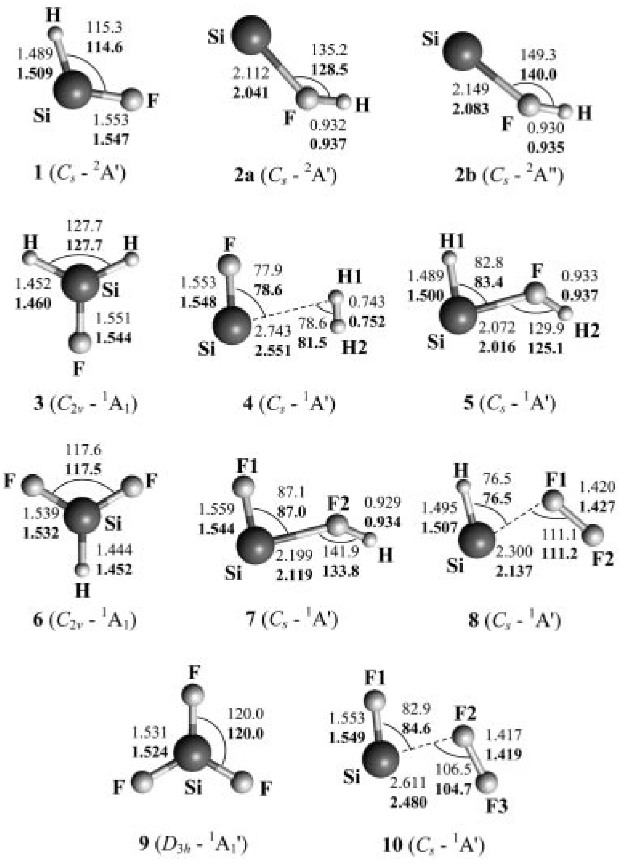

Figure 1. MP2(full)/6-311G(d,p) and CCSD(T,full)/cc-pVTZ-optimised (bold) geometries [Å and °] of the $(Si,H,F)^+$ and $(Si,H_n,F_{3-n})^+$ isomeric ions (n = 0–3).

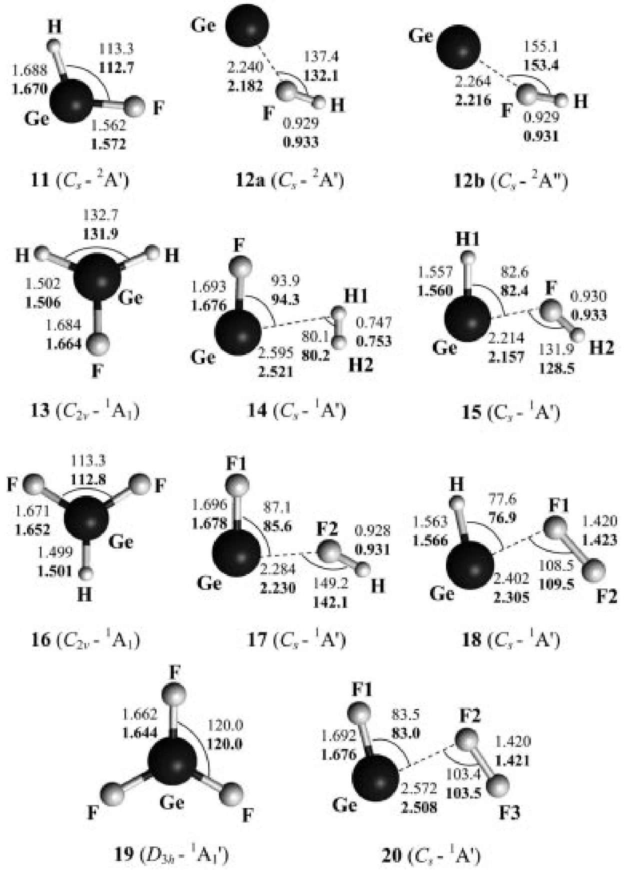

Figure 2. MP2(full)/6-311G(d,p) and CCSD(T,full)/cc-pVTZ-optimised (bold) geometries [Å and °] of the $(Ge,H,F)^+$ and $(Ge,H_n,F_{3-n})^+$ isomeric ions (n = 0–3).

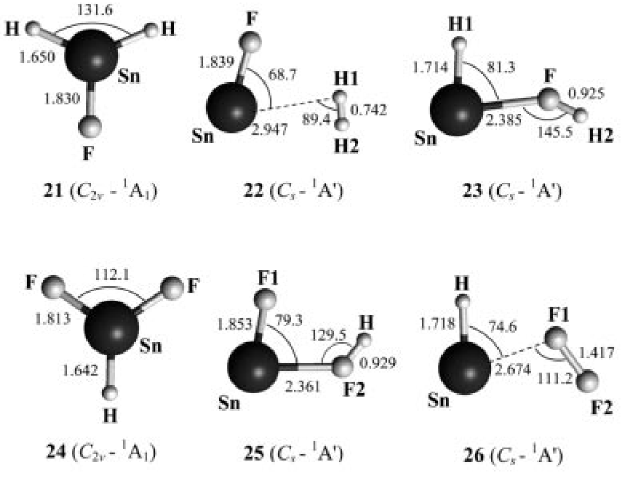

Figure 3. MP2(full)/6-311G(d,p)/LANL2DZ-optimised geometries [Å and °] of the $(Sn,H_2,F)^+$ and $(Sn,H,F_2)^+$ isomeric ions.

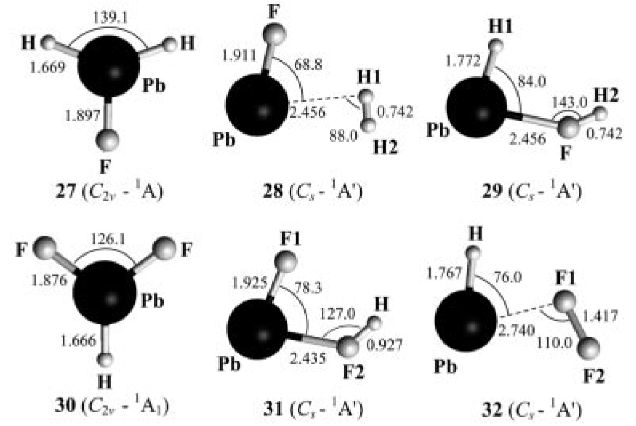

Figure 4. MP2(full)/6-311G(d,p)/LANL2DZ-optimised geometries [Å and °] of the $(Pb,H_2,F)^+$ and $(Pb,H,F_2)^+$ isomeric ions.

plexes by about 4–6 kcal mol^{-1} for the silicon-containing ions and by about 10–12 kcal mol^{-1} for the germanium-containing ions. On the other hand, from Table 3, the large energy differences of up to some tens of kilocalories per mole predicted at the MP2(full)/6-311G(d,p)/LANL2DZ level of theory between the various $(A,H_2,F)^+$ and $(A,H,F_2)^+$ (A = Sn and Pb) isomeric structures are confirmed, within a few kilocalories per mole, by CCSD(T) single-point calculations.

Structure and Stability of the $(Si,H,F)^+$ and $(Si,H_n,F_{3-n})^+$ Isomeric Ions (n = 0–3)

The optimised parameters and the harmonic frequencies of the bent H–Si–F$^+$ isomer **1**[13] are in very good agreement with previous HF/6-31G(d) data[14,15] and identify the cat-

Table 1. Total energies (atomic units), zero-point energies (ZPE, atomic units), thermal corrections (TC, atomic units) and total entropies (S, cal·mol^{-1} K^{-1}) of the $(Si,H,F)^+$ and $(Si,H_n,F_{3-n})^+$ (n = 0–3) isomeric ions (see Figure 1).

Species	CCSD(T,full)/aug-cc-pVTZ[a]	ZPE[b]	TC (298.15 K)[b]	S (298.15 K)[c]	ΔE (0 K)[d]	ΔG (298.15 K)[d]
			$(Si,H,F)^+$			
1	–389.12644	0.00890	0.00297	58.1	0.0 (0.0)	0.0 (0.0)
2a	–389.09152	0.01073	0.00353	59.8	+23.1 (+17.2)	+22.9 (+17.0)
2b	–389.08922	0.01036	0.00373	60.0	+24.3 (+18.0)	+24.2 (+17.9)
			$(Si,H_2,F)^+$			
3	–389.78084	0.01917	0.00310	56.6	0.0 (0.0)	0.0 (0.0)
4	–389.76142	0.01463	0.00497	67.0	+9.3 (+8.9)	+7.4 (+7.0)
5	–389.71984	0.01868	0.00388	61.3	+38.0 (+34.2)	+37.1 (+33.3)
			$(Si,H,F_2)^+$			
6	–489.00399	0.01445	0.00352	61.9	0.0 (0.0)	0.0 (0.0)
7	–488.97642	0.01373	0.00484	69.6	+16.9 (+10.8)	+15.4 (+9.3)
8	–488.67361	0.00967	0.00490	70.4	+204.3 (+203.5)	+202.7 (+201.9)
			$(Si,F_3)^+$			
9	–588.21217	0.00959	0.00412	64.7	0.0 (0.0)	0.0 (0.0)
10	–587.93165	0.00521	0.00596	81.1	+173.3 (+169.1)	+169.5 (+165.3)

[a] At the CCSD(T,full)/cc-pVTZ-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)/aug-cc-pVTZ//CCSD(T)/cc-pVTZ level of theory. The MP2(full)/6-311G(d,p) values are given in parentheses.

Table 2. Total energies (atomic units), zero-point energies (ZPE, atomic units), thermal corrections (TC, atomic units) and total entropies (S, cal·mol^{-1} K^{-1}) of the $(Ge,H,F)^+$ and $(Ge,H_n,F_{3-n})^+$ (n = 0–3) isomeric ions (see Figure 2).

Species	CCSD(T,full)/aug-cc-pVTZ[a]	ZPE[b]	TC (298.15 K)[b]	S (298.15 K)[c]	ΔE (0 K)[d]	ΔG (298.15 K)[d]
			$(Ge,H,F)^+$			
11	–2175.66017	0.00740	0.00308	61.5	0.0 (0.0)	0.0 (0.0)
12a	–2175.66498	0.01057	0.00365	63.1	–1.0 (–13.9)	–1.2 (–14.1)
12b	–2175.66326	0.01018	0.00389	63.2	–0.2 (–13.4)	–0.2 (–13.4)
			$(Ge,H_2,F)^+$			
13	–2176.30594	0.01731	0.00325	59.9	0.0 (0.0)	0.0 (0.0)
14	–2176.30696	0.01459	0.00469	68.2	–2.4 (–8.7)	–4.0 (–10.3)
15	–2176.28782	0.01765	0.00414	65.2	+11.6 (+0.6)	+10.6 (–0.4)
			$(Ge,H,F_2)^+$			
16	–2275.49306	0.01225	0.00383	65.5	0.0 (0.0)	0.0 (0.0)
17	–2275.52119	0.01266	0.00525	74.2	–17.4 (–29.6)	–19.1 (–31.3)
18	–2275.24304	0.00893	0.00507	74.0	+154.8 (+145.9)	+153.1 (+144.2)
			$(Ge,F_3)^+$			
19	–2374.66216	0.00722	0.00464	68.7	0.0 (0.0)	0.0 (0.0)
20	–2374.47694	0.00463	0.00602	83.4	+114.6 (+104.6)	+111.1 (+101.1)

[a] At the CCSD(T,full)/cc-pVTZ-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)/aug-cc-pVTZ//CCSD(T)/cc-pVTZ level of theory. The MP2(full)/6-311G(d,p) values are given in parentheses.

Table 3. MP2(full)/6-311G(d,p)/LANL2DZ total energies (*E*, atomic units), zero-point energies (ZPE, atomic units), thermal corrections (TC, atomic units) and total entropies (*S*, cal·mol^{-1} K^{-1}) of the $(M,H_2,F)^+$ and $(M,H,F_2)^+$ isomeric ions (M = Sn and Pb) (see Figures 3 and 4).

Species	*E*	ZPE	TC (298.15 K)	*S* (298.15 K)	Δ*E* (0 K)[a]	Δ*G* (298.15 K)[a]
			$(Sn,H_2,F)^+$			
21	–103.87133	0.01560	0.00340	62.1	0.0 (0.0)	0.0 (0.0)
22	–103.91097	0.01373	0.00512	72.2	–26.0 (–27.2)	–28.0 (–29.2)
23	–103.89916	0.01649	0.00450	68.4	–16.9 (–19.6)	–18.1 (–20.8)
			$(Sn,H,F_2)^+$			
24	–202.98699	0.01079	0.00406	68.0	0.0 (0.0)	0.0 (0.0)
25	–203.06645	0.01323	0.00480	73.5	–48.3 (–50.6)	–49.5 (–51.8)
26	–202.78237	0.00797	0.00538	77.6	+126.6 (+113.6)	+124.6 (+111.6)
			$(Pb,H_2,F)^+$			
27	–103.93178	0.01498	0.00347	64.1	0.0 (0.0)	0.0 (0.0)
28	–104.01583	0.01379	0.00504	73.5	–53.5 (–52.8)	–55.3 (–54.6)
29	–104.00859	0.01634	0.00445	70.0	–47.3 (–48.6)	–48.5 (–49.8)
			$(Pb,H,F_2)^+$			
30	–203.03090	0.00987	0.00426	70.4	0.0 (0.0)	0.0 (0.0)
31	–203.16985	0.01303	0.00492	76.0	–85.2 (–86.0)	–86.5 (–87.3)
32	–202.89244	0.00757	0.00551	80.3	+85.4 (+73.7)	+83.3 (+71.6)

[a] The values in parentheses are based on CCSD(T,full)/6-311G(d,p)/LANL2DZ single-point calculations.

ion as a typical covalent structure, with Si–H and Si–F bond lengths of about 1.5 Å and corresponding stretching frequencies around 2150 and 1050 cm^{-1}, respectively. On the other hand, the geometries and harmonic frequencies of the nearly degenerate Si^+–(HF) isomers **2a** and **2b**, located as distinct minima on the A′ and A′′ doublet potential energy surface, point to ion-dipole complexes between Si^+ and HF. The Si–F bond lengths are longer than 2.0 Å, the corresponding stretching frequencies range around 250 cm^{-1} and the CCSD(T,full)/aug-cc-pVTZ//CCSD(T,full)/cc-pVTZ dissociation energies into $Si^+(^2P)$ and HF amount to 22.3 kcal mol^{-1} for isomer **2a** and 21.1 kcal mol^{-1} for isomer **2b**. At the same computational level, the two ions are less stable than **1** by 23.1 and 24.3 kcal mol^{-1}, respectively. This difference is larger than the energy gap between SiH_2^+ (C_{2v}) and Si^+–(H_2), obtained so far as 11.5 kcal mol^{-1} at the complete active space SCF level of theory followed by second-order CI (CASSCF–SOCI)[5] and presently confirmed as 11.4 kcal mol^{-1} at the CCSD(T,full)/aug-cc-pVTZ//CCSD(T,full)/cc-pVTZ level of theory.

The geometries and harmonic frequencies of the F–SiH_2^+ isomer **3** and of the H–SiF_2^+ isomer **6** of C_{2v} symmetry are also in good agreement with previous HF,[14–16] MP2[10,17] and CASSCF[18] ab initio studies and are again typical of covalent structures. On the other hand, the bond lengths, harmonic frequencies and dissociation energies of the $(Si,H_2,F)^+$ isomers **4** and **5**, and of the $(Si,H,F_2)^+$ isomers **7** and **8**, point to ion-molecule complexes between ground-state $SiF^+(^1\Sigma^+)$[19] and H_2 (**4**) or HF (**7**), and ground-state $SiH^+(^1\Sigma^+)$[20] and HF (**5**) or F_2 (**8**). The bond lengths between the constituting moieties range from about 2.0 Å (isomer **5**) to about 2.6 Å (isomer **4**), and their CCSD(T,full)/aug-cc-pVTZ//CCSD(T,full)/cc-pVTZ interaction energies, computed as 3.3 kcal mol^{-1} for isomer **4**, 8.4 kcal mol^{-1} for isomer **8**, and 22.1 and 18.6 kcal mol^{-1}, respectively, for isomers **5** and **7**, parallel the increasing solvation ability of H_2, F_2 and HF. From Table 1, these ions are less stable than the corresponding covalent structures **3** or **6** by 9.3 kcal mol^{-1} (isomer **4**), 38.0 kcal mol^{-1} (isomer **5**), 16.9 kcal mol^{-1} (isomer **7**) and 204.3 kcal mol^{-1} (isomer **8**) (in the context of the protonation of SiF_2, the energy difference between isomers **6** and **7** has been obtained[21] as 15.9 kcal mol^{-1} at the G2 level of theory). These energy differences and orders of stabilities, namely FSi^+–(H_2) > HSi^+–(HF) and FSi^+–(HF) >> HSi^+–(F_2), reflect a balance of several factors, including the different strength of the Si–H$^+$ and Si–F$^+$ covalent bonds[22] (75 vs. 151 kcal mol^{-1}), the different thermodynamic stability of H_2, HF and F_2, and the different solvation ability of these ligands. Consistently, the ion-molecule complex **10**, arising from the weak interaction [5.5 kcal mol^{-1} at the CCSD(T,full)/aug-cc-pVTZ//CCSD(T,full)/cc-pVTZ level of theory] between SiF^+ and the highly unstable, poorly solvating F_2, is less stable than SiF_3^+ (D_{3h}) by more than 170 kcal mol^{-1}.

Structure and Stability of the $(Ge,H,F)^+$ and $(Ge,H_n,F_{3-n})^+$ Isomeric Ions (n = 0–3)

As already pointed out in the Introduction, the energy difference of about 28 kcal mol^{-1} between SiH_3^+ (D_{3h}) and HSi^+–(H_2)[1] is reduced to about 10 kcal mol^{-1} for GeH_3^+ and HGe^+–(H_2).[4] Similarly, H–Si–H$^+$ (C_{2v}) is more stable than Si^+–(H_2) by about 11 kcal mol^{-1},[5] but, according to highly accurate ab initio calculations,[4] H–Ge–H$^+$ and Ge^+–(H_2) are nearly degenerate. Therefore, passing from $(Si,H,F)^+$ and $(Si,H_n,F_{3-n})^+$ (n = 0–3) to $(Ge,H,F)^+$ and $(Ge,H_n,F_{3-n})^+$ (n = 0–3), one expects an overall stabilisation of the ion-molecule complexes with respect to the corresponding covalent structures. From Table 2, the clearest confirmation of this qualitative expectation is the high stability of the FGe^+–(HF) isomer **17**, which is more stable than the covalent H–GeF_2^+ (**16**) by more than 17 kcal mol^{-1} at the CCSD(T,full)/aug-cc-pVTZ//CCSD(T,full)/cc-pVTZ level of theory. The $FGe^+–(H_2)$ isomer **14** is also more stable than $F–GeH_2^+$ (**13**) by about 2 kcal mol^{-1}, while the two $Ge^+–(HF)$ isomers **12a** and **12b**, located as distinct energy minima on the A′ and A′′ doublet potential energy surfaces, are nearly degenerate with the $H–Ge–F^+$ cation **11**. Ions **12a**, **12b**, **14** and **17**, as well as the $HGe^+–(HF)$ isomer **15** and the $HGe^+–(F_2)$ isomer **18** feature bond lengths, bond angles and harmonic frequencies that point to ion-molecule complexes between ground state $Ge^+(^2P)$, $GeH^+(^1\Sigma^+)$[23] and $GeF^+(^1\Sigma^+)$,[24] and H_2, HF or F_2. Similar to their silicon congeners, the distances between the constituting moieties range in fact from about 2.0 Å to more than 2.5 Å and the CCSD(T,full)/aug-cc-pVTZ//CCSD(T,full)/cc-pVTZ interaction energies regularly increase from the H_2 complex **14** (4.6 kcal mol^{-1}) to the F_2 complex **18** (8.6 kcal mol^{-1}), and arrive at about 20–22 kcal mol^{-1} for the HF complexes **12**, **15** and **17**. In addition, the orders of stability of these isomers, namely $FGe^+–(H_2) > HGe^+–(HF)$ and $FGe^+–(HF) >> HGe^+–(F_2)$, parallel that of their silicon congeners and again reflect the increasing strength of $Ge–H^+$ and $Ge–F^+$ covalent bonds (68 vs. 125 kcal mol^{-1}), and the different thermodynamic stability and solvation ability of H_2, HF and F_2. It is therefore not surprising that the $FGe^+–(F_2)$ loosely bound complex **20** (the interaction between GeF^+ and F_2 amounts to 7.0 kcal mol^{-1}) is less stable than GeF_3^+ (D_{3h}) by 114.6 kcal mol^{-1}.

Structure and Stability of the $(A,H_2,F)^+$ and $(A,H,F_2)^+$ Isomeric Ions (A = Sn and Pb)

Passing to the tin- and lead-containing ions $(A,H_2,F)^+$ and $(A,H,F_2)^+$ (A = Sn and Pb), with the only exception of the $HSn^+–(F_2)$ isomer **26** and the $HPb^+–(F_2)$ isomer **32**, all the $FA^+–(H_2)$, $HA^+–(HF)$ and $FA^+–(HF)$ isomers, **22**, **23**, **25**, **28**, **29** and **31** (A = Sn and Pb), become appreciably more stable than the corresponding covalent structures **21** ($F–SnH_2^+$), **24** ($H–SnF_2^+$), **27** ($F–PbH_2^+$) and **30** ($H–PbF_2^+$). The MP2(full)/6-311G(d,p)/LANL2D energy differences amount to about 17 kcal mol^{-1} for $HSn^+–(HF)$ and 26.0 kcal mol^{-1} for $FSn^+–(H_2)$, range around 50 kcal mol^{-1} for $FSn^+–(HF)$, $FPb^+–(H_2)$ and $HPb^+–(HF)$, and become as large as about 85 kcal mol^{-1} for the $FPb^+–(HF)$ isomer. The values obtained by CCSD(T) single-point calculations are essentially similar, but these estimates could be in principle appreciably affected by geometry optimisations. We note in fact from Figure 1 and Figure 2 that, for the Si and Ge analogues, the MP2 distances of the ion-neutral complexes are considerably larger than the CCSD(T) values.

From Figure 3 and Figure 4, any $FA^+–(H_2)$, $HA^+–(HF)$, $HA^+–(F_2)$ and $FA^+–(HF)$ isomeric structure (A = Sn and Pb) features bond lengths between the constituting moieties that are typical of ion-molecule complexes. In addition, similar to their silicon and germanium congeners, their stabilisation energies with respect to the separated ions and neutrals, computed as about 0.5 kcal mol^{-1} for isomers **22** and **28**, about 3 kcal mol^{-1} for isomers **26** and **32**, and about 17–24 kcal mol^{-1} for isomers **23**, **25**, **29** and **31**, are again related to the increasing solvation ability of their constituting H_2, F_2 or HF neutral moieties. They also follow the orders of stability already noted for Si and Ge, namely $FA^+–(H_2) > HA^+–(HF)$ and $FA^+–(HF) >> HA^+–(F_2)$ (A = Sn and Pb).

Concluding Remarks

The benchmark theoretical study by Schleyer and coworkers[1] on cationic hydrides of group XIV first disclosed a periodic structural switch from covalent structures to ion-molecule complexes, which results in particular in the higher stability of $HSn^+–(H_2)$ and $HPb^+–(H_2)$ with respect to SnH_3^+ and PbH_3^+. The results of our calculations indicate that, for the fluorine-substituted cations, this structural switch occurs even earlier and ion-molecule complexes such as $FGe^+–(H_2)$ and $FGe^+–(HF)$, as well as $Ge^+–(HF)$, are already more stable than their corresponding covalent structures. In addition, for the tin- and lead-containing analogues, the energy differences become as large as some tens of kilocalories per mole. From a general point of view, these findings suggest that the covalent structure of even the simplest AH_2X^+- or AHX_2^+-substituted cations of group XIV cannot be taken for granted, and, especially for the ions containing germanium, tin and lead, the role of ion-molecule complexes such as $A^+–(HX)$, $AH^+–(HX)$ or $AX^+–(H_2)$ must be carefully investigated.

Computational Details

The quantum chemical calculations were performed using Unix versions of the Gaussian03[25] and MOLPRO 2000.1[26] sets of programs installed on an Alphaserver 1200 and an HP Proliant DL585 machine. The geometries of all the silicon- and germanium-containing ions were first optimised, using the 6-311G(d,p) basis set,[27] at the second-order Møller-Plesset level of theory with inclusion of the inner electrons, MP2(full),[28] and subsequently refined, using the Dunning's correlation consistent triple-zeta basis set (cc-pVTZ) [29] 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).[30,31] To evaluate the influence of diffuse functions, single-point calculations were finally performed at the CCSD(T,full) level of theory with the aug-cc-pVTZ basis set. For the doublet state species, we used the spin-restricted coupled cluster theory as implemented in MOLPRO.[32,33] The MP2(full)/6-311G(d,p) unscaled frequencies were 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.[34] The overall TC term was finally obtained by adding the translational (3/2 RT) and rotational (RT) contributions at this temperature. The structure and harmonic frequencies of the tin- and lead-containing species were computed at the MP2(full) level of theory using the 6-311G(d,p) basis set for H and F and the Los Alamos ECP plus DZ (LANL2DZ) for Sn and Pb.[35]

Supporting Information (see footnote on the first page of this article): Tables 1S–4S containing the MP2(full)/6-311G(d,p) and

MP2(full)/6-311G(d,p)/LANL2DZ harmonic frequencies of the presently investigated ions.

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