

Ab initio prediction of the structure, harmonic vibrational frequencies, and dissociation energy of the $\text{H}_2\text{-GeH}^+ 3\text{-H}_2$ cluster ion

Edet F. Archibong, Peter F. Schreiner, Jerzy Leszczyński, Paul von Rague Schleyer, Henry F. Schaefer III, and Richard Sullivan

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Ab initio prediction of the structure, harmonic vibrational frequencies, and dissociation energy of the $\text{H}_2\text{-GeH}_3^+\text{-H}_2$ cluster ion

Edet F. Archibong

Jackson State University, Department of Chemistry, 1400 Lynch Street, Jackson, Mississippi 39217

Peter F. Schreiner

University of Georgia, Center for Computational Quantum Chemistry, Athens Georgia 30602 and Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany

Jerzy Leszczyński^{a)}

Jackson State University, Department of Chemistry, 1400 Lynch Street, Jackson, Mississippi 39217

Paul von Rague Schleyer

Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany

Henry F. Schaefer III

University of Georgia, Center for Computational Quantum Chemistry, Athens, Georgia 30602

Richard Sullivan

Jackson State University, Department of Chemistry, 1400 Lynch Street, Jackson, Mississippi 39217

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Ab initio predictions of the molecular geometry, harmonic vibrational frequencies, and dissociation energies are reported for the germanium hydride cluster ion GeH_7^+ . Seven stationary points were located on the potential energy surface (PES) of GeH_7^+ using the self-consistent field (SCF), configuration interaction including single and double excitations (CISD), and coupled cluster including single, double, and perturbatively included triple excitations [CCSD(T)] methods in conjunction with a double- ζ plus polarization (DZP) and a triple- ζ plus polarization TZ(3d1f,1p) quality basis set. The most stable structure has a C_2 symmetry with the two H_2 subunits rotating freely about the symmetry axis of the GeH_3^+ fragment. Our best estimate of the dissociation energy for GeH_7^+ , taking into account the zero point vibrational energy (ZPVE) is 3.10 kcal/mol compared to 4.6 and 1.2 kcal/mol obtained, respectively, for the SiH_7^+ and CH_7^+ cluster ions. © 1995 American Institute of Physics.

INTRODUCTION

The need and the very recent efforts to determine experimentally the structures and spectroscopic parameters of the methonium ion CH_5^+ ,¹ and the silanium ion SiH_5^+ ,² have resulted in the theoretical determination of the structures and energetics of the weakly bound $\text{CH}_5^+\text{-H}_2^3$ and $\text{H}_2\text{-SiH}_3^+\text{-H}_2^{4-5}$ cations. Despite their importance in chemistry as the simplest prototypes for nonclassical carbonium and silanium ions, experimental geometrical and spectroscopic parameters of CH_5^+ and SiH_5^+ have not been ascertained due to difficulties encountered in detecting and assigning their spectra. Theoretical studies⁶⁻⁸ on CH_5^+ have established that the lowest energy structures of the ion (two C_s and one C_{2v}) have nearly identical energy. Thus the potential energy surface of this system is very flat and experimental detection and assignment of its infrared (ir) spectrum is virtually impossible. In a recent article, Schreiner *et al.*⁸ concluded that CH_5^+ is an example of highly fluxional systems, unique, and without a definite structure. On the other hand, *ab initio* geometry predictions of SiH_5^+ ⁹ and GeH_5^+ ¹⁰ established that the global minimum structures for both clus-

ter ions have a similar C_s geometry with one H_2 ligand bound sideways to the XH_3^+ ($\text{X}=\text{Si,Ge}$) fragment. Furthermore, the energy barrier for hydrogen scrambling (pseudorotation) via the C_{2v} transition structure, was predicted to be 26 and 31 kcal/mol above the energy of the minimum C_s structure in SiH_5^+ and GeH_5^+ , respectively. Consequently, the occurrence of pseudorotation is very unlikely in SiH_5^+ and GeH_5^+ , in marked contrast to CH_5^+ where the three lowest energy structures cluster together on the potential energy surface.⁶⁻⁸

Currently, there are experimental efforts using infrared absorption spectroscopy based upon vibrational dissociation to study CH_5^+ and SiH_5^+ indirectly, by investigating corresponding infrared spectra of the weakly bound $\text{CH}_5^+\text{-H}_2^1$ and $\text{SiH}_5^+\text{-H}_2^2$. It is assumed that attachment of H_2 ligand would stabilize the fluxional CH_5^+ , and SiH_5^+ ions without serious alteration in the basic structural features of the cations. Thus the structures and vibrational frequencies of CH_5^+ and SiH_5^+ in weakly bound clusters of $\text{CH}_5^+\text{-H}_2$ and $\text{SiH}_5^+\text{-H}_2$, respectively, are expected to be similar to those of free CH_5^+ and SiH_5^+ systems. The only theoretical study³ on $\text{CH}_5^+\text{-H}_2$ unfortunately concluded that attachment of H_2 does not stabilize CH_5^+ well enough to allow straightforward analysis of the vibrational spectrum. Similarly, the theoretical results on

^{a)} Author to whom correspondence should be addressed.

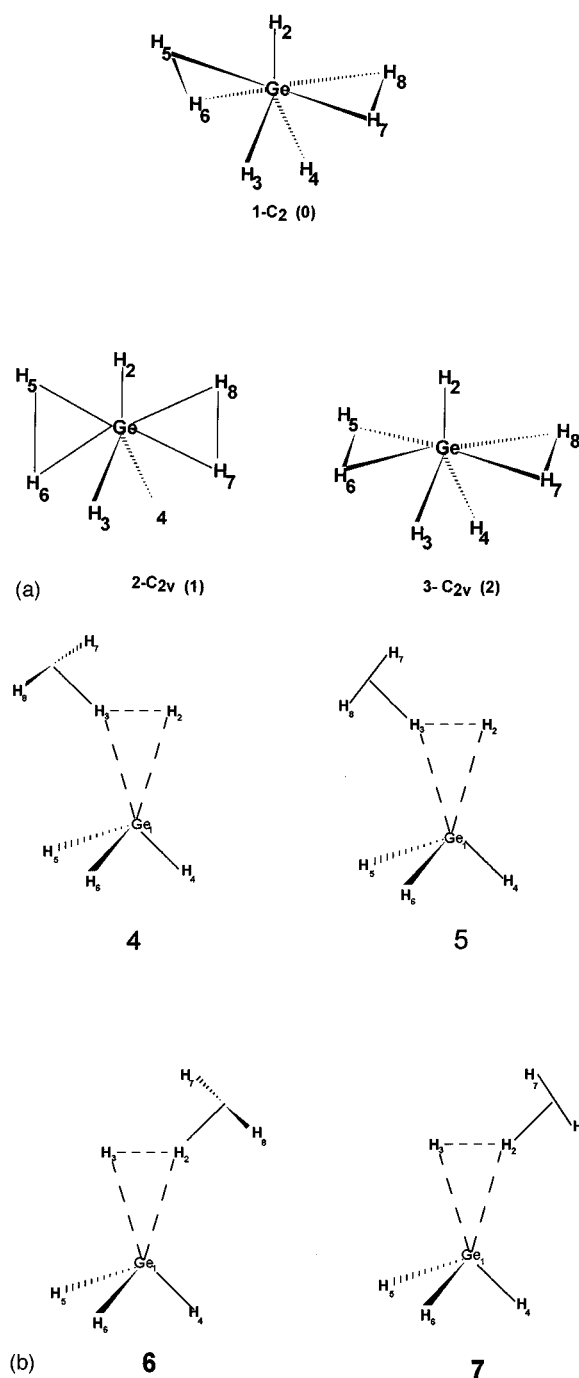


FIG. 1. (a) Sketches of the $\text{H}_2\text{-GeH}_3^+-\text{H}_2$ isomers. The numbers in parenthesis denote the Hessian index. Geometrical parameters are summarized in Table I. (b) Four $\text{GeH}_5^+-\text{H}_2$ stationary points of C_s symmetry. The numbers in parenthesis denote the Hessian index. Geometrical parameters are summarized in Table II.

SiH_7^+ ($\text{H}_2\text{-SiH}_3^+-\text{H}_2$)^{4,5} have shown that the internal rotation of the H_2 units has essentially a zero potential barrier. The results of these theoretical calculations suggest it may be difficult experimentally to obtain the spectra of XH_5^+ ($\text{X}=\text{C}, \text{Si}$) ions through H_2 stabilization.

As part of our efforts to elucidate the structures of weakly bound clusters, we have examined the potential energy surface of GeH_7^+ the germanium analog of CH_7^+ and SiH_7^+ . The molecular structures of CH_7^+ and SiH_7^+ are

markedly different. In CH_7^+ the global minimum is a C_s structure with one H_2 unit weakly attached to one of the two hydrogen atoms of the nonclassical $3c-2e$ bond of the $\text{CH}_5^+(C_s)$ fragment.³ On the other hand, two theoretical studies^{4,5} predicted that SiH_7^+ has a C_2 geometry with two symmetry equivalent H_2 moieties bound to the planar SiH_3^+ fragment on opposite faces and equidistant from Si. This theoretical description of SiH_7^+ structure agrees with the suggestion derived from earlier experimental ir studies.² Investigation of the structure and energetics of GeH_7^+ is therefore timely and will certainly lead to a better understanding of the molecular geometries and properties of this class of hypervalent ions. The electronegativity of germanium is between that of carbon and silicon; thus is the structure of GeH_7^+ unique, does it resemble that of CH_7^+ (that is, $\text{GeH}_5^+-\text{H}_2$) or will it more likely be isostructural with SiH_7^+ ($\text{H}_2\text{-GeH}_3^+-\text{H}_2$)? Primarily, our goal is to shed more light on the molecular structures of XH_n^+ ($\text{X}=\text{C}, \text{Si}, \text{Ge}; n=5,7$) ions,^{3,5,7-10} provide estimates of the binding energies, and furnish spectroscopic parameters which may be useful for experimental endeavours. To our knowledge there are no structural reports on the GeH_7^+ ion.

THEORETICAL METHODS

We employed three one-particle basis sets in this study. One of the basis sets was a medium sized double- ζ plus polarization basis set derived from Dunning's $\text{Ge}(14s11p5d)$ and $\text{H}(4s1p)$ primitive set¹¹ contracted to $\text{Ge}[7s5p2d]$ and $\text{H}[2s1p]$. This contracted set is then augmented by a set of d -type polarization functions on germanium with orbital exponent $\alpha_d(\text{Ge})=0.25$ to give a $[7s5p3d/2s1p]$ set labeled DZP. The second basis set was of triple- ζ plus f -type polarization function TZ($3d1f,1p$) quality. It consists of the above basis set more flexibly contracted to $[10s8p3d1f/3s1p]$. The orbital exponents of the polarization functions are $[\alpha_d(\text{Ge})=0.25, \alpha_f(\text{Ge})=0.45, \text{ and } \alpha_p(\text{H})=0.75]$. The d functions in the basis sets are the six-component spherical harmonic functions, and the f functions in the TZ($3d1f,1p$) set are the ten-component spherical harmonics. The construction of the third basis set is different from the DZP and TZ($3d1f,1p$) basis sets, and also smaller than the latter. It consists of Huzinaga's¹² germanium $[4333/433/4]$ set loosely uncontracted to $[433111/43111/4]$. Then two sets of five-membered d -type polarization functions with orbital exponents $\alpha_d(\text{Ge})=0.108$ and 0.382 , and one set of seven-membered f -type polarization functions $[\alpha_f(\text{Ge})=0.45]$ were added to give a $6s5p3d1f [433111/43111/411/1]$ set. For hydrogen, we employed Huzinaga-Dunning-Hay¹³⁻¹⁴ triple- ζ basis augmented with two sets of p -type polarization functions with orbital exponents $\alpha_p(\text{H})=1.5$ and 0.375 . We labeled this $[6s5p3d1f/3s2p]$ basis set as TZ2P for convenience, and it was employed for all the MP2 calculations.

Geometry optimizations were carried out at the Hartree-Fock level using analytical gradients. Utilizing the SCF geometries and force constants, the structures were reoptimized at the second-order Moller-Plesset perturbation (MP2) level (only for TZ2P). Further geometry optimizations employing

TABLE I. Selected geometrical parameters for the GeH_7^+ isomers (1–3). Distances in Å and angles in degrees.

		SCF		CISD		CCSD		CCSD(T)		MP2(FC)	MP2(FC9)
		DZP	TZ(3d1f,1p)	DZP	TZ(3d1f,1p)	DZP	TZ(3d1f,1p)	DZP	TZ(3d1f,1p)	TZ2P	TZ2P
1- C_2	Ge–H ₂	1.509	1.507	1.513	1.514	1.517	1.518	1.518	1.519	1.505	1.491
	Ge–H ₅	2.311	2.285	2.225	2.199	2.223	2.196	2.216	2.189	2.192	2.143
	Ge–H ₆	2.310	2.284	2.224	2.198	2.223	2.195	2.215	2.188	2.190	2.140
	H ₅ –H ₆	0.748	0.748	0.757	0.757	0.759	0.760	0.760	0.761	0.754	0.754
	H ₂ GeH ₅	83.6	83.4	83.2	83.1	83.2	83.0	83.2	83.0	83.2	83.0
2- C_{2v}	Ge–H ₂	1.509	1.507	1.514	1.515						
	Ge–H ₃	1.508	1.506	1.513	1.513						
	Ge–H ₅	2.311	2.285	2.225	2.198						
	Ge–H ₆	2.312	2.286	2.226	2.200						
	H ₅ –H ₆	0.748	0.748	0.756	0.756						
3- C_{2v}	H ₂ GeH ₅	80.2	80.1	79.7	79.6						
	Ge–H ₂	1.508	1.506	1.513	1.512						
	Ge–H ₃	1.509	1.507	1.514	1.513						
	Ge–H ₅	2.311	2.285	2.240	2.261						
	H ₅ –H ₆	0.748	0.748	0.757	0.750						
	H ₂ GeH ₅	90.4	90.4	90.7	90.3						

the DZP and TZ(3d1f,1p) basis sets were also carried using configuration interaction (CI),¹⁵ coupled cluster including all single and double excitations (CCSD)¹⁶ analytic gradient methods, and CCSD method with the effect of connected triple excitations included perturbatively [CCSD(T)].¹⁷ The configurations in the CI expansion included single and double substitutions with respect to the Hartree–Fock reference determinant (CISD), and the effect of unlinked quadruple excitations on the CISD energies were estimated by incorporating Davidson correction¹⁸ (CISD+Q). Residual Cartesian and internal coordinate gradients were always less than 10^{-6} for the stationary points. The harmonic vibrational frequencies were obtained from analytic second derivative methods at the SCF and MP2 levels, whereas they were determined by finite central differences of analytic gradients in the configuration interaction and the coupled cluster calculations. To account for anharmonicity and electron correlation, the harmonic vibrational frequencies and zero-point vibrational energies obtained at the SCF level were scaled by a

factor of 0.91. At the correlated level, the scaling factor was 0.95 to correct primarily for anharmonicity.

Only the valence electrons were correlated, that is, 14 lowest occupied molecular orbitals (Ge 1s, 2s, 2p, 3s, 3p, 3d-like orbitals) were kept doubly occupied, and the six highest virtual molecular orbitals (Ge 1s*, 2s*, 2p*, 3s*) were deleted in the CI and CC procedures. The MP2 calculations with the TZ2P basis set was undertaken to study the effect of germanium 3d electrons on the geometrical parameters and dissociation energies. Thus in one set of calculations at the MP2 level, 14 lowest molecular orbitals were kept doubly occupied (we shall refer to this as MP2FC), and in another set only 9 lowest molecular orbitals were frozen (we shall refer to this approximation as MP2FC9 for convenience). We estimate the basis-set superposition error (BSSE) by the “counterpoise” procedure of Boys and Bernardi.¹⁹ In this method, the BSSE is approximated by the difference between the energy of the monomers calculated in the pure monomer basis sets and in the dimer basis set. All the MP2 calculations were done using Gaussian 92 program.²⁰ The CI and coupled cluster calculations were carried out with the program PSI2.0.8.²¹

TABLE II. Geometrical parameters of the C_s isomers at the CCSD/TZ(3d1f,1p) level.^a

	4- C_s	5- C_s	6- C_s	7- C_s
r_{12}	2.022	2.019	2.026	2.026
r_{13}	2.028	2.025	2.019	2.018
r_{14}	1.517	1.517	1.516	1.516
r_{15}	1.515	1.515	1.515	1.515
r_{23}	0.767	0.768	0.768	0.768
r_{2c}^b			2.481	2.486
r_{3c}^b	2.544	2.502		
r_{78}	0.742	0.742	0.742	0.742
θ_{12c}^b			127.5	131.2
θ_{13c}	101.0	113.1		
θ_{214}	82.4	82.5	82.2	82.2
θ_{415}	119.3	119.3	119.4	119.3
θ_{516}	119.9	119.8	119.7	119.8

^aBond lengths in angstroms, angles in degrees.

^bThe subscript c refers to the center of the H₂ moiety in $\text{GeH}_3^+(\text{H}_2)$.

RESULTS AND DISCUSSION

Previous theoretical studies on CH_7^+ ($\text{CH}_5^+ - \text{H}_2$)³ and SiH_7^+ ($\text{H}_2 - \text{SiH}_3^+ - \text{H}_2$)^{4,5} have shown that the structures of these two cations are remarkably different, and the larger size of Si among other factors have been attributed⁵ to this difference. Since Ge is even larger than Si, it is reasonable to investigate the potential energy surface of GeH_7^+ starting from the geometries located on the PES of $\text{H}_2 - \text{SiH}_3^+ - \text{H}_2$. Thus initially we considered five structures (one C_2 , two C_s , and two C_{2v}) in which the two hydrogen moieties are symmetry equivalent. However, optimization of the two C_s structures (with the hydrogen subunits in or out of plane) always converged to the corresponding in or out of plane C_{2v} structures. Definition of three structures (one C_2 and two C_{2v}) of

TABLE III. Selected geometrical parameters of GeH₇⁺ (C₂), GeH₅⁺ (C_s), GeH₃⁺ (D_{3h}), and H₂. Distances in Å and angles in degrees.

		SCF/TZ(3d1f,1p)	CISD/TZ(3d1f,1p)	CCSD(T)/TZ(3d1f,1p)	MP2(FC)/TZ2P	MP2(FC9)/TZ2P
GeH ₇ ⁺						
C ₂	Ge-H ₂	1.507	1.514	1.519	1.505	1.491
	Ge-H ₅	2.285	2.199	2.189	2.192	2.143
	Ge-H ₆	2.284	2.198	2.188	2.190	2.140
	H ₅ -H ₆	0.748	0.757	0.761	0.754	0.754
	H ₂ GeH ₅	83.4	83.1	83.0	83.2	83.0
GeH ₅ ⁺						
C _s	Ge-H ₂	1.509	1.517	1.522	1.508	1.494
	Ge-H ₃	1.508	1.516	1.521	1.507	1.493
	Ge-H ₅	2.105	2.032	2.024	2.007	1.949
	Ge-H ₆	2.107	2.035	2.027	2.011	1.954
	H ₅ -H ₆	0.756	0.768	0.772	0.765	0.767
	H ₂ GeH ₅	82.6	82.2	82.1	81.9	81.5
GeH ₃ ⁺						
D _{3h}	Ge-H	1.510	1.520	1.523	1.508	1.495
H ₂	H-H	0.743	0.743	0.743	0.737	

the type H₂-GeH₃⁺-H₂ located on the PES of GeH₇⁺ are shown in Fig. 1(a) (structures 1–3). Included in parenthesis are the numbers of imaginary frequency (Hessian index) characterising each stationary point. The optimized geometry of the C₂ structure 1 has a positive definite hessian for all calculations at the correlated level. The C_{2v} structure 2 has one imaginary frequency and represents the transition state for the internal rotations of the H₂ units about the GeH₃⁺ symmetry axis, while structure 3 (C_{2v}) has two imaginary frequencies.

Table I contains selected geometrical parameters for structures 1–3 in Fig. 1(a). The table shows that the difference in predicted geometrical parameters for the DZP and TZ(3d1f,1p) is not substantial. Generally, for conformers 1–3, the bond lengths predicted by the two basis sets at all levels of theory do not vary more than 0.028 Å, and the angles differ not more than 0.2°. Note also the effects of electron correlation on the geometrical parameters. At the correlated levels, the interaction between the H₂ subunits and the GeH₃⁺ fragment becomes stronger [shortening of the Ge-H₅ and GeH₆ distances; Fig. 1(a)], and the bond distance within the H₂ subunits (for example, H₅-H₆) becomes longer. This is consistent with the fact that electron correlation strongly favour complexlike structures.^{7,22} In going from

SCF/TZ(3d1f,1p) to the correlated levels, the change in the bond distances for structures 1–3 is generally less than 0.1 Å, and the largest increase in the angles is 0.5°.

Also included in Table I are the MP2(FC) and MP2(FC9) (respectively, excluding and including germanium 3d correlation effects) results using the TZ2P basis set. The table shows that correlating the 3d orbitals on germanium, shortened the Ge-H bond lengths of the GeH₃⁺ fragment in GeH₇⁺ roughly by 0.014 Å, and the distances of the H₂ ligands from Ge by 0.05 Å.

In addition to structures 1–3, we also examined structures similar to those located on the PES of CH₇⁺,³ and indeed, we located C_s structures 4–7 of the type GeH₅⁺-H₂. As shown below, these structures are higher in energy compared to the C₂ and the two C_{2v} structures 1–3. Note that attempts to locate similar structures for SiH₇⁺ have not been successful. The geometries of the C_s structures are defined in Fig. 1(b) and Table II. Only structure 4 is a minimum, while the remaining structures are characterized by one or more imaginary frequencies.

In Table III we present the geometrical parameters of the GeH_n⁺ (n=3,5,7) cations together with the H-H bond length. Comparison of the Ge-H distances in free GeH₃⁺, with those of GeH₃⁺ fragments in GeH₅⁺ (Ge-H₂ and Ge-H₃) and GeH₇⁺

TABLE IV. Absolute energies (in -a.u.) of GeH₇⁺ isomers.

Optimization level	1-C ₂	2-C _{2v}	3-C _{2v}	4-C _s	5-C _s	6-C _s	7-C _s
SCF/DZP	2078.951 894	2078.951 881	2078.951 880	2078.945 842	2078.947 061	2078.946 881	2078.946 746
SCF/TZ(3d1f,1p)	2079.048 545	2079.048 536	2079.048 536	2079.043 707	2079.043 546	2079.043 542	2079.043 453
CISD/DZP	2079.123 435	2079.123 416	2079.123 416	2079.117 451	2079.117 154	2079.116 898	2079.116 814
CISD+Q/DZP	2079.136 84	2079.136 82	2079.136 82	2079.130 66	2079.130 36	2079.130 09	2079.130 02
CISD/TZ(3d1f,1p)	2079.230 890	2079.230 856	2079.230 856	2079.224 007	2079.223 791	2079.223 736	2079.223 668
CISD+Q/TZ(3d1f,1p)	2079.245 76	2079.245 72	2079.245 72	2079.238 62	2079.238 40	2079.238 34	2079.238 28
CCSD/DZP	2079.134 722						
CCSD/TZ(3d1f,1p)	2079.243 416						
CCSD(T)/DZP	2079.137 020						
CCSD(T)/TZ(3d1f,1p)	2079.246 358						

TABLE V. Relative energies (in kcal/mol) including ZPVE (in parenthesis) of GeH_7^+ isomers.

Optimization level	1- C_2	2- C_{2v}	3- C_{2v}	4- C_s	5- C_s	6- C_s	7- C_s
SCF/DZP	0.00	0.01(−0.09)	0.01(−0.09)	3.80	3.03	3.15	3.23
SCF/TZ(3d1f,1p)	0.00	0.01(−0.09)	0.01(−0.09)	3.04	3.14	3.14	3.20
CISD/DZP	0.00	0.01(−0.09)	0.01(−0.09)	3.76	3.94	4.10	4.15
CISD+Q/DZP	0.00	0.01(−0.09)	0.01(−0.09)	3.38	4.07	4.24	4.28
CISD/TZ(3d1f,1p)	0.00	0.02(−0.08)	0.02(−0.08)	4.32	4.45	4.49	4.53
CISD+Q/TZ(3d1f,1p)	0.00	0.03(−0.07)	0.02(−0.07)	4.48	4.62	4.66	4.69

(Ge–H₂) indicate a difference of not more than 0.006 Å, and from the results of Table III, it appears these Ge–H distances are generally shorter in the larger clusters. On the other hand, the distances of the H₂ subunits from Ge are larger in GeH_7^+ compared to GeH_5^+ . For example, the Ge–H(5) and Ge–H(6) bond distances are roughly 2.2 Å in GeH_7^+ and 2.0 Å in GeH_5^+ . Next consider the H–H distance of the H₂ ligands in GeH_7^+ . The H–H distance in isolated H₂ is 0.743 Å at all levels using the TZ(3d1f,1p) basis set. The corresponding distance for the weakly attached H₂ units in GeH_7^+ ranges from 0.748 Å [SCF/TZ(3d1f,1p)] to 0.761 Å [CCSD(T)/TZ(3d1f,1p)]. Note that the H₂ units are less perturbed in GeH_7^+ , in comparison to GeH_5^+ where the H–H distance is 0.756 Å at SCF/TZ(3d1f,1p) and 0.772 Å at CCSD(T) level with the same basis set.

Table IV contains the absolute energies for all seven structures of GeH_7^+ , and the relative energies are presented in Table V. The results of Table IV show that the C_2 structure is the lowest in energy at all levels of theory. However, the energy difference between the C_{2v} structures 2 and 3 and the C_2 global minimum structure is less than 0.1 kcal/mol (including correction for ZPVE). Note that electron correlation only has a moderate effect on the relative energies of 1–3. The results also show that the C_s isomers are much higher in

energy (relative to C_2). Electron correlation significantly stabilizes the C_2 minimum structure compared to the C_s isomers 4–7.

Theoretical harmonic vibrational frequencies have always been a useful source of information for experimental detection and assignment of infrared spectra. The computed harmonic vibrational frequencies for structure 1 are presented in Table VI. The SCF results and the correlated results are scaled by 0.91 and 0.95, respectively. Also included in the tables are the harmonic vibrational frequencies for free H₂, and H₂ stretching frequency within GeH_5^+ . The vibrational frequency analyses at the correlated levels indicate that structure 1 has no imaginary frequency (see Table VI). Employing the CCSD(T)/TZ(3d1f,1p) data, the intense ω_{10} mode at 3974 cm^{−1} corresponds to the antisymmetric H–H stretching mode. The symmetric H–H stretching mode at 3991 cm^{−1} has zero oscillator strength and may not be observed experimentally. Comparison of the H–H stretching mode of free H₂ at 4190 cm^{−1} [CCSD(T)/TZ(3d1f,1p)] with the ω_{10} mode at 3974 cm^{−1} indicates a frequency shift of 216 cm^{−1}. In previous studies involving attachment of an H₂ ligand to XH_n^+ (X=C, Si, Ge; n=3,5) ions,^{1–10} the frequency shift of the H–H stretching mode in the complex from the free H₂, have been used empirically to indicate the

TABLE VI. Harmonic vibrational frequencies (cm^{−1}) and intensity (km/mol) of the C_2 minimum structure of GeH_7^+ . (SCF frequencies scaled by 0.91; correlated frequencies scaled by 0.95).

	SCF/DZP	SCF/TZ(3d1f,1p)	CCSD(T)/TZ(3d1f,1p)	MP2/TZ2P
A				
ω_1	4018(0.0)	4021(0.0)	3991(0.0)	4071(0.0)
ω_2	2174(4.8)	2169(4.3)	2173(39.6)	2247(3.4)
ω_3	2148(0.0)	2140(0.0)	2134(0.0)	2209(0.0)
ω_4	844(50.3)	834(55.4)	802(128.9)	832(37.4)
ω_5	676(26.0)	722(21.9)	766(19.5)	726(18.4)
ω_6	551(0.0)	568(0.0)	623(0.0)	620(0.5)
ω_7	380(0.0)	424(0.0)	551(0.0)	508(0.0)
ω_8	229(3.9)	240(5.0)	284(30.5)	280(6.9)
ω_9	34(0.0)	28(0.1)	64(0.3)	81(0.3)
B				
ω_{10}	4006(312.0)	4009(355.6)	3974(345.8)	4053(357.2)
ω_{11}	2173(4.8)	2169(4.3)	2172(39.7)	2246(2.9)
ω_{12}	844(50.6)	834(55.7)	803(127.5)	832(37.1)
ω_{13}	801(102.0)	806(97.5)	790(147.4)	806(84.3)
ω_{14}	676(27.7)	722(21.2)	766(19.5)	726(20.1)
ω_{15}	551(0.0)	568(0.0)	623(0.0)	621(0.6)
ω_{16}	229(23.4)	253(167.2)	348(594.5)	295(154.7)
ω_{17}	221(133.1)	238(14.0)	283(33.2)	276(16.7)
ω_{18}	1i(0.0)	1i(0.0)	9(0.0)	8(0.0)
H ₂	4223	4172	4190	4302
H ₂ in GeH_5^+	3912	3911	3854	3876

TABLE VII. Harmonic vibrational frequencies (cm^{-1}) and intensity (km/mol) of the C_{2v} structures of GeH_7^+ at SCF/TZ(3d1f,1p) level. The frequencies are scaled by 0.91.

	2- C_{2v}	3- C_{2v}
ω_1	4022(0.1)	4022(0.1)
ω_2	4009(355.1)	4009(355.2)
ω_3	2170(5.1)	2170(5.1)
ω_4	2168(3.5)	2168(3.5)
ω_5	2140(0.0)	2140(0.0)
ω_6	835(62.2)	835(62.1)
ω_7	833(49.2)	834(49.3)
ω_8	807(96.9)	807(96.9)
ω_9	723(0.0)	723(0.0)
ω_{10}	719(43.6)	719(43.6)
ω_{11}	571(0.5)	571(0.0)
ω_{12}	566(0.0)	566(0.5)
ω_{13}	424(0.0)	424(0.0)
ω_{14}	251(176.0)	251(176.1)
ω_{15}	241(4.9)	240(5.0)
ω_{16}	238(5.3)	239(5.2)
ω_{17}	9(0.1)	10i(3.3)
ω_{18}	29i(0.0)	32i(0.0)

TABLE VIII. Harmonic vibrational frequencies (cm^{-1}) and intensity (km/mol) of the C_s structures of GeH_7^+ at SCF/TZ(3d1f,1p) level. Frequencies are scaled by 0.91.

	4- C_s	5- C_s	6- C_s	7- C_s
ω_1	4163(6.2)	4166(6.2)	4165(5.5)	4167(5.3)
ω_2	3908(225.0)	3906(223.9)	3905(240.5)	3905(240.3)
ω_3	2165(3.4)	2164(3.5)	2163(3.5)	2163(3.6)
ω_4	2161(3.2)	2160(2.9)	2162(2.7)	2161(2.9)
ω_5	2133(0.2)	2133(0.2)	2133(0.2)	2133(0.2)
ω_6	881(23.2)	885(25.4)	879(25.6)	881(26.8)
ω_7	841(56.3)	840(58.8)	840(58.8)	840(59.4)
ω_8	839(62.8)	839(61.7)	839(62.3)	839(61.0)
ω_9	805(62.4)	805(60.1)	805(61.3)	805(61.5)
ω_{10}	516(0.2)	517(11.3)	522(26.7)	523(29.6)
ω_{11}	515(6.3)	517(0.2)	519(0.3)	519(0.3)
ω_{12}	498(91.1)	501(87.0)	498(71.6)	500(67.8)
ω_{13}	267(6.2)	241(6.6)	261(4.2)	247(4.7)
ω_{14}	127(1.0)	134(0.1)	139(0.4)	137(0.1)
ω_{15}	113(8.1)	107(8.6)	105(8.8)	102(8.9)
ω_{16}	90(0.9)	41(2.0)	69(0.8)	48(3.1)
ω_{17}	66(0.9)	35(3.3)	51(3.1)	22i(3.2)
ω_{18}	54(3.1)	83i(0.0)	20i(2.9)	65i(0.0)

strength of the XH_n^+-H_2 interaction. The larger the shift, the more perturbed the attached H_2 , and consequently the tighter the complex. Thus the strength of H_2 attachment in GeH_7^+ and GeH_5^+ can be assessed by comparing, respectively, the shifts of the H-H vibrational frequency of the complexes from the free H_2 stretching mode. Relative to free H_2 , the frequency shift of H-H stretching mode in GeH_5^+ is 330 cm^{-1} .^{10(b)} Comparison of this latter shift with the H-H frequency shifts in $\text{H}_2\text{-GeH}_3^+-\text{H}_2$ (216 cm^{-1}) indicates a stronger attachment of the H_2 unit in GeH_5^+ . Similar comparison with the frequency shift in $\text{H}_2\text{-SiH}_3^+-\text{H}_2$ (259 cm^{-1})⁵ indicates that the GeH_3^+ cation has a weaker interaction with the H_2 subunits.

Table VII and VIII contain the scaled harmonic vibrational frequencies for the C_{2v} and the C_s structures, respectively. The C_{2v} structure 2 is a transition state for the H_2 subunit rotations, and the rotational barrier is essentially zero. Table VIII shows that C_s structure 4 [Fig. 1(b)] is a local minimum, and structure 5 a transition state for the H_2 rotation. Note that structure 6 has one imaginary frequency, however, a similar structure is a minimum on the PES of CH_5^+-H_2 .

Next consider the dissociation energies D_e and D_0 (including correction for zero-point energy) of GeH_7^+ . Table IX lists the total energies of GeH_7^+ , GeH_5^+ , and H_2 calculated at their optimized geometries. From these data, the dissociation

energies listed in Table X were estimated, at different levels of theory, as the energy difference for the reaction



The dissociation energy, D_e , at the SCF/TZ(3d1f,1p) level is 3.6 kcal/mol. Correction for the zero-point energy lowers D_e by 96% to D_0 value of 0.1 kcal/mol. The effect of electron correlation on the dissociation energies is not negligible. The SCF/TZ(3d1f,1p) values of D_e (3.6 kcal/mol) is raised to CCSD(T)/TZ(3d1f,1p) value of 5.6 kcal/mol, and the D_0 enormously increased from 0.1 kcal/mol [SCF/TZ(3d1f,1p)] to 3.1 kcal/mol at the CCSD(T)/TZ(3d1f,1p) level.

The MP2 calculations with only nine core orbitals frozen (FC9) were undertaken in order to investigate the effects of freezing the inner 3d electrons on the predicted dissociation energies. The difference between the FC and FC9 results for D_e is not more than 2%. Similarly, the variation in D_0 values at the MP2 level for FC and FC9 is not larger than 3%. An important conclusion from these MP2 results is that correlating the 3d orbitals on germanium does not have a significant effect on the dissociation energy of GeH_7^+ . At the CCSD(T)/TZ(3d1f,1p) level, our estimate of the BSSE is 0.22 kcal/mol (4%). A wealth of experience³ suggests that a BSSE correction this small will only serve to yield poorer agree-

TABLE IX. Absolute energies (in hartrees) of $\text{H}_2\text{-GeH}_3^+-\text{H}_2$, $\text{GeH}_3^+(\text{H}_2)$, and GeH_3^+ at various levels of theory.

Optimization level	$\text{H}_2\text{-GeH}_3^+-\text{H}_2$	$\text{GeH}_3^+-\text{H}_2$	GeH_3^+	H_2
SCF/DZP	-2078.951 894	-2077.814 748	-2076.670 110	-1.131 089
SCF/TZ(3d1f,1p)	-2079.048 545	-2077.910 312	-2076.765 712	-1.132 486
CCSD/DZP	-2079.134 722	-2077.959 884	-2076.777 451	-1.166 708
CCSD/TZ(3d1f,1p)	-2079.243 416	-2078.066 497	-2076.880 734	-1.168 332
CCSD(T)/DZP	-2079.137 020	-2077.961 949	-2076.778 992	-1.166 708
CCSD(T)/TZ(3d1f,1p)	-2079.246 358	-2078.069 106	-2076.882 671	-1.168 332

TABLE X. Dissociation energies (kcal/mol) of GeH_7^+ at selected levels of theory.

$\text{GeH}_7^+ \rightarrow \text{GeH}_5^+ + \text{H}_2$		
	D_e	D_0
SCF		
DZP	3.8	0.5
TZ(3d1f,1p)	3.6	0.1
MP2		
MP2(FC)/TZ2P ^a	5.8	3.8
MP2(FC9)/TZ2P ^b	5.9	3.9
CCSD		
DZP	5.1	1.8
TZ(3d1f,1p)	5.4	1.9
CCSD(T)		
DZP	5.3	2.0
TZ(3d1f,1p)	5.6	3.1 ^c

^aThe total energies of GeH_7^+ , GeH_5^+ , and GeH_3^+ at (MP2FC)/TZ2P level are $-2077.390\,668$, $-2076.210\,607$, and $-2075.021\,031$, respectively.

^bThe total energies of GeH_7^+ , GeH_5^+ , and GeH_3^+ at (MP2FC9)/TZ2P level are $-2077.454\,868$, $-2076.274\,662$, and $-2075.082\,436$, respectively.

^cBSSE=0.22 kcal/mol.

ment with the experimental dissociation energy (not available in this case). Consequently, the BSSE is included to indicate basis set incompleteness and is not taken into account in the final prediction of the dissociation energy. Thus for GeH_7^+ our best estimate for the dissociation energy, D_0 , is 3.1 kcal/mol obtained from the frozen core CCSD(T)/TZ(3d1f,1p) prediction.

The dissociation energies, D_0 , of the XH_n^+ ($\text{X}=\text{C}, \text{Si}, \text{Ge}$; $n=5,7$) ions are presented in Table XI. This table shows that D_0 consistently decreases from carbon to germanium for the pentacoordinate clusters ($n=5$), an indication of increasing stability of the XH_3^+ cations as the central Group IV atom becomes bigger. However, for $n=7$, the order of decreasing D_0 is $\text{SiH}_7^+ > \text{GeH}_7^+ > \text{CH}_7^+$; a reflection of considerable thermodynamic stability of the methonium ion, CH_5^+ , compared to the SiH_5^+ and GeH_5^+ analogues.

In summary, a C_2 structure has been located as the global energy minimum on the potential energy surface of the GeH_7^+ cluster ion. The H_2 ligands bind at a distance of about 2.2 Å from Ge, and rotate with essentially zero barrier. Comparison of predicted structures with those available in the literature show that the bonding schemes for GeH_7^+ and SiH_7^+

TABLE XI. Comparison of theoretical dissociation energies (kcal/mol) of XH_n^+ ($\text{X}=\text{C}, \text{Si}, \text{Ge}$; $n=5,7$).

	CH_n^+	SiH_n^+	GeH_n^+
n	D_0	D_0	D_0
5	42.0 ^a	10.0 ^c	9.7 ^e
7	1.5 ^b	4.6 ^d	3.1 ^f

^aReference 7; QCISD/6-311++G(3df,3pd)//MP2(fu)/6-311++G(2df,2pd).

^bReference 3; CCSD(T)/TZ2P+d.

^cReference 9; CCSD/TZ2P.

^dReference 5; CCSD/TZ2P(f,d).

^eReference 10(a); CCSD(T)/TZ2P//MP2/TZ2P.

^fThis work; CCSD(T)/TZ(3d1f,1p).

are similar. Four stationary points analogous to those located on the PES of CH_7^+ were also found, but they are higher in energy compared to the global C_2 structure, and the two C_{2v} transition structures lying 0.1 kcal/mol above the global minimum structure. Our calculated dissociation energy, D_e , for GeH_7^+ is 5.6 kcal/mol, and D_0 is 3.1 kcal/mol.

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