Cationic Germanium Fluorides: A Theoretical Investigation on the Structure, Stability, and Thermochemistry of GeF_n/GeF_n^+ ($n = 1-3$)

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The structure, harmonic frequencies, enthalpies of formation, and dissociation energies of the GeF_n^+ cations ($n = 1-3$) and of their neutral counterparts GeF_n have been investigated at the MP2 and CCSD(T) levels of theory and discussed in connection with previous experimental and theoretical data. The CCSD(T,full)/cc-pVTZ-optimized geometries and MP2(full)/6-311G(d) harmonic frequencies are 1.744 Å and 668.0 cm^{-1} for GeF($^2\Pi$), 1.670 Å and 798.6 cm^{-1} for GeF^+($^1\Sigma^+$), 1.731 Å/97.4° and 267.0 (a_1)/673.1 (b_2)/690.6 (a_1) cm^{-1} for GeF_2(C_{2v},$^1A_1$), 1.666 Å/116.9° and 202.3 (a_1)/769.6 (a_1)/834.6 (b_2) cm^{-1} for GeF_2^+(C_{2v},$^2A_1$), 1.706 Å/112.2° and 214.4 (e)/273.1 (a_1)/699.6 (a_1)/734.1 (e) cm^{-1} for GeF_3(C_{3v},$^2A_1$), and 1.644 Å and 211.4 (e′)/229.9 (a_2'')/757.4 (a_1')/879.3 (e′) cm^{-1} for GeF_3^+(D_{3h},$^1A_1$). These calculated values are in excellent agreement with the experimental data reported for GeF, GeF^+, and GeF_2, and should be therefore of good predictive value for the still unexplored GeF_2^+, GeF_3, and GeF_3^+. The comparison of the CCSD(T,full)/cc-pVTZ enthalpies of formation at 298.15 K, −11.6 (GeF), −125.9 (GeF_2), −180.4 (GeF_3), 158.4 (GeF^+), 134.1 (GeF_2^+), and 44.8 (GeF_3^+) kcal mol^{-1}, with the available experimental data, especially for the cations, shows discrepancies which suggest the need for novel and more refined measurements. On the other hand, the computed adiabatic ionization potentials of GeF, 7.3 eV, GeF_2, 11.2 eV, and GeF_3, 9.7 eV, are in good agreement with the available experimental estimates.

1. Introduction

The properties of neutral germanium fluorides GeF_n ($n = 1-5$) have been intensively investigated over the years by various experimental and theoretical methods,[1−51] not only for fundamental reasons but also for their active role in the fine processing of semiconductors.[52−54] More recently, the structure, stability, and thermochemistry of the corresponding anionic species GeF_n^- ($n = 1-5$) have been systematically investigated by density functional methods,[41] and discussed in connection with previous related experimental and theoretical data.[3j,k,35−37,55−60] As for cationic germanium fluorides, experimental and theoretical studies[55a,61] 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.[55a] The GeF^+ and GeF_2^+ ions have also been investigated by spectroscopic methods,[19a,62] and various calculations, at different levels of theory, have been performed over the years to investigate the properties of GeF_n^+ ($n = 1-3$).[32,36,63−65] However, a comparative theoretical study on the structure, stability, and thermochemistry of these species, performed at a uniform and accurate level of theory, is still missing. Therefore, as part of our continuing interest in the chemistry of fluorinated inorganic ions,[66] we decided to undertake the computational investigation of GeF_n^+ ($n = 1-3$) and of their neutral counterparts GeF_n. The obtained results will be discussed in the present paper.

2. Computational Methods

The quantum chemical calculations have been performed using Unix versions of the Gaussian03[67] and MOLPRO 2000.1[68] sets of programs installed on an Alphaserver 1200 and an HP Proliant DL585 machine. The geometries of GeF_n and GeF_n^+ ($n = 1-3$) were first optimized, using the 6-311G(d) basis set,[69] at the second-order Møller−Plesset level of theory with inclusion of the inner electrons, MP2(full),[70] and subsequently refined, using Dunning's correlation-consistent triple-ζ basis set (cc-pVTZ),[71] 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).[72,73] For the doublet-state species, we used the spin-restricted coupled cluster theory as implemented in MOLPRO.[74,75] The MP2(full)/6-311G(d) unscaled frequencies were used to calculate the zero-point vibrational energies (ZPEs) of the investigated species and the vibrational contribution to their thermal correction (TC), obtained at 298.15 K by standard statistical mechanics formulas.[76] The overall TC term was finally obtained by adding the translational ($^3/_2$(RT)) and rotational (RT) contributions at this temperature. The enthalpies of formation were determined by the atomization energy procedure,[77] taking from the JANAF-NIST tables[78] the enthalpies of formation at 298.15 K of Ge, Ge^+, F, and F^+.

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3. Results and Discussion

The optimized geometries and harmonic vibrational frequencies of GeF_n and GeF_n^+ ($n = 1-3$) are collected in Tables 1 and 2, and their absolute energies, reported in Table 3, have been used to derive the thermochemical data collected in Tables 4−6. We have included in particular the adiabatic ionization potentials (IPs) of GeF_n ($n = 1-3$), obtained as the difference between the absolute energies of GeF_n^+ and GeF_n, the bond dissociation enthalpies (BDHs) of GeF_n and GeF_n^+, namely, the enthalpy changes of the reactions (all reagents and products in their ground state)

$$GeF_n \rightarrow GeF_{n-1} + F \qquad (1)$$

$$GeF_n^+ \rightarrow GeF_{n-1}^+ + F \qquad (2)$$

and the enthalpies of formation ($\Delta_f H_{298.15}$) of GeF_n and GeF_n^+. The values of the neutral species have been obtained by combining the CCSD(T,full)/cc-pVTZ enthalpy change at 298.15 K of the atomization reaction

$$GeF_n \rightarrow Ge(^3P) + nF(^2P)$$

with the experimental enthalpies of formation[78] of Ge, 89 kcal mol^{-1}, and F, 18.97 kcal mol^{-1}. For the cationic species, they are the average of the two independent estimates obtained by combining the CCSD(T,full)/cc-pVTZ enthalpy changes of the dissociations

$$GeF_n^+ \rightarrow Ge^+(^2P) + nF(^2P)$$

$$GeF_n^+ \rightarrow Ge(^3P) + F^+(^3P) + (n-1)F(^2P)$$

with the experimental enthalpies of formation of Ge, Ge^+, 271.2 kcal mol^{-1}, F, and F^+, 415.6 kcal mol^{-1}. For comparative purposes, we have also reported in Tables 1, 2, and 4−6 relevant information from previous experimental and theoretical studies.

3.a. Ge and Ge^+. The CCSD(T,full)/cc-pVTZ IP of ground-state $Ge(^3P)$ is 7.9 eV and is in perfect agreement with the two most accurate experimental values of 7.899 eV[79] and 7.89944 ± 0.00002 eV[80] obtained from spectroscopic methods.

TABLE 1: Theoretical and Experimental (in Parentheses) Geometrical Parameters of GeF_n and GeF_n^+ ($n = 1-3$)[a]

species	sym	Ge−F	F−Ge−F
$GeF(^2\Pi)$	$C_{\infty v}$	1.744[b]	
		1.727[c]	
		1.760[d]	
		1.736[e]	
		(1.745)[f]	
		(1.7495)[g]	
$GeF^+(^1\Sigma^+)$	$C_{\infty v}$	1.670[b]	
		1.669[h]	
		(1.665)[i]	
$GeF_2(^1A_1)$	C_{2v}	1.731[b]	97.4[b]
		1.745[d]	97.2[d]
		1.727[e]	97.8[e]
		1.723[j]	97.1[j]
		1.732[k]	97.6[k]
		1.750[l]	97.8[l]
		(1.73 ± 0.05)[m]	(94 ± 4)[m]
		(1.732)[n]	(97.15)[n]
$GeF_2^+(^2A_1)$	C_{2v}	1.666[b]	116.9[b]
		1.651[j]	117.2[j]
		1.777[o]	127.0[o]
$GeF_3(^2A_1)$	C_{3v}	1.706[b]	112.2[b]
		1.716[d]	106.4[d]
		1.706[e]	106.6[e]
$GeF_3^+(^1A_1)$	D_{3h}	1.644[b]	
		1.677[p]	

[a] Bond lengths in angstroms and bond angles in degrees. [b] CCSD(T,full)/cc-pVTZ, present work. [c] CASSCF/second-order CI, ref 31. [d] BHLYP/DZP++, ref 41. [e] MP2(full)/6-31G(2df), ref 48. [f] From microwave spectroscopy, ref 8a. [g] From microwave spectroscopy, ref 20. [h] CASSCF/second-order CI, ref 64. [i] From infrared diode laser spectroscopy, ref 62a. [j] MRSDCI(+Q) with relativistic ECPs of Christiansen et al., ref 32. [k] CCSD/DZP(2f), ref 33. [l] CCSD(T) with relativistic ECPs of the Stuttgart/Bonn group, ref 47. [m] From infrared spectroscopy, ref 3d. [n] From microwave spectroscopy, ref 6b. [o] Nonlocal spin density/Perdew−Yang functional, ref 36. [p] MP2/VDZ+P, ref 65.

TABLE 2: Harmonic Vibrational Frequencies (cm^{-1}) of GeF_n and GeF_n^+ ($n = 1-3$)

species	sym	type	theory	expt
GeF	σ	stretch	668.0,[a] 633,[b] 662.3,[c] 710[d]	665.7,[e] 662.4,[f] 670 ± 80[g]
GeF^+	σ	stretch	798.6,[a] 770[h]	815.6[i]
$GeF_2(C_{2v})$	a_1	bend	267.0,[a] 253.1,[c] 250[d]	263,[j] 265,[k] 263.9[l]
	b_2	stretch	673.1,[a] 662.1,[c] 689[d]	663,[j] 677[k]
	a_1	stretch	690.6,[a] 686.3,[c] 709[d]	692,[j] 707[k]
$GeF_2^+(C_{2v})$	a_1	bend	202.3[a]	
	a_1	stretch	769.6[a]	
	b_2	stretch	834.6[a]	
$GeF_3(C_{3v})$	e	deformation	214.4,[a] 210.0,[c] 209[d]	
	a_1	umbrella	273.1,[a] 268.3,[c] 260[d]	
	a_1	stretch	699.6,[a] 700.9,[c] 703[d]	
	e	stretch	734.1,[a] 729.5,[c] 739[d]	
$GeF_3^+(D_{3h})$	e′	deformation	211.4[a]	
	a_2''	umbrella	229.9[a]	
	a_1'	stretch	757.4[a]	
	e′	stretch	879.3[a]	

[a] MP2(full)/6-311G(d), present work. [b] CASSCF/second-order CI, ref 31. [c] BHLYP/DZP++, ref 41. [d] MP2(full)/6-31G(2df), ref 48. [e] From microwave spectroscopy, ref 8a. [f] From microwave spectroscopy, ref 20. [g] From the photoelectron spectrum of GeF^-, ref 35. [h] CASSCF/second-order CI, ref 64. [i] From infrared diode laser spectroscopy, ref 62a. [j] From infrared spectroscopy, ref 3d. [k] From microwave spectroscopy, ref 6b. [l] From laser-induced emission excitation spectroscopy, ref 33.

3.b. GeF and GeF^+. The GeF radical has a doublet ground state, $^2\Pi$,[31] and our CCSD(T,full)/cc-pVTZ bond distance of 1.744 Å is in very good agreement with the two experimental values of 1.745 Å[8a] and 1.7495 Å[20] obtained from microwave spectroscopy. Our MP2(full)/6-311G(d) harmonic frequency of 668.0 cm^{-1} is also in excellent agreement with the three independent experimental values of 665.7 cm^{-1},[8a] 662.4 cm^{-1},[20] and 670 ± 80 cm^{-1},[35] obtained from the microwave spectrum of GeF and the photoelectron spectrum of GeF^-. The CCSD(T,full)/cc-pVTZ bond distance of GeF^+, 1.670 Å, is shorter than that of GeF by ca. 0.07 Å, and the MP2(full)/6-311G(d) harmonic frequency, 798.6 cm^{-1}, is higher than that of GeF by ca. 130 cm^{-1}. These values are consistent with previous estimates[64] of 1.669 Å and 770 cm^{-1} obtained at the complete active space SCF level of theory followed by second-order CI (CASSCF/SOCI), and are also in very good agreement with the experimental values of 1.665 Å and 815.6 cm^{-1} obtained by infrared diode laser spectroscopy.[62a] The structural differences between GeF and GeF^+ parallel the difference in their electronic structure. In particular, as part of their detailed investigation of the various electronic states of GeF[31] and GeF^+,[64] Liao and Balasubramanian found that the CASSCF/first-order CI (CASSCF/FOCI) wave functions of ground-state GeF and GeF^+ are by far dominated (95%) by the $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1$ and $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$ distributions of the valence electrons, respectively (the validity of a monodeterminantal

TABLE 3: Absolute Energies[a] and Zero-Point Energies[b] (au) of GeF_n and GeF_n^+ (n = 1−3)

species	0 K	298.15 K	ZPE
$GeF(^2\Pi)$	−2175.37246	−2175.36997	0.00249
$GeF^+(^1\Sigma^+)$	−2175.10281	−2175.10037	0.00244
$GeF_2(^1A_1)$	−2275.21557	−2275.21204	0.00354
$GeF_2^+(^2A_1)$	−2274.80269	−2274.79914	0.00355
$GeF_3(^2A_1)$	−2374.96363	−2374.95896	0.00468
$GeF_3^+(^1A_1)$	−2374.60600	−2374.60136	0.00464
$Ge(^3P)$	−2075.55103	−2075.54961	
$Ge^+(^2P)$	−2075.26131	−2075.25989	
$F(^2P)$	−99.63211	−99.63069	
$F^+(^3P)$	−99.00212	−99.00070	

[a] CCSD(T,full)/cc-pVTZ. [b] MP2(full)/6-311G(d).

TABLE 4: Theoretical and Experimental Dissociation Enthalpies (298.15 K, kcal mol^{-1}) of GeF_n and GeF_n^+ (n = 1−3) (All Molecules and Ions in Their Electronic Ground State)

dissociation	theory	expt
$GeF \rightarrow Ge + F$	119.6,[a] 116.2,[b] 110.1,[c] 121.1[d]	113.0,[e] 116.2 ± 4.6,[f] 115.3,[g] 119.9[h]
$GeF^+ \rightarrow Ge^+ + F$	132.2,[a] 128.7[i]	129,[j] 131.4[k]
$GeF_2 \rightarrow GeF + F$	133.2,[a] 119.4,[c] 131.4,[d] 120.4[l]	115.3 ± 18.4,[f] 147.6,[k] 100[g]
$GeF_2^+ \rightarrow GeF^+ + F$	43.3[a]	64.6[k]
$GeF_3 \rightarrow GeF_2 + F$	73.6,[a] 59.4,[c] 68.3[d]	106.1,[k] 61.4[g]
$GeF_3^+ \rightarrow GeF_2^+ + F$	108.2[a]	117.6[k]

[a] CCSD(T,full)/cc-pVTZ, present work. [b] CASSCF/second-order CI + Q and 0 K, ref 31. [c] BHLYP/DZP++ with no ZPE, ref 41. [d] G3//DFT and 0 K, ref 48. [e] From the emission spectra of GeF, ref 1a. [f] From mass spectrometric measurements under Knudsen conditions, ref 3a. [g] Reference 3j. [h] From the spectroscopic study of GeF at 0 K, ref 8c. [i] CASSCF/second-order CI + Q with no ZPE, ref 64. [j] From the study of the Rydberg states of GeF, ref 1b. [k] From mass spectrometric measurements, ref 55a. [l] MRSDCI(+Q) with relativistic ECPs of Christiansen et al. with no ZPE, ref 32.

TABLE 5: Theoretical and Experimental Enthalpies of Formation (298.15 K, kcal mol^{-1}) of GeF_n and GeF_n^+ (n = 1−3)

species	theory	expt
GeF	−11.6,[a] −13.2[b]	
GeF^+	158.4[a]	≤154.5 ± 16.1[c]
GeF_2	−125.9,[a] −126.6[b]	−136.9[d]
GeF_2^+	134.1[a]	≤110.7 ± 6.9[c]
GeF_3	−180.4,[a] −176.5[b]	−180 ± 5[e]
GeF_3^+	44.8[a]	≤13.8 ± 6.9[c]

[a] CCSD(T,full)/cc-pVTZ, present work. [b] G3//DFT, ref 48. [c] From mass spectrometric measurements, ref 55a. [d] From the enthalpy of sublimation of GeF_2, ref 3h. [e] From the appearance potential of GeF_3^-, ref 3j.

TABLE 6: Theoretical and Experimental Ionization Potentials (298.15 K, kcal mol^{-1}) of GeF_n (n = 1−3) and Ge

species	theory	expt
GeF	7.3[a]	7.28,[b] 7.8 ± 0.4,[c] 7.46,[d] 7.44,[e] ≤7.0[f]
GeF_2	11.2,[a] 11.24,[g] 11.6[h]	11.6 ± 0.3,[i] 11.8 ± 0.1,[j] 11.65,[k] ≤10.8 ± 0.6[f]
GeF_3	9.7[a]	≤10.3 ± 0.3[f]
Ge	7.9[a]	7.899,[l] 7.89944 ± 0.00002[m]

[a] CCSD(T,full)/cc-pVTZ adiabatic values, present work. [b] From the energy of the Rydberg states of GeF, ref 1b. [c] From the electron impact ionization of GeF, ref 3a. [d] From the energy of the Rydberg states of GeF, ref 8c. [e] From the energy of the Rydberg states of GeF, ref 22. [f] From mass spectrometric measurements, ref 55a. [g] MRSDCI(+Q) with no ZPE, ref 32. [h] G3//DFT and 0 K, ref 48. [i] From the electron impact ionization of GeF_2, ref 3a. [j] From the electron impact ionization of GeF_2, ref 3b. [k] From the photoelectron spectrum of GeF_2, ref 19a. [l] From spectroscopic measurements, ref 79. [m] From spectroscopic measurements, ref 80.

description of the reference wave function of GeF and GeF^+ is confirmed here by the fact that, similarly to all the other presently investigated GeF_n and GeF_n^+, their CCSD(T,full)/cc-pVTZ T1 diagnostic[81] is computed as ca. 0.012 and is lower than the usually accepted threshold of 0.02). The antibonding character of the 2π outer orbital of GeF suggests that, passing from GeF to GeF^+, the bond distance should decrease and the vibrational frequency should increase. We note also from Table 4 that the CCSD(T,full)/cc-pVTZ BDH of GeF^+, 132.2 kcal mol^{-1}, is larger than that of GeF, 119.6 kcal mol^{-1}, and both these values are in good agreement, within their combined uncertainties, with previous available experimental[1a,b,3a,j,8c,31,55a] and theoretical[31,48,64] estimates (the only somewhat larger deviation is the BHLYP/DZP++ theoretical estimate of 110.1 kcal mol^{-1} of the bond dissociation energy (BDE) of GeF[41]). The CCSD(T,full)/cc-pVTZ BDH of GeF results in a $\Delta_f H_{298.15}$ of −11.6 kcal mol^{-1}, which is in very good agreement with the recent G3//DFT theoretical estimate of −13.2 kcal mol^{-1}.[48] In addition, we have derived an average $\Delta_f H_{298.15}$ of GeF^+ of 158.4 kcal mol^{-1}, which compares quite favorably with a reported experimental value of 154.5 ± 16.1 kcal mol^{-1}.[55a] However, as already noted by other authors,[3j,41] the thermochemical data on GeF_n and GeF_n^+ (n = 1−4) obtained so far by Harland, Cradock, and Thynne[55a] by measuring the appearance potentials (APs) of GeF_n^+ (n = 0−4) from the electron bombardment of GeF_4 should be regarded as of only limited value, since they are unavoidably affected by hardly evaluable contributions from excess kinetic and/or excitation energy arising from the ionization event.

The difference between the $\Delta_f H_{298.15}$ values of GeF and GeF^+ furnishs an adiabatic IP of GeF of 7.37 eV, which is practically coincident with the value of 7.34 eV obtained from the difference between their CCSD(T,full)/cc-pVTZ absolute energies. This calculated IP of GeF is the first theoretical confirmation of the three experimental evaluations of 7.28 eV,[1b] 7.46 eV,[8c] and 7.44 eV[22] based on the study of the Rydberg states of the GeF radical, and is also in agreement, within combined uncertainties, with the value of 7.8 ± 0.4 eV obtained from the electron impact ionization of GeF.[3a] On the other hand, the upper limit of 7.0 eV obtained from AP measurements from GeF_4[55a] appears slightly underestimated.

3.c. GeF_2 and GeF_2^+. The infrared and microwave spectra of gaseous GeF_2, produced from the volatilization of solid germanium difluoride, have been so far investigated by Hastie, Hauge, and Margrave,[3d] and by Takeo, Curl, and Wilson.[6] The molecule has a bent structure of C_{2v} symmetry, with a Ge−F distance and a F−Ge−F angle obtained as 1.73 ± 0.05 Å and 94 ± 4°, respectively, by IR spectroscopy,[3d] and refined as 1.732 Å and 97.15° by MW spectroscopy.[6b] Our CCSD(T,full)/cc-pVTZ-computed values of 1.731 Å and 97.4° are in excellent agreement with these measurements. In addition, from Table 2, the MP2(full)/6-311G(d) harmonic frequencies of 267.0, 673.1, and 690.6 cm^{-1} compare quite favorably with the available experimental values,[3d,6,33] and consistent with the other theoretical assignments,[41,48] we confirm the asymmetric stretching (b_2) to be lower in energy than the symmetric one (a_1). Concerning the thermochemistry of GeF_2, its BDH is presently computed as 133.2 kcal mol^{-1} at the CCSD(T,full)/cc-pVTZ level of theory and compares quite favorably with the value of 131.4 kcal mol^{-1} recently obtained at the G3//DFT level of theory and 0 K.[48] Within combined uncertainties, both these values are also consistent with the probably most accurate (see Table 4) available experimental estimate of 115.3 ± 18.4 kcal mol^{-1} obtained so far by mass spectrometric measurements under Knudsen conditions.[48] On the other hand, they are somewhat larger than other two theoretical values of 119.4 and 120.4 kcal mol^{-1} obtained, respectively, at the BHLYP/DZP++[41] and at the multireference CI levels of theory, with inclusion of single and double excitations and of the Davidson correction for uncoupled quadruple clusters, MRCISD(+Q).[32] In addition, from Table 5, the CCSD(T,full)/cc-pVTZ and the G3//DFT values of the $\Delta_f H_{298.15}$ of GeF_2 range around −126 kcal mol^{-1} and are almost 10 kcal mol^{-1} higher than the experimental estimate of −136.9 kcal mol^{-1} obtained so far[3h] from the standard enthalpy of sublimation of solid GeF_2. We note however that, in this experiment, gaseous GeF_2 was detected as GeF_2^+ at an AP of 12.9 ± 0.3 eV, which is significantly higher (vide infra) than the IP of GeF_2 and suggests the conceivable interfering presence of additional parent neutrals and ions such as $(GeF_2)_2$ and $(GeF_2)_2^+$.

The structure of GeF_2^+ is still experimentally unknown, and to date, the most accurate theoretical investigation has been performed by Balasubramanian et al.[32] at the CASSCF level of theory followed by MRSDCI(+Q). The ground state of GeF_2^+, $^2A_1$, has an MRSDCI(+Q) bond distance and bond angle of 1.651 Å and 117.2°, respectively, and is predicted to be more stable than the $^2B_1$ state by about 3 eV. Our CCSD(T,full)/cc-pVTZ-optimized parameters of 1.666 Å and 116.9° are in good agreement with these previous estimates and confirm that the values of 1.777 Å and 127.0° obtained by nonlocal spin density calculations (NLSD/PP)[32] are indeed overestimated. The harmonic frequencies of GeF_2^+ have not yet been theoretically investigated, and our MP2(full)/6-311G(d) calculations furnish a bending frequency of 202.3 cm^{-1}, a symmetric stretching frequency of 769.6 cm^{-1}, and an asymmetric stretching frequency of 834.6 cm^{-1}. Therefore, with respect to GeF_2, the order of the two stretching motions is expected to be reversed. In addition, we note from Tables 1 and 2 that the structural differences between GeF_2 and GeF_2^+ parallel those discussed for neutral and ionized GeF. Thus, at both the MRSDCI(+Q) and CCSD(T,full)/cc-pVTZ levels of theory, the bond distance of GeF_2^+ is shorter than that of GeF_2 by ca. 0.07 Å and the bond angle is larger by ca. 20°. In addition, the bending frequency of GeF_2^+ is lower than that of GeF_2 by ca. 65 cm^{-1}, and the symmetric and asymmetric stretching motions are higher than those of GeF_2 by ca. 80 and ca. 160 cm^{-1}, respectively. Concerning the thermochemistry of GeF_2^+, its BDH has been so far obtained by Harland, Cradock, and Thynne[55a] as 64.6 kcal mol^{-1}, and the $\Delta_f H_{298.15}$ of GeF_2^+ has been derived as ≤110.7 ± 6.9 kcal mol^{-1}. Not surprisingly, these probably less accurate experimental estimates significantly deviate from our CCSD(T,full)/cc-pVTZ-computed values of 43.3 and 134.1 kcal mol^{-1}, respectively. On the other hand, from Table 6, our computed adiabatic IP of GeF_2, 11.2 eV, is lower than the experimental value, obtained as 11.65 eV from the photoelectron spectrum of GeF_2[19a] and 11.6 ± 0.3 and 11.8 ± 0.1 eV from the electron impact ionization of GeF_2.[3a,b] It is also practically coincident with the MRSDCI(+Q) estimate of 11.24 eV[32] but lower than the G3//DFT value of 11.6 eV.[48]

3.d. GeF_3 and GeF_3^+. The structure and harmonic frequencies of both GeF_3 and GeF_3^+ are still experimentally unknown. For GeF_3, they have been recently theoretically investigated at the density functional (BHLYP/DZP++)[41] and MP2(full)/6-31G(2df) levels of theory.[48] In line with previous HF calculations,[27b] both these methods predict a minimum-energy structure of C_{3v} symmetry, with a bond angle of ca. 106.5° and a bond length of 1.716 Å (BHLYP/DZP++) or 1.706 Å (MP2(full)/6-31G(2df)). Our CCSD(T,full)/cc-pVTZ calculations confirm a bond length of 1.706 Å but predict a somewhat larger bond angle of 112.2°. In addition, from Table 2, our MP2(full)/6-311G(d) harmonic frequencies are in qualitative and quantitative agreement with the BHLYP/DZP++ and the MP2(full)/6-31G(2df) estimates. Our calculated values include in particular two degenerate bending motions at 214.4 cm^{-1}, the "umbrella" motion at 273.1 cm^{-1}, and three stretching frequencies at 699.6 (a_1) and 734.1 (e) cm^{-1}. Concerning the thermochemistry of GeF_3, its enthalpy of formation has been so far measured by Wang, Margrave, and Franklin[3j] as −180 ± 5 kcal mol^{-1} by combining the appearance energies of GeF_3^- and F^- from the electron bombardment of GeF_4 with a spectroscopic estimation of the electronic excitation energy of GeF_3. Our CCSD(T,full)/cc-pVTZ estimate of −180.4 kcal mol^{-1} is in full agreement with this value, and is also consistent with the G3//DFT estimate of −176.5 kcal mol^{-1}.[48] In addition, the discrepancy between our calculated BDH of GeF_3, 73.6 kcal mol^{-1}, and the value of 61.4 kcal mol^{-1} reported by Wang, Margrave, and Franklin[3j] comes from their employed enthalpy of formation of GeF_2 of ca. −137 kcal mol^{-1}. As discussed above, this value is probably underestimated by ca. 10−12 kcal mol^{-1}. Once again, the old estimate[55a] of 106.1 kcal mol^{-1} for the BDH of GeF_3 is probably less accurate.

The removal of the outer electron of GeF_3 leads to a fully planar GeF_3^+ (D_{3h} symmetry), whose CCSD(T,full)/cc-pVTZ bond distance of 1.644 Å is shorter than that of GeF_3 by ca. 0.06 Å. In addition, from Table 2, passing from GeF_3 to GeF_3^+, the stretching frequencies of a_1 and e symmetry increase by ca. 60 and ca. 150 cm^{-1}, respectively, whereas the "umbrella" motion decreases by ca. 40 cm^{-1}. These structural differences between neutral and ionized GeF_3 parallel those already discussed for GeF/GeF^+ and GeF_2/GeF_2^+ and likely reflect an increase, passing from GeF_3 to GeF_3^+, of the total σ donation from Ge to the fluorine atoms. This suggestion comes from the detailed theoretical investigation by Frenking and co-workers[65] on the π-donor ability of the halogens in the AX_3^+ cations (A = C, Si, Ge, Sn, Pb; X = F, Cl, Br, I). It has been found in particular that the p(π) population of atom A always decreases from iodine to fluorine, and amounts to less than 0.25e for GeF_3^+. On the other hand, all the halogens are strong σ acceptors in SiX_3^+−PbX_3^+, with the trend F ≫ Cl > Br > I. Concerning the thermochemistry of GeF_3^+, its BDH is computed as 108.2 kcal mol^{-1} at the CCSD(T,full)/cc-pVTZ level of theory. This value is not far from the estimate of 117.6 kcal mol^{-1} obtained by Harland, Cradock, and Thynne from mass spectrometric measurements,[55a] and their upper limit of 10.3 ± 0.3 eV for the IP of GeF_3 is also not inconsistent with our CCSD(T,full)/cc-pVTZ-computed value of 9.7 eV. However, their upper limit of 13.8 ± 6.9 kcal mol^{-1} for the $\Delta_f H_{298.15}$ of GeF_3^+ appears underestimated with respect to our computed value of 44.8 kcal mol^{-1}.

4. Concluding Remarks

All the GeF_n^+ have been observed in the gas phase from the electron impact fragmentation of GeF_4,[55a] and from the direct ionization of GeF and GeF_2.[3a,b] Consistently, all the ground-state GeF_n^+ are predicted to reside in potential energy wells on the MP2(full)/6-311G(d) surface and to be thermodynamically stable, at the CCSD(T,full)/cc-pVTZ level of theory, with respect to the loss of atomic and molecular fluorine. The CCSD(T,full)/cc-pVTZ bond distance of GeF^+, 1.670 Å, and its MP2(full)/6-311G(d) harmonic frequency of 798.6 cm^{-1} compare quite favorably with the experimental values of 1.665 Å and

815.6 cm^{-1},[62a] and an even better agreement between theory and experiment is found for GeF and GeF_2. Therefore, our computed geometries and harmonic frequencies of GeF_2^+, GeF_3, and GeF_3^+ should be of good predictive value to help their still unreported experimental measurement.

Passing from GeF_n to GeF_n^+, the Ge−F bond distances are invariably shorter by ca. 0.07 Å, and the F−Ge−F bond angles of GeF_2^+ and GeF_3^+ are wider than those of their neutral counterparts by ca. 20 and ca. 8°, respectively. Parallel to these geometric changes, the stretching frequencies of GeF_n^+ are higher than those of their corresponding neutrals, and the bending frequencies of GeF_2^+ and GeF_3^+ are lower than those of GeF_2 and GeF_3. These findings indicate that the positive ionization of GeF, GeF_2, and GeF_3 produces structural effects which are opposite those resulting from the addition of the electron. Thus, in the GeF_n/GeF_n^- series ($n = 1-3$),[48] the bond lengths and the bond angles of the anions are invariably longer and smaller, respectively, than those of the neutrals, and the stretching frequencies of GeF_n^- are invariably smaller than those of GeF_n.

Concerning the thermochemistry of GeF_n and GeF_n^+, our calculated IPs of GeF, 7.3 eV, GeF_2, 11.2 eV, and GeF_3, 9.7 eV, are in good agreement with the available experimental values. In addition, our calculated dissociation enthalpies and enthalpies of formation of GeF_n favorably compare with the most accurate available experimental values. On the other hand, for GeF_n^+ these thermochemical quantities only roughly compare to, and sometimes strongly deviate from, the experimental values reported so far by Harland, Cradock, and Thynne.[55a] They must be therefore regarded as only upper/lower estimates, and more accurate experiments are probably required to evaluate the thermochemistry of GeF_n^+. We hope that our investigation could stimulate future experimental work along this direction.

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