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Calculation of the Proton and Electron Affinity of Simple Ge-Containing Species Using Density Functional Theory

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Basis sets developed using the generator coordinate method and a pseudopotential have been adapted to density functional theory to calculate the proton affinity of GeH_4, GeH_3-, GeF_3^-, $CH_3GeH_2^-$, and $Ge(OH)_3^-$ and the electron affinity of $\cdot GeH_3$ and $\cdot GeF_3$. The proton affinity of GeH_4 is calculated to be 673.9 kJ mol^{-1} at 298 K, while values for GeH_3^- (1505.0 kJ mol^{-1}) and $CH_3GeH_2^-$ (1529.0 kJ mol^{-1}) are in excellent agreement with experimental values. The electron affinity of $\cdot GeF_3$ is predicted to be in the range of 3.5−3.7 eV by calculations using different functionals and ab initio methods. The present calculations reveal that the B3P86 method can yield proton affinities comparable to those obtained with other high-quality methods but consistently overestimates electron affinities of simple Ge radicals.

Introduction

The thermochemical, bonding, and reactivity properties of simple Ge-containing radicals and ions are expected to play a key role in the mechanisms of chemical deposition processes leading to film formation and synthesis of new ceramic materials.[1] In the particular case of gas-phase ion chemistry, a detailed knowledge of proton affinities (PA) and electron affinities (EA) is essential to understand ion reactivity patterns. Unfortunately, and despite recent work on gas-phase radical[2,3] and ionic reactions[4−6] in organogermanes, a detailed characterization of structural and thermochemical parameters of simple Ge radicals and ions remains largely unknown.

In the absence of experimental data, theoretical methods can nowadays be used to estimate structural and thermochemical parameters with remarkable accuracy provided that a reliable approach is developed for calculating these properties. Thus, the quest for high-quality basis sets for Ge is a growing concern,[7,8] and ab initio calculations on reactive Ge systems[9−11] enjoy a lively interplay with experimental information. In recent years, our group has increasingly explored the use of the generator coordinate method (GCM) to develop basis functions adapted to pseudopotentials that considerably reduces computational cost without loss of accuracy.[12] This methodology has been shown[13] to yield proton affinities with a mean absolute deviation of 3.3 kJ mol^{-1} from experimental values and to outperform the G2 method for a large number of hydride-type anions.

In this paper, the GCM procedure is explored in conjunction with density functional theory (DFT) to calculate the proton affinities of GeH_4, GeX_3^- (X = H, F, OH), and $CH_3GeH_2^-$ species and the electron affinities of a few selected Ge radicals. The main objective of these calculations is to provide theoretical support for ongoing experimental work in different laboratories. A comparison of these results with those obtained by other high level calculations, and with available experimental data, clearly reinforces the usefulness of the GCM methodology for deriving thermochemical information.

Computational Methodology

The basic methodology involved in the use of the discrete version of the GCM has been previously described in detail.[12,13] Briefly, this method adapted to the Gaussian 94 program[14] initially involves an analysis of the best representation for the basis functions using as a criterion the ground-state electron energy of the atoms. Polarization and diffuse functions (s, p, d, and f type) are then added until convergence is achieved for the weight functions of the outer atomic orbitals. The actual procedure in the present case involved three steps that can be illustrated for the B3P86 functional:

(1) The valence basis sets were first determined from the 7s, 5p, and 1d set of functions adapted to the pseudopotential (ECP) of Stevens and co-workers[15] for C and Ge and 4s/1p for H. In the first attempts, this set was coupled to the B3P86 method using the Becke exchange functional[16] and the Perdew correlation potential.[17] Numerical integrations were performed with a grid of 77 (radial part) and 302 points (angular part) per shell. A similar procedure was adopted with other functionals as described below.

(2) The above basis sets were then contracted by reoptimizing the exponent of the primitive functions (4111/311/1 for C and Ge and 31/1 for H). Diffuse functions (s and p type) were then added to the valence region to yield a (41111/3111/1) set for C and Ge and (311/1) sets for H. The functions thus obtained define the GCM/ECP basis set.

(3) For more refined energy calculations, the set was augmented with additional polarization functions (p for H and d and f for C and Ge) to yield a (3111/11) set for H and a (41111/3111/11/11) set for C and Ge. This set is referred to as the (GCM/ECP+) basis set.

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TABLE 1: GCM/ECP+ Basis Set (41111/3111/11/11) for C, O, F, and Ge[a]

	C		O		F		Ge	
type	exp.	coeff.	exp.	coeff.	exp.	coeff.	exp.	coeff.
s	0.036 88	1.000 00	0.066 68	1.000 00	0.086 92	1.000 00	0.033 05	1.000 00
s	0.097 17	1.000 00	0.179 15	1.000 00	0.231 17	1.000 00	0.085 06	1.000 00
s	0.256 04	1.000 00	0.481 29	1.000 00	0.614 81	1.000 00	0.218 90	1.000 00
s	0.674 64	1.000 00	1.293 03	1.000 00	1.635 09	1.000 00	0.563 32	1.000 00
s	1.772 47	−0.081 66	3.413 39	0.080 01	4.227 65	−0.065 22	1.328 27	−0.395 04
	4.558 71	−0.116 54	8.879 17	−0.116 35	10.899 33	−0.120 21	3.355 19	0.066 03
	11.724 77	0.004 80	23.090 35	0.004 50	28.099 61	0.002 90	8.475 14	−0.011 07
	30.155 53	−0.004 62	60.046 66	−0.004 33	72.443 71	−0.005 06	21.408 00	0.001 36
p	0.035 36	1.000 00	0.056 63	1.000 00	0.069 75	1.000 00	0.024 96	1.000 00
p	0.117 50	1.000 00	0.198 14	1.000 00	0.248 03	1.000 00	0.086 32	1.000 00
p	0.390 47	1.000 00	0.693 27	1.000 00	0.881 99	1.000 00	0.298 46	1.000 00
p	1.277 42	0.293 54	2.399 89	0.327 62	2.988 20	0.277 18	1.093 78	−0.069 82
	4.261 67	0.077 55	7.995 51	0.091 60	10.329 74	0.079 01	3.856 14	−0.004 46
	14.217 66	0.016 95	27.438 20	0.018 31	35.708 29	0.015 39	13.594 89	−0.001 29
d	0.390 47	1.000 00	0.693 27	1.000 00	0.881 99	1.000 00	0.086 32	1.000 00
d	0.573 08	1.000 00	1.160 21	1.000 00	1.452 70	1.000 00	0.259 76	1.000 00
f	0.390 47	1.000 00	0.693 27	1.000 00	0.881 99	1.000 00	0.086 32	1.000 00
f	0.573 08	1.000 00	1.160 21	1.000 00	1.452 70	1.000 00	0.259 76	1.000 00

[a] The pseudopotentials were obtained from ref 14. The basis set for H (3111/11) is available from the authors upon request.

TABLE 2: Bond Distances (in Å) Obtained by Geometry Optimization of Tetrahedral GeH_4

method	QCISD(T)	B3P86/ (ECP/GCM)	B3PW91/ (ECP/GCM)	exptl[a]
R(Ge−H)	1.525	1.535	1.537	1.525

[a] Reference 23.

An analogous procedure was used for O and F in the appropriate systems. A complete description of the valence basis set is given in Table 1.

Geometries were fully optimized at the level of theory defined as B3P86/(GCM/ECP) and stationary points were characterized by computing the vibrational frequencies (Nimag = 0). These unscaled frequencies were then used to calculate zero-point energies and temperature corrections for the thermodynamic functions. Total electronic energies were calculated with the more extended basis (GCM/ECP+) resulting in a B3P86/(GCM/ECP+)//B3P86/(GCM/ECP) level of calculation.

The Gaussian 94 suite of programs[14] was used throughout this work. For comparison purposes, calculations were also performed with different functionals of DFT and with the G2 and G2MP2 methods.

Results and Discussion

Proton Affinity of GeH_4. The proton affinity of GeH_4 was originally proposed[18] to be in the range of 678−686 kJ mol^{-1} on the basis of a limited number of proton-transfer reactions bracketing experiments. However, a revised estimate of 713.4 kJ mol^{-1} has been recommended in a recent compilation of ion thermochemistry values,[19] although a definitive experimental value has yet to be determined. An early CI calculation[20] placed the proton affinity of GeH_4 at 703 kJ mol^{-1}, while a more recent calculation[21] at the CCSD(T)//TZV+f level predicts a value of 654.4 kJ mol^{-1} at 0 K. Thus, the calculation of the PA of GeH_4 was considered an important test for our methodology.

The fully optimized geometrical parameters obtained for the tetrahedral GeH_4 using different methods are shown in Table 2. They are in very close agreement with the geometries reported by other recent ab initio calculations[21,22] and with the experimental results.[23] The geometry of the GeH_5^+ species is a subject of considerable interest since good quality calculations consistently predict this species to be best represented as a loose complex of GeH_3^+ with molecular H_2.[21,24] The optimized geometries for GeH_5^+ obtained at the B3P86/(ECP/GCM) and the G2 (MP2(full)/6-31Gd)) levels are shown in Figure 1.

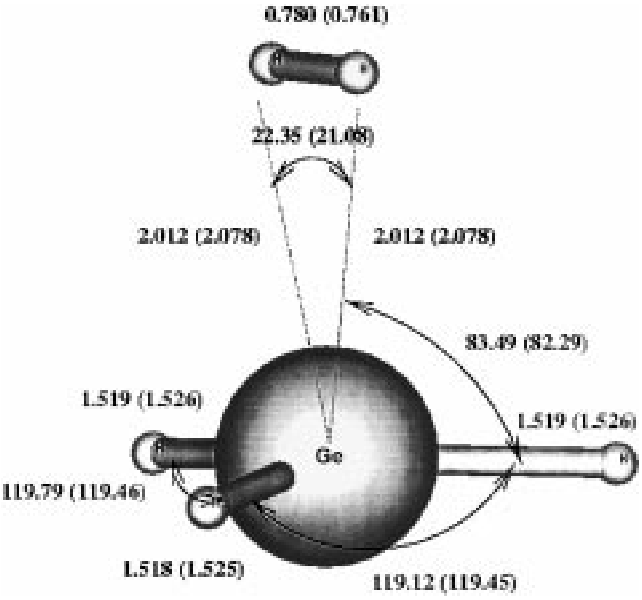

Figure 1. Optimized geometry for the GeH_5^+ ion. The bond distances and angles refer to values obtained at the B3P86/(ECP/GCM) level. Values quoted in parentheses refer to the geometry optimized at the G2(MP2(full)/6-31G(d)). The hydrogen molecule is slightly tilted from the plane by a dihedral angle of 7.56° (6.97°).

Electronic and zero-point energies calculated with the (GCM/ECP+) basis set for the optimized geometries of GeH_4 and GeH_5^+ are displayed in Table 3. These results lead to a proton affinity of 673.9 kJ mol^{-1} for GeH_4 at 298.15 K. By comparison, calculations at the G2(MP2) and G2 levels, with zero-point energy corrections scaled by 0.8929, yield 673.8 and 672.8 kJ mol^{-1}, respectively. The close agreement between the results of the density functional calculations using our basis set and those obtained by G2 calculations strongly suggests that the proton affinity of GeH_4 is probably lower than the revised estimate.[19] This conclusion is based on the fact that our methodology and G2 calculations can generally reproduce experimental proton affinities within "chemical accuracy" (better than ±10 kJ mol^{-1}).[13]

The quality of the calculated proton affinity for GeH_4 was also verified by calculating the proton affinity of the C and Si

TABLE 3: Calculated Energies (au), Zero-Point Energies (kJ mol^{-1}), and Proton Affinities at 298 K (in kJ mol^{-1}) for GeH_4 Species

	B3P86/(ECP/GCM)		G2		G2MP2	
	GeH_4	GeH_5^+	GeH_4	GeH_5^+	GeH_4	GeH_5^+
electronic energy	−6.393 91	−6.656 40	−2077.798 900 4	−2078.054 380 3	−2077.796 659	−2078.052 810 8
ZPE[a]	77.11	95.27	80.54	98.07		
PA at 298 K	673.9		672.8		673.8	
exptl PA	(713)[b]					

[a] Frequencies unscaled for the B3P86 calculation and scaled by 0.8929 for the G2 and G2MP2 calculations. [b] Revised value proposed in ref 19.

TABLE 4: Optimized Bond Distances (in Å) and Bond Angles (in deg) Obtained for GeX_3^-, $\cdot GeX_3$, and GeX_3H at the B3P86/(GCM/ECP) Level

	GeH_3^-	**$\cdot GeH_3$**	**GeH_4**
R(Ge−H)	1.623	1.542	1.535
∠HGeH	93.23	110.76	109.47
	GeF_3^-	**$\cdot GeF_3$**	**GeF_3H**
R(Ge−F)	1.829	1.720	1.701
∠FGeF	95.87	106.76	106.55
	$Ge(OH)_3^-$	**$Ge(OH)_3H$**	
R(Ge−O)	1.895	1.761	
∠OGeO	94.33	108.23	

TABLE 5: Calculated Energies (au), Zero-Point Energies[a] (kJ mol^{-1}), Proton Affinities (kJ mol^{-1}), and Electron Affinities (eV) for GeH_n Species

method	GeH_3	GeH_3^-	GeH_4
QCISD(T)/ (GCM/ECP+)[b]	−5.548 34	−5.602 78	−6.185 54
ZPE	49.66	43.76	73.14
EA	1.54		
PA		1507.0	
B3PW91/ (GCM/ECP+)[c]	−5.604 00	−5.660 71	−6.243 73
ZPE	51.96	46.11	76.94
EA	1.60		
PA		1506.0	
B3P86/ (GCM/ECP+)[c]	−5.734 11	−5.811 16	−6.393 91
ZPE	52.09	46.27	77.11
EA	2.16		
PA		1505.0	
exptl EA	1.739 ± 0.043		
exptl PA		1502.0 ± 5.1	

[a] Frequencies scaled by 0.8929 and 1.000 for ab initio and DFT calculations, respectively. [b] E[QCISD(T)] calculated as described in refs 12 and 13. [c] E is the total electronic energy calculated with the functionals B3PW91 and B3P86.

analogues. Using a similar computational approach as that described above, a proton affinity of 557 kJ mol^{-1} is obtained for CH_4 (recommended[19] experimental value 544 kJ mol^{-1}) and 647 kJ mol^{-1} for SiH_4 (recommended[19] experimental value 640 kJ mol^{-1}), both at 298 K. Likewise, our optimized geometries for SiH_5^+ and CH_5^+ can be compared with those obtained in other high-quality calculations. We find that the SiH_5^+ structure resembles that of the GeH_5+ ion (see Figure 1): the H_a-H_b distance of the H_2 moiety is calculated to be 0.79 Å, the angle $\angle H_aSiH_b$ is 24° (as opposed to 22° in GeH_5^+ in Figure 1), and the SiH_3^+ ionic moiety is almost planar. This is very similar to the structure obtained in a calculation at the TZ2P CCSD level of theory.[25] Likewise, the optimized geometry for CH_5^+ displays considerable $CH_3^+(H_2)$ character with the H_a-H_b distance of the H_2 moiety lengthened to 1.07 Å, with the angle $\angle H_aCH_b = 54°$, and leading to a more pyramidal CH_3^+. These findings are in very good agreement with the C_s geometry previously obtained at the TZ2P+f CCSD(T) level of theory.[26]

Proton Affinity and Electron Affinity of GeX_3^- (X = H, F, OH). The gas-phase proton affinity of GeH_3^- has only been established in recent years by a series of bracketing experiments leading to a value of 1502 ± 5.1 kJ mol^{-1} at 298 K.[27] Previously, an upper bound of 1.739 ± 0.043 eV was determined for the electron affinity of $\cdot GeH_3$ on the basis of some early photodetachment experiments.[28] Theoretical calculations at the G2 level have addressed the question of these important thermochemical parameters and conclude the proton affinity of GeH_3^- to be 1518.4 kJ mol^{-1} at 298 K and the electron affinity of $\cdot GeH_3$ to be 1.60 eV.[29] A much earlier calculation using electron propagator theory concluded the vertical and adiabatic ionization energy of GeH_3^- to be 2.01 and 1.39 eV, respectively.[30]

Previous studies have shown that different methods of DFT can also reproduce experimental proton affinities of simple anions with remarkable accuracy.[31] Our initial attempts at the B3P86 level revealed that very good agreement could be achieved with the experimental proton affinity of GeH_3^- (see below), but not with the reported electron affinity of $\cdot GeH_3$. It was therefore necessary to carry out a careful comparison of different levels of DFT[32] and other ab initio methods in order to establish a reliable protocol for the calculation of electron affinities.

Geometries optimized at the B3P86/(GCM/ECP) level for different GeX_3^- anions and their conjugate acids are shown in Table 4. Similar results are obtained with the B3PW91 and B3LYP methods, and no significant differences were found for optimized geometries by the G2 and G2MP2 methods. At the QCISD(T) level, the optimized geometries consistently result in shorter bond lengths (0.01−0.03 Å).

The energies calculated by different methods for GeH_3^-, and related species, are shown in Table 5 along with the calculated proton affinities and electron affinities of the corresponding radical. The QCISD(T)/(GCM/ECP+) is a high-level calculation for the electronic energy that is obtained through additive approximations of simpler calculations as outlined previously.[12c,13] All three methods reported in Table 5 yield proton affinities within 1 kJ mol^{-1} of each other and agree with the experimental value better than the G2 calculation.[29] On the other hand, significantly different values are obtained for the electron affinity of $\cdot GeH_3$. For example, the QCISD(T) and B3LYP calculations predict values of 1.54 and 1.60 eV, respectively, for the electron affinity of $\cdot GeH_3$, in close agreement with the G2 value.[29] By comparison, the B3P86 method is observed to overestimate considerably the electron affinity leading to a value of 2.16 eV.

An even more extensive comparison of methods is shown in Table 6 for GeF_3^-. The proton affinity at 298 K is calculated to be 1322 kJ mol^{-1} by the B3P86/(GCM/ECP+) method and 1348 kJ mol^{-1} by the G2MP2 method. However, a large difference is again observed for the calculated electron affinities. The electron affinity calculated for $\cdot GeF_3$ at the B3P86/(GCM/ECP+) level appears to be unusually high (4.12 eV). By comparison, calculations at the B3PW91 and B3LYP levels, using either the (GCM/ECP+) or the 6-311G(3df,2p) basis sets, yield electron affinities for $\cdot GeF_3$ ranging from 3.56 to 3.79

TABLE 6: Calculated Energies (au), Zero-Point Energies[a] (kJ mol^{-1}), Proton Affinities (kJ mol^{-1}), and Electron Affinities (eV) for GeF$_3$ Species

method	GeF_3	GeF_3^-	GeF_3H	method	GeF_3	GeF_3^-
QCISD(T)/(GCM/ECP+)[b]	−76.485 58	−76.613 52		B3PW91/(GCM/ECP+)[c]	−76.894 69	−76.764 80
ZPE	16.07	15.65		ZPE	13.14	15.82
EA	3.51			EA	3.56	
B3PW91/6-311G(3df,2p)//6-31G(d)	−2376.581 31	−2376.714 11		B3P86/6-311G(3df,2p)//6-31G(d)	−2377.910 56	−2378.064 56
ZPE	15.82	16.90		ZPE	16.90	15.90
EA	3.62			EA	4.20	
B3LYP/(GCM/ECP+)[c]	−76.740 57	−76.873 24		B3LYP/6-311G(3df,2p)//6-31G(d)	−2376.727 52	−2376.866 41
ZPE	15.69	13.01		ZPE	17.07	15.69
EA	3.64			EA	3.79	
B3P86/(GCM/ECP+)	−77.267 79	−77.418 30	−77.929 03	G2MP2	−2374.758 062	−2374.891 222
ZPE	15.90	13.26	38.74	ZPE	19.12	17.11
EA	4.12			EA	3.62	
PA		1322.0		PA		1348.0

[a] Frequencies scaled by 0.8929 and 1.000 for ab initio and DFT calculations, respectively. [b] E[QCISD(T)], see ref 13.

eV. Likewise, the value calculated at the G2MP2 level of 3.62 eV is within this range and close to most of the values calculated by the above density functional methods. Unfortunately, these predictions cannot be properly compared with experimental results since such different values as 1.1,[33] 1.6,[34] and 3.1 eV[35] have been claimed from appearance potential measurements.

The possible effects due to the use of different basis sets, a pseudopotential, and different functionals were also explored in our work. The results for the calculated electron affinity of $\cdot GeF_3$ are displayed in Table 6. First, the basis set, GCM/ECP+, was observed to be well-adjusted to the pseudopotential and to describe adequately both radical and anionic systems. This basis set yields consistent results for the electron affinity using QCISD(T) (3.51 eV), or DFT methods such as B3PW91 (3.56 eV) and B3LYP (3.64 eV). Second, the use of the pseudopotential fares extremely well when compared with calculations (DFT and G2MP2) that consider explicitly all the electrons. For example, the electron affinity of $\cdot GeF_3$ is calculated to be 3.62 eV at the B3PW91/6-311+G(3df,2p)//6-31G(d) level, 3.64 eV at the B3LYP/6-311+G(3df,2p)//6-31G-(d) level, and 3.62 eV at the G2MP2. These values are in excellent agreement with those obtained with the pseudopotential. Finally, the B3P86 method is observed to overestimate the electron affinity whether the calculation is carried out with a pseudopotential (4.12 eV) or includes all the electrons (4.20 eV). On the other hand, differences in calculated proton affinities are much less sensitive to the method. Thus, we can conclude that the B3P86 method yields proton affinities comparable to those obtained with ab initio methods but appears to be inadequate for calculating electron affinities. This conclusion is important in order to extend our approach to germanium−fluorine cluster anions for which vertical and threshold photodetachment energies have been recently measured experimentally.[36]

The proton affinities of $CH_3GeH_2^-$ and $Ge(OH)_3^-$ were also determined using our methodology. The PA of $CH_3GeH_2^-$ has been measured experimentally to be 1536.6 kJ mol^{-1} indicating that methyl substitution decreases the gas-phase acidity of monogermane.[27] Our calculations at the B3P86/(GCM/ECP+) level are shown in Table 7 and yield a proton affinity of 1529.0 kJ mol^{-1} at 298 K. By comparison, a value of 1532.2 kJ mol^{-1} is calculated at the G2 level and 1532.8 kJ mol^{-1} at the G2MP2 level for the proton affinity of $CH_3GeH_2^-$. All three values agree closely with the experimental value. Finally, calculations for $Ge(OH)_3^-$ system, chosen as a model for the ubiquitous $Ge(OCH_3)_3^-$ species in the gas-phase ion chemistry of alkoxygermanes,[6] lead to an estimated proton affinity of 1432.0 kJ mol^{-1} at the B3P86/(GCM/ECP+) level and 1451.7 kJ mol^{-1} at the G2MP2 (Table 7).

TABLE 7: Calculated Energies (au), Zero-Point Energies[a] (kJ mol^{-1}) and Proton Affinities at 298 K (kJ mol^{-1}) for $MeGeH_2^-$ and $Ge(OH)_3^-$ at the B3P86/(GCM/ECP+) Level

	$MeGeH_2^-$	$MeGeH_3$	$Ge(OH)_3^-$	$HGe(OH)_3$
electronic energy	−12.82437	−13.41616	−54.43945	−54.99239
ZPE	123.97	154.72	101.84	126.98
PA	1529.0		1432.0	
exptl PA	1536.6		?	

[a] Frequencies unscaled.

Conclusions

The present calculations represent an important extension of the capabilities of the GCM methodology coupled with DFT for obtaining thermochemical parameters of Ge species. While different functionals can be used to obtain the proton affinity of Ge neutral and anionic species, the B3P86 functional seems to be inadequate for calculating electron affinities, and estimates obtained by this method should be viewed with caution. A comparison of the electron affinities obtained with other common functionals (B3PW91 and B3LYP) with our adapted basis set leads us to believe that for radicals of high electron affinity (for example, $\cdot GeF_3$) values are probably within 0.25 eV of the experimental value. Further work is in progress in order to better understand the limitations of B3P86 functional in predicting electron affinities.

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