

Comparison of the Standard 6-31G and Binning-Curtiss Basis Sets for Third Row Elements

Shahidul M. Islam, Stephanie D. Huelin, Margot Dawe, and Raymond A. Poirier*

*Department of Chemistry, Memorial University,
St. John's, Newfoundland, Canada A1B 3X7*

Received September 4, 2007

Abstract: Ab initio calculations were carried out for isogyric reactions involving the third row elements, Ga, Ge, As, Se, and Br. Geometries of all the reactants and products were optimized at the HF, MP2, and B3LYP levels of theory using the 6-31G(d) and 6-31G(d,p) basis sets. For molecules containing third row elements geometries, frequencies and thermodynamic properties were calculated using both the standard 6-31G and the Binning-Curtiss (BC6-31G) basis sets. In order to determine the performance of these basis sets, the calculated thermodynamic properties were compared to G3MP2 values and where possible to experimental values. Geometries and frequencies calculated with the standard 6-31G and the BC6-31G basis sets were found to differ significantly. Frequencies calculated with the standard 6-31G basis set were generally in better agreement with the experimental values (MAD=40.1 cm⁻¹ at B3LYP/6-31G-(d,p) and 94.2 cm⁻¹ at MP2/6-31G(d,p) for unscaled frequencies and 29.6 cm⁻¹ and 24.4 cm⁻¹, respectively, for scaled frequencies). For all the reactions investigated, the thermodynamic properties calculated with the standard 6-31G basis set were found to consistently be in better agreement with the G3MP2 and the available experimental results. However, the BC6-31G basis set performs poorly for the reactions involving both second and third row elements. Since, in general, the standard 6-31G basis set performs well for all the reactions, we recommend that the standard 6-31G basis set be used for calculations involving third row elements. Using G3MP2 enthalpies of reaction and available experimental heats of formation (ΔH_f°), previously unknown ΔH_f° for CH₃SeH, SiH₃SeH, CH₃AsH₂, SiH₃AsH₂, CH₃GeH₃, and SiH₃GeH₃ were found to be 18.3, 18.0, 38.4, 82.4, 41.9, and 117.4 kJ mol⁻¹, respectively.

1. Introduction

Calculations for compounds containing first and second row elements are now very common. However, fewer calculations have been performed for compounds containing third row main group elements. Such computations require basis sets that are consistent with those used for the first and second row elements in order to obtain accurate and reliable results.¹ For third row elements the Binning-Curtiss (BC6-31G) basis set² has been used in combination with the standard 6-31G basis set in most electronic structure packages (for example, Gaussian³ and GAMESS⁴). However, this basis set does not

actually meet the definition of the standard 6-31G basis set, but it is constructed from a contraction of the Dunning basis set.² The core functions are highly contracted with respect to those which represent the valence region which are kept uncontracted in order to maintain flexibility. For example, for the BC6-31G basis set, the s, p, and d shells consist of six (821111), four (6311), and one (5) contracted functions, respectively, which gives a total of 24 basis functions. Rassolov et al.⁵ have developed a standard 6-31G basis set for the third row elements to use in G3 theories,⁶ where the 3d orbitals are included in the valence space of the third row elements, resulting in a total of 29 basis functions. However, very little has been reported^{7,8} on the use of the

* Corresponding author phone: (709) 737-8609; fax: (709) 737-3702; e-mail: rpoirier@mun.ca.

standard 6-31G basis set vs the BC6-31G basis set for lower levels of theory (e.g., HF, MP2, and B3LYP) for compounds containing third row elements. No detailed investigation of geometries and frequencies for compounds containing third row elements have been performed using the standard 6-31G basis set. From our previous study,⁷ thermodynamic properties for $\text{SiH}_3\text{Br} + \text{HCN} \rightarrow \text{SiH}_3\text{CN} + \text{HBr}$ and $\text{SiHBr} + \text{H}_2 \rightarrow \text{SiH}_2 + \text{HBr}$, calculated at HF, MP2, and B3LYP levels using the standard 6-31G basis set, were found to be in better agreement with Gaussian-n theories compared to values obtained using the BC6-31G basis set for bromine with the same levels of theory. However, in a later study⁸ on the reaction of alkenes with bromine, the thermodynamic properties obtained with the standard 6-31G basis set were found to agree very well with the values obtained with the BC6-31G basis set. In this study, we have extended the study to encompass other third row main group elements. G3MP2 theory⁹ and experimental results where available are used in this study in evaluating the performance of the standard 6-31G and the BC6-31G basis sets for compounds containing first row and second row elements in combination with the third row elements Ga, Ge, As, Se, and Br. The results are compared, contrasted, and evaluated at the HF, MP2, and B3LYP levels of theory.

2. Method

In this study, the performance of the third row basis sets is evaluated by comparing the thermodynamics properties for the following isogyric reactions:



where X = Ga, Ge, As, Se, and Br and $n = 2, 3, 2, 1$, and 0, respectively, and for



The geometries and frequencies for molecules containing third row atoms are also investigated. All the electronic structure calculations were carried out with Gaussian03.³ The geometries of all reactants and products were fully optimized at the HF, MP2, and B3LYP levels of theory using both the 6-31G(d) and 6-31G(d,p) basis sets. For third row elements, Ga, Ge, As, Se, and Br, both the standard 6-31G⁵ and BC6-31G² basis sets are used throughout. Geometries of all the compounds were optimized ensuring all had their expected symmetries. From our previous work,^{7,8} it was found that the enthalpies of reaction calculated by using G3MP2,⁹ G3B3,¹⁰ and G3MP2B3¹⁰ levels of theory all agreed to within 5.3 kJ mol⁻¹. Therefore, the G3MP2 level of theory is used in this study which is expected to adequately reproduce the experimental data. G3MP2 theory is based on geometry optimizations performed at the MP2(full) level of theory using the standard 6-31G(d) basis set for first, second, and third row elements. In some cases G3MP2 calculations were

also performed using the BC6-31G(d) basis set for third row elements. For the standard 6-31G(d) basis set, the G3MP2 energy is the summation of the following single point energies

$$E[\text{QCISD(T)}/6\text{-}31\text{G(d)}] + \Delta E_{\text{MP2}} + \Delta E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE})$$

where

$$(\Delta E_{\text{MP2}}) = [E(\text{MP2}/\text{G3MP2Large})] - [E(\text{MP2}/6\text{-}31\text{G(d)})]$$

While the G3MP2 energy calculated using the BC6-31G(d) basis set is given by

$$E[\text{QCISD(T)}/\text{BC6-}31\text{G(d)}] + \Delta E_{\text{MP2}} + \Delta E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE})$$

where

$$(\Delta E_{\text{MP2}}) = [E(\text{MP2}/\text{G3MP2Large})] - [E(\text{MP2}/\text{BC6-}31\text{G(d)})]$$

For all the third row elements the G3MP2Large basis set,^{1,11} which is not yet incorporated in Gaussian03, was used for G3MP2 calculations. Frequencies were calculated for all structures to ensure the absence of imaginary frequencies in the minima.

3. Results and Discussion

The optimized geometries, frequencies, the thermodynamic properties of the isogyric reactions, and heats of formation of some energetically stable compounds containing third row elements are presented in Tables 1–9.

3.1. Geometries of Molecules Containing Third Row Elements. Bond lengths and angles calculated at the MP2 and B3LYP levels of theory using the standard 6-31G(d,p) and BC6-31G(d,p) basis sets for all the structures containing third row elements are listed in Table 1 along with the experimental data where available.

The geometric parameters calculated with the standard 6-31G(d,p) and BC6-31G(d,p) basis sets are quite different. The MP2 bond lengths are always shorter than the B3LYP bond lengths, and with a few exceptions ($\angle\text{H}-\text{C}-\text{H}$ in $\text{CH}_3\text{-Br}$, CH_3SeH , CH_3AsH_2 , and CH_3GaH_2 and $\angle\text{H}-\text{Si}-\text{X}$ (X=Br, Ga) in SiH_3Br and SiH_3GaH_2) the MP2 bond angles are larger or almost equal to B3LYP angles. However, for all the levels of theory the agreement with experiment is similar to that found for compounds containing first and second row elements.

Table 2 lists the mean absolute deviations (MAD) in bond lengths and angles from experiment and calculations. A total of 25 experimental bond lengths and 18 experimental bond angles were used to calculate the mean absolute deviations from experiment. A total of 36 bond lengths and 36 bond angles were used to calculate the mean absolute deviations between the values calculated at the MP2 and the B3LYP level of theory using the standard 6-31G(d,p) and BC6-31G(d,p) basis sets. For bond lengths the MAD is ~0.012 Å except for B3LYP/6-31G(d,p) which has a MAD of 0.019 Å. The lowest MAD (0.0118 Å) is given by MP2/6-31G(d).

Table 1. Optimized and Experimental Structural Parameters for Compounds Containing Third Row Elements^a

molecules	point group	geometric parameter	MP2			B3LYP			exptl
			/6-31G(d,p)	/BC6-31G(d,p)	Δ^s	/6-31G(d,p)	/BC6-31G(d,p)	Δ^s	
HBr	$C_{\infty v}$	H–Br	1.4075	1.4057	0.0018	1.4269	1.4171	0.0098	1.4144, ^a 1.4129 ^b
SeH ₂	C_{2v}	Se–H	1.4527	1.4480	0.0047	1.4738	1.4614	0.0124	1.4600, ^a 1.4605 ^b
		\angle H–Se–H	91.6	91.5	0.1	91.2	91.0	0.2	90 ^c
AsH ₃	C_{3v}	As–H	1.5042	1.5043	–0.0001	1.5271	1.5181	0.009	1.5108, ^a 1.5187 ^b
		\angle H–As–H	93.0	92.2	0.8	91.9	91.2	0.7	90 ^c
GeH ₄	T_d	Ge–H	1.5219	1.5285	–0.0066	1.5369	1.5306	0.0063	1.5151, ^a 1.5293, ^b 1.514 ^d
		\angle H–Ge–H	109.5	109.5	0.0	109.5	109.5	0.0	109.5 ^c
GaH ₃	D_{3h}	Ga–H	1.5579	1.5785	–0.0206	1.5700	1.5733	–0.0033	1.560, ^a 1.5505 ^e
		\angle H–Ga–H	120.0	120.0	0.0	120.0	120.0	0.0	
PH ₂ Br	Cs	P–Br	2.2474	2.2440	0.0034	2.2775	2.2612	0.0163	2.234, ^f 2.230 ^f
		P–H	1.4067	1.4063	0.0004	1.4248	1.4242	0.0006	1.425, ^f 1.412 ^f
		Br–H	2.7894	2.7847	0.0047	2.8183	2.8106	0.0077	
		\angle H–P–Br	96.8	96.7	0.1	96.4	96.8	–0.4	96.1 ^f
		\angle H–P–H	93.5	93.4	0.1	92.2	92.1	0.1	92.4 ^f
SiHBr	Cs	Si–Br	2.2529	2.2470	0.0059	2.2809	2.2601	0.0208	2.237, ^g 2.231 ^h
		Si–H	1.5086	1.5082	0.0004	1.5308	1.5309	–0.0001	1.518, ^g 1.561 ^h
		\angle H–Si–Br	94.5	94.6	–0.1	94.2	94.6	–0.4	93.4 ^g
CH ₃ Br	C_{3v}	C–Br	1.9424	1.9480	–0.0056	1.9658	1.9625	0.0033	1.939, ⁱ 1.934, ^j 1.933 ^k
		C–H	1.0832	1.0834	–0.0002	1.0879	1.0878	0.0001	1.113, ⁱ 1.082, ^j 1.086 ^k
		\angle H–C–Br	108.1	107.8	0.3	107.7	107.7	0.0	107.7 ^j
		\angle H–C–H	110.8	111.1	–0.3	111.2	111.2	0.0	111.2, ^j 111.17 ^k
SiH ₃ Br	C_{3v}	Si–Br	2.2294	2.2249	0.0045	2.2484	2.2299	0.0185	2.212, ^l 2.210 ^m
		Si–H	1.4690	1.4686	0.0004	1.4808	1.4808	0.0	1.474, ^l 1.487 ^m
		\angle H–Si–Br	108.4	108.4	0.0	108.5	108.7	–0.2	108.2 ^l
		\angle H–Si–H	110.5	110.5	0.0	110.4	110.2	0.2	
CH ₃ SeH	Cs	C–Se	1.9610	1.9503	0.0107	1.9812	1.9633	0.0179	1.976 ⁿ
		C–H	1.0896	1.0899	–0.0003	1.0909	1.0912	–0.0003	1.10 ⁿ
		Se–H	1.4730	1.4799	–0.0069	1.4827	1.4848	–0.0021	1.48 ⁿ
		\angle H–C–H	110.7	110.9	–0.2	110.9	110.9	0.0	111 ⁿ
		\angle C–Se–H	95.0	95.8	–0.8	94.9	95.6	–0.7	95 ⁿ
SiH ₃ SeH	Cs	Si–Se	2.2909	2.2895	0.0014	2.3086	2.2963	0.0123	
		Si–H	1.4816	1.4810	0.0006	1.4851	1.4846	0.0005	
		Se–H	1.4741	1.4812	–0.0071	1.4829	1.4849	–0.0020	
		\angle H–Si–H	110.2	110.3	–0.1	109.9	109.9	0.0	
		\angle Si–Se–H	93.9	94.5	–0.6	93.6	94.2	–0.6	
CH ₃ AsH ₂	Cs	C–As	1.9798	1.9607	0.0191	1.999	1.983	0.016	1.92 ^o
		C–H	1.0924	1.0928	–0.0004	1.0920	1.0916	0.0004	1.09 ^o
		As–H	1.5248	1.5354	–0.0106	1.5300	1.5205	0.0095	
		\angle H–C–H	109.4	109.2	0.2	109.6	109.9	–0.3	
		\angle C–As–H	96.0	96.5	–0.5	95.6	95.1	0.5	
SiH ₃ AsH ₂	Cs	Si–As	2.3705	2.3672	0.0033	2.3949	2.3698	0.0251	
		Si–H	1.4838	1.4836	0.0002	1.4873	1.4857	0.0016	
		As–H	1.5243	1.5357	–0.0114	1.5347	1.5186	0.0161	1.52 ^o
		\angle H–Si–H	109.1	109.2	–0.1	108.8	108.8	0.0	109.28 ^o
		\angle Si–As–H	93.6	93.8	–0.2	92.8	93.5	–0.7	94 ^o
CH ₃ GeH ₃	C_{3v}	C–Ge	1.9540	1.9474	0.0066	1.9692	1.9515	0.0177	1.9490, ^p 1.9453 ^q
		C–H	1.0873	1.0874	–0.0001	1.0924	1.0924	0.0	1.0921, ^p 1.083 ^q
		Ge–H	1.5264	1.5324	–0.0060	1.5414	1.5361	0.0053	1.5285, ^p 1.529 ^q
		\angle H–C–H	108.7	108.8	–0.1	108.7	108.7	0.0	108.841, ^p 108.4 ^q
		\angle C–Ge–H	110.3	110.6	–0.3	110.2	110.6	–0.4	109.3 ^q
SiH ₃ GeH ₃	C_{3v}	\angle H–Ge–H	108.5	108.3	0.2	108.4	108.3	0.1	108.776 ^p
		Si–Ge	2.3838	2.3828	0.0010	2.3987	2.3795	0.0192	2.36 ^r
		Si–H	1.4761	1.4758	0.0003	1.4872	1.4868	0.0004	1.49 ^r
		Ge–H	1.5252	1.5337	–0.0085	1.5400	1.5372	0.0028	1.53 ^r
		\angle Si–Ge–H	110.7	110.7	0.0	110.8	110.8	0.0	
CH ₃ GaH ₂	Cs	\angle H–Si–H	108.8	108.9	–0.1	108.6	108.6	0.0	108.8 ^r
		\angle H–Ge–H	108.2	108.2	0.0	108.1	108.1	0.0	108.8 ^r
		C–Ga	1.9686	1.9874	–0.0188	1.9796	1.9771	0.0025	
		Ga–H	1.5636	1.5840	–0.0204	1.5769	1.5800	–0.0031	

Table 1. (Continued)

molecules	point group	geometric parameter	MP2			B3LYP			exptl
			/6-31G(d,p)	/BC6-31G(d,p)	Δ^s	/6-31G(d,p)	/BC6-31G(d,p)	Δ^s	
SiH ₃ GaH ₂	Cs	C–H	1.0919	1.0928	–0.0009	1.0974	1.0980	–0.0006	
		\angle C–Ga–H	120.6	120.9	–0.3	120.6	121.0	–0.4	
		\angle H–Ga–H	118.8	118.2	0.6	118.7	118.0	0.7	
		\angle Ga–C–H	108.6	109.1	–0.5	108.6	108.9	–0.3	
		\angle Ga–C–H	111.9	112.2	–0.3	111.8	112.1	–0.3	
		\angle H–C–H	107.5	107.1	0.4	107.5	107.2	0.3	
		\angle H–C–H	109.3	108.9	0.4	109.5	109.1	0.4	
		Si–Ga	2.4212	2.4199	0.0013	2.4315	2.4004	0.0311	
		Ga–H	1.5626	1.5830	–0.0204	1.5762	1.5789	–0.0027	
		Si–H	1.4808	1.4816	–0.0008	1.4922	1.4929	–0.0007	
		\angle Si–Ga–H	121.0	121.5	–0.5	121.0	121.6	–0.6	
		\angle H–Ga–H	118.1	116.9	1.2	117.9	116.7	1.2	
		\angle Ga–Si–H	108.8	108.8	0.0	108.7	108.6	0.1	
		\angle Ga–Si–H	112.0	112.1	–0.1	112.4	112.6	–0.2	
		\angle H–Si–H	107.8	107.7	0.1	107.5	107.4	0.1	
		\angle H–Si–H	108.3	108.3	0.0	108.2	108.1	0.1	

^a Reference 14. ^b Reference 15. ^c Reference 16. ^d Reference 17. ^e Reference 18. ^f Reference 19. ^g Reference 20. ^h Reference 21. ⁱ Reference 22. ^j Reference 23. ^k Reference 24. ^l Reference 25. ^m Reference 26. ⁿ Reference 27. ^o Reference 28. ^p Reference 29. ^q Reference 30. ^r Reference 31. ^s Δ represents the difference between parameters calculated with the standard 6-31G(d,p) and the BC6-31G(d,p) basis sets. ^t Bond lengths are in Å and angles are in deg.

Table 2. Mean Absolute Deviations for Bond Lengths and Angles^a

comparison	MAD (bond lengths)	MAD (angles)
experiment vs		
MP2/6-31G(d,p)	0.0118	0.6
MP2/BC6-31G(d,p)	0.0124	0.6
B3LYP/6-31G(d,p)	0.0187	0.5
B3LYP/BC6-31G(d,p)	0.0124	0.5
MP2/6-31G(d,p) vs		
MP2/BC6-31G(d,p)	0.0057	0.3
B3LYP/BC6-31G(d,p) vs		
B3LYP/6-31G(d,p)	0.0078	0.3

^a Mean absolute deviations from experiment were calculated from 25 bond lengths and 18 bond angles, while 36 bond lengths and 36 bond angles were used to calculate the MAD between the calculated bond lengths and angles. Bond lengths are in Å, and angles are in deg.

For bond angles the MAD (18 of bond angles) is 0.5–0.6. Changes in bond lengths with a change in basis set are generally larger at B3LYP (0.0078 Å) than at MP2 (MAD=0.0057 Å). For example in HBr, the difference in bond lengths calculated at B3LYP/6-31G(d,p) and B3LYP/BC6-31G(d,p) is 0.0098 Å, while the difference at MP2/6-31G(d,p) and MP2/BC6-31G(d,p) is 0.0018 Å. However, the difference due to a change of basis set at the MP2 level for X–H bond distances in GaH₃, CH₃SeH, SiH₃SeH, SiH₃GeH₃, CH₃GaG₂, and SiH₃GaH₂ and C–X bond distances in CH₃Br and CH₃AsH₂ are larger than the respective B3LYP values.

3.2. Frequencies of Molecules Containing Third Row Elements. Frequencies for the molecules containing third row elements at MP2/6-31G(d,p), MP2/BC6-31G(d,p), B3LYP/6-31G(d,p), and B3LYP/BC6-31G(d,p) are listed in Table 3 along with the experimental frequencies where available. MAD values for the frequencies are given in Table 4. A total of 145 frequencies of compounds containing third

row elements were used to calculate the MAD between calculated frequencies and 73 to calculate the MAD between experimental and calculated frequencies. In most cases the B3LYP/6-31G(d,p) frequencies are in better agreement with experimental frequencies (Tables 3 and 4), with a MAD of 40.1 cm^{–1} compared to 57.8 cm^{–1} for B3LYP/BC6-31G(d,p) and 94.2 cm^{–1} and 105.4 cm^{–1} for MP2/6-31G(d,p) and MP2/BC6-31G(d,p), respectively. Therefore, for both MP2 and B3LYP the standard 6-31G basis set gives the best agreement, and overall the B3LYP with the standard 6-31G(d,p) basis set performs the best in calculating frequencies for molecules containing third row elements. B3LYP frequencies are found to be slightly more sensitive to the basis set than MP2 frequencies, i.e., the differences between the frequencies calculated at B3LYP/6-31G(d,p) and B3LYP/BC6-31G(d,p), $\Delta\nu(\text{B3LYP})$, are generally larger than the differences between the frequencies calculated at MP2/6-31G(d,p) and MP2/BC6-31G(d,p), $\Delta\nu(\text{MP2})$ (Table 3). For unscaled frequencies the MAD between MP2/6-31G(d,p) and MP2/BC6-31G(d,p) is 16.4 cm^{–1}, while between B3LYP/6-31G(d,p) and B3LYP/BC6-31G(d,p) the MAD is 20.3 cm^{–1}. The MAD between the MP2/6-31G(d,p) and B3LYP/6-31G(d,p) is 58.9 cm^{–1}, while the MAD between the MP2/BC6-31G(d,p) and B3LYP/BC6-31G(d,p) is 51.8 cm^{–1}, when unscaled frequencies are used. Standard frequency scaling factors for compounds containing first and second row elements are available in the literature.^{12,13} The MAD for scaled frequencies using the standard scale factors are also given in Table 4. Scaling improves the frequencies significantly at all levels of theory and basis sets. After scaling MP2/6-31G(d,p) now has the lowest MAD (24.4 cm^{–1}) from experiment. For B3LYP/6-31G(d,p) and B3LYP/BC6-31G(d,p) the MAD are lowered to 29.6 and 29.3 kJ mol^{–1}, respectively, when frequencies are scaled. The MAD between B3LYP/6-31G(d,p) and B3LYP/BC6-31G(d,p) is 19.5 cm^{–1}, while MP2/6-31G(d,p) and MP2/BC6-31G(d,p) is 15.3 cm^{–1}.

Table 3. Calculated and Experimental Frequencies (in cm^{-1}) for Compounds Containing Third Row Elements^a

molecules	point group	freq	MP2			B3LYP			expt
			/6-31G(d,p)	/BC6-31G(d,p)	$\Delta\nu^m$	/6-31G(d,p)	/BC6-31G(d,p)	$\Delta\nu^m$	
HBr	$C_{\infty v}$	ν_1	2759.3	2765.6	-6.3	2622.9	2663.3	-40.4	2558.5 ^b
SeH ₂	C_{2v}	ν_1	1125.1	1162.3	-37.2	1074.5	1131.5	-57.0	1034.2 ^c
		ν_2	2544.3	2595.3	-51.0	2395.5	2449.6	-54.1	2344.5 ^c
		ν_3	2564.0	2611.8	-47.8	2412.3	2466.2	-53.9	2357.8 ^c
AsH ₃	C_{3v}	ν_1	980.8	986.7	-5.9	946.3	968.7	-22.4	906.0 ^c
		$\nu_2(\text{e})$	1079.2	1116.0	-36.8	1031.1	1071.7	-40.6	1003 ^c
		ν_3	2315.1	2380.0	-64.9	2182.4	2261.6	-79.2	2116.1 ^c
		$\nu_4(\text{e})$	2332.4	2395.0	-62.6	2200.7	2282.3	-81.6	2123.0 ^c
GeH ₄	T_d	$\nu_1(\text{t}_2)$	861.3	851.3	10.0	823.6	820.1	3.5	819 ^d
		$\nu_2(\text{e})$	965.1	956.3	8.8	928.9	935.3	-6.4	931 ^d
		ν_3	2245.8	2332.0	-86.2	2138.3	2252.0	-113.7	2114 ^d
		$\nu_4(\text{t}_2)$	2247.4	2340.1	-92.7	2148.7	2273.6	-124.9	
GaH ₃	D_{3h}	ν_1	750.4	730.1	20.3	718.4	711.3	7.1	717.4 ^{e,f}
		$\nu_2(\text{e})$	792.5	784.3	8.2	762.5	776.5	-14.0	758.7 ^{e,g}
		$\nu_3(\text{e})$	2033.8	2039.8	-6.0	1966.6	2018.2	-51.6	1923.2 ^{e,g}
		ν_4	2038.2	2049.9	-11.7	1961.3	2012.2	-50.9	
PH ₂ Br	C_s	ν_1	412.8	423.9	-11.1	383.0	398.7	-15.7	399.79 ^h
		ν_2	818.7	821.4	-2.7	784.9	794.2	-9.3	794.90 ^h
		ν_3	863.9	869.8	-5.9	819.1	831.1	-12.0	812.46 ^h
		ν_4	1165.6	1165.8	-0.2	1135.5	1138.1	-2.6	
		ν_5	2524.0	2522.6	1.4	2389.0	2387.2	1.8	
		ν_6	2537.7	2537.2	0.5	2401.9	2400.9	1.0	
SiHBr	C_s	ν_1	422.7	432.4	-9.6	394.9	410.1	-15.2	424.3 ⁱ
		ν_2	815.7	820.7	-5.0	774.7	785.3	-10.6	553.6 ^j
		ν_3	2164.4	2164.8	-0.4	2039.7	2038.1	1.6	1970.9 ^j
CH ₃ Br	C_{3v}	ν_1	639.0	632.0	7.0	588.4	592.8	-4.4	617, ^j 611 ^{k,c}
		$\nu_2(\text{e})$	1009.3	1003.9	5.4	968.1	967.6	0.5	974 ^j
		ν_3	1405.2	1394.9	10.3	1345.8	1343.2	2.6	1333 ^j
		$\nu_4(\text{e})$	1536.5	1540.4	-3.9	1487.7	1490.5	-2.8	1472 ^j
		ν_5	3177.4	3173.9	3.5	3097.2	3096.1	1.1	3082, ^j 2972 ^k
		$\nu_6(\text{e})$	3304.2	3302.5	1.7	3211.4	3210.0	1.4	3184 ^j
SiH ₃ Br	C_{3v}	ν_1	441.9	448.1	-6.2	414.9	429.2	-14.3	430 ^c
		$\nu_2(\text{e})$	655.4	668.4	-13	628.9	643.8	-14.9	633 ^c
		ν_3	991.4	1000.1	-8.7	944.5	957.9	-13.4	930 ^c
		$\nu_4(\text{e})$	999.0	1001.4	-2.4	954.9	955.2	-0.3	950 ^c
		ν_5	2356.2	2360.1	-3.9	2253.3	2254.7	-1.4	2200 ^c
		$\nu_6(\text{e})$	2374.5	2378.1	-3.6	2271.7	2271.8	-0.1	2196 ^c
CH ₃ SeH	C_s	ν_1	212.0	229.3	-17.3	198.3	181.2	17.1	145 ^l
		ν_2	614.0	606.1	7.9	572.8	571.1	1.7	584 ^l
		ν_3	744.9	764.2	-19.3	715.1	744.3	-29.2	712 ^l
		ν_4	961.1	950.2	10.9	919.5	914.7	4.8	921 ^l
		ν_5	1046.8	1052.0	-5.2	1009.7	1022.8	-13.1	980 ^l
		ν_6	1386.1	1379.2	6.9	1329.8	1329.7	0.1	1288 ^l
		ν_7	1530.0	1536.9	-6.9	1485.1	1490.4	-5.3	1433 ^l
		ν_8	1543.0	1548.0	-5.0	1494.6	1498.5	-3.9	1447 ^l
		ν_9	2535.1	2582.3	-47.2	2378.9	2425.4	-46.5	2330 ^l
		ν_{10}	3163.0	3162.5	0.5	3083.6	3082.4	1.2	2955 ^l
		ν_{11}	3277.1	3277.2	-0.1	3182.4	3181.0	1.4	3027 ^l
		ν_{12}	3284.0	3286.7	-2.7	3190.6	3190.6	0.0	3032 ^l
SiH ₃ SeH	C_s	ν_1	184.4	175.2	9.2	175.9	102.1	73.8	
		ν_2	412.3	420.6	-8.3	386.7	399.8	-13.1	
		ν_3	529.2	554.5	-25.3	507.6	537.4	-29.8	
		ν_4	626.4	641.3	-14.9	598.2	615.0	-16.8	
		ν_5	779.1	802.4	-23.3	754.6	784.4	-29.8	
		ν_6	972.9	981.9	-9.0	924.4	937.2	-12.8	
		ν_7	982.0	983.2	-1.2	939.5	938.2	1.3	
		ν_8	1014.8	1020.1	-5.3	970.9	976.5	-5.6	
		ν_9	2336.4	2337.6	-1.2	2235.1	2235.3	-0.2	
		ν_{10}	2346.3	2347.0	-0.7	2244.5	2243.6	0.9	

Table 3. (Continued)

molecules	point group	freq	MP2			B3LYP			exptl
			/6-31G(d,p)	/BC6-31G(d,p)	$\Delta\nu^m$	/6-31G(d,p)	/BC6-31G(d,p)	$\Delta\nu^m$	
CH ₃ AsH ₂	Cs	ν_{11}	2361.3	2365.0	−3.7	2260.4	2262.6	−2.2	
		ν_{12}	2527.4	2561.9	−34.5	2378.8	2409.5	−30.7	
		ν_1	206.2	238.4	−32.2	195.4	224.1	−28.7	
		ν_2	589.7	590.0	−0.3	554.1	555.5	−1.4	
		ν_3	667.2	699.3	−32.1	651.3	680.6	−29.3	
		ν_4	703.5	726.0	−22.5	678.6	701.7	−23.1	
		ν_5	966.8	959.3	7.5	932.3	930.3	2.0	
		ν_6	999.6	1015.4	−15.8	964.8	985.2	−20.4	
		ν_7	1057.8	1097.6	−39.8	1009.9	1050.9	−41.0	
		ν_8	1356.8	1351.4	5.4	1305.4	1305.9	−0.5	
		ν_9	1530.6	1542.1	−11.5	1488.4	1497.6	−9.2	
		ν_{10}	1534.9	1544.3	−9.4	1490.2	1498.4	−8.2	
		ν_{11}	2297.1	2365.1	−68.0	2157.8	2227.9	−70.1	
		ν_{12}	2309.7	2374.2	−64.5	2172.4	2241.9	−69.5	
SiH ₃ AsH ₂	Cs	ν_{13}	3152.3	3154.0	−1.7	3070.9	3071.2	−0.3	
		ν_{12}	3259.2	3262.0	−2.8	3157.7	3160.3	−2.6	
		ν_{13}	3272.0	3278.0	−6.0	3178.2	3179.4	−1.2	
		ν_1	162.4	143.9	18.5	135.7	128.6	7.1	
		ν_2	376.6	379.7	−3.1	350.0	357.1	−7.1	
		ν_3	462.5	500.8	−38.3	444.1	485.8	−41.7	
		ν_4	481.2	515.3	−34.1	458.9	497.9	−39	
		ν_5	704.6	748.5	−43.9	681.4	732.1	−50.7	
		ν_6	758.9	805.7	−46.8	726.0	778.3	−52.3	
		ν_7	950.3	956.1	−5.8	902.7	912.6	−9.9	
		ν_8	990.0	992.7	−2.7	950.0	951.6	−1.6	
		ν_9	1000.3	1002.2	−1.9	958.4	959.8	−1.4	
		ν_{10}	1046.4	1084.8	−38.4	996.8	1046.5	−49.7	
		ν_{11}	2298.1	2324.2	−26.1	2173.2	2225.7	−52.5	
CH ₃ GeH ₃	C _{3v}	ν_{12}	2312.1	2338.8	−26.7	2187.5	2238.3	−50.8	
		ν_{13}	2322.5	2341.8	−19.3	2223.6	2240.6	−17.0	
		ν_{12}	2337.6	2368.8	−31.2	2239.1	2250.8	−11.7	
		ν_{13}	2341.3	2376.5	−35.2	2241.1	2261.6	−20.5	
		ν_1	177.9	193.0	−15.1	158.3	183.0	−24.7	157 ^c
		$\nu_2(e)$	506.9	496.3	10.6	493.4	490.1	3.3	506 ^c
		ν_3	616.0	637.3	−21.3	586.0	613.9	−27.9	602 ^{c,m}
		ν_4	882.4	872.4	10.0	848.1	845.4	2.7	843 ^{c,m}
		$\nu_5(e)$	886.7	876.8	9.9	857.4	857.5	−0.1	848 ^c
		$\nu_6(e)$	942.0	934.0	8.0	905.1	913.7	−8.6	900 ^c
		ν_7	1340.7	1332.6	8.1	1297.0	1295.4	1.6	1254 ^{c,m}
		$\nu_8(e)$	1525.5	1528.4	−2.9	1484.0	1486.7	−2.7	1428 ^c
		$\nu_9(e)$	2222.4	2312.4	−90	2126.0	2244.6	−118.6	2085 ^{c,m}
		ν_{10}	2223.9	2317.3	−93.4	2129.3	2259.2	−129.9	2084 ^c
SiH ₃ GeH ₃	C _{3v}	ν_{11}	3147.0	3147.2	−0.2	3063.8	3065.2	−1.4	2938 ^{c,m}
		$\nu_{12}(e)$	3255.7	3257.0	−1.3	3153.4	3154.9	−1.5	2997 ^c
		ν_1	122.2	122.3	−0.1	109.2	131.5	−22.3	144 ⁿ
		ν_2	370.1	356.6	13.5	348.4	340.1	8.3	312, ⁿ 318 ^m
		$\nu_3(e)$	376.7	369.5	7.2	370.2	371.0	−0.8	371 ⁿ
		$\nu_4(e)$	627.1	619.5	7.6	600.1	602.5	−2.4	550 ⁿ
		ν_5	825.3	818.1	7.2	794.2	796.2	−2.0	780, ⁿ 785.2 ^m
		$\nu_6(e)$	926.6	916.0	10.6	889.3	899.1	−9.8	881 ⁿ
		ν_7	948.9	943.9	5.0	904.6	905.9	−1.3	890, ⁿ 890.3 ^m
		$\nu_8(e)$	997.6	997.2	0.4	955.5	955.4	0.1	930 ⁿ
		ν_9	2218.7	2294.8	−76.1	2124.5	2221.3	−96.8	2052, ⁿ 2076.6 ^m
		$\nu_{10}(e)$	2223.9	2305.7	−81.8	2134.1	2235.2	−101.1	2069 ⁿ
		ν_{11}	2319.3	2319.2	0.1	2222.5	2235.7	−13.2	2151, ⁿ 2163.1 ^m
		$\nu_{12}(e)$	2334.0	2334.5	−0.5	2236.9	2254.8	−17.9	2160 ⁿ
CH ₃ GaH ₂	Cs	ν_1	10.5	36.4	−25.9	37.3	30.2	7.1	
		ν_2	430.2	417.5	12.7	418.2	419.2	−1.0	
		ν_3	519.2	514.1	5.1	501.8	498.7	3.1	

Table 3. (Continued)

molecules	point group	freq	MP2			B3LYP			exptl
			/6-31G(d,p)	/BC6-31G(d,p)	$\Delta\nu^m$	/6-31G(d,p)	/BC6-31G(d,p)	$\Delta\nu^m$	
SiH ₃ GaH ₂	Cs	ν_4	586.4	597.3	-10.9	560.0	578.9	-18.9	
		ν_5	769.1	758.1	11.0	750.4	748.9	1.5	
		ν_6	805.2	792.5	12.7	773.9	781.2	-7.3	
		ν_7	821.1	806.0	15.1	800.0	792.4	7.6	
		ν_8	1299.5	1293.8	5.7	1256.1	1254.0	2.1	
		ν_9	1510.7	1510.3	0.4	1470.2	1468.6	1.6	
		ν_{10}	1520.7	1518.9	1.8	1477.0	1475.4	1.6	
		ν_{11}	2004.7	2019.9	-15.2	1933.4	1993.3	-59.9	1892.0 ^g
		ν_{12}	2012.1	2030.1	-18.0	1935.6	1994.3	-58.7	1898.0 ^g
		ν_{13}	3127.6	3123.8	3.8	3039.5	3038.6	0.9	
		ν_{14}	3221.7	3214.6	7.1	3115.0	3111.7	3.3	
		ν_{15}	3253.5	3245.4	8.1	3148.2	3144.9	3.3	
		ν_1	6.6	13.0	-6.4	29.5	35.6	-6.1	
		ν_2	336.7	326.1	10.6	318.6	323.9	-5.3	
		ν_3	339.8	334.8	5.0	325.9	332.5	-6.6	
		ν_4	407.3	394.2	13.1	379.8	381.0	-1.2	
		ν_5	573.2	562.7	10.5	544.7	549.4	-4.7	
		ν_6	618.5	604.9	13.6	591.3	591.5	-0.2	
		ν_7	781.7	772.5	9.2	753.0	769.5	-16.5	
		ν_8	933.1	929.5	3.6	884.3	888.8	-4.5	
		ν_9	991.1	990.0	1.1	947.7	946.1	1.6	
		ν_{10}	999.3	998.7	0.6	956.5	956.1	0.4	
		ν_{11}	2006.3	2023.9	-17.6	1932.6	1994.8	-62.2	
		ν_{12}	2009.2	2026.2	-17	1940.7	2001.5	-60.8	
		ν_{13}	2297.2	2293.0	4.2	2198.4	2195.5	2.9	
		ν_{14}	2314.2	2311.0	3.2	2216.5	2215.2	1.3	
		ν_{15}	2321.0	2318.3	2.7	2224.2	2222.9	1.3	

^a Calculated frequencies are not scaled. ^b Reference 32. ^c Reference 33. ^d Reference 34. ^e Reference 35. ^f Reference 36. ^g Reference 37. ^h Reference 38. ⁱ Reference 20. ^j Reference 39. ^k Reference 22. ^l Reference 27. ^m Reference 40. ⁿ Reference 31(b). ^m Δ represents the difference between frequencies calculated with the standard 6-31G(d,p) and the BC6-31G(d,p) basis sets.

Table 4. Mean Absolute Deviations for Frequencies (in cm⁻¹)^a

comparison (unscaled frequencies)	MAD	comparison (scaled frequencies)	MAD
experiment vs		experiment vs	
MP2/6-31G(d,p)	94.2	MP2/6-31G(d,p)	24.4
MP2/BC6-31G(d,p)	105.4	MP2/BC6-31G(d,p)	35.4
B3LYP/6-31G(d,p)	40.1	B3LYP/6-31G(d,p)	29.6
B3LYP/BC6-31G(d,p)	57.8	B3LYP/BC6-31G(d,p)	29.3
MP2/6-31G(d,p) vs		MP2/6-31G(d,p) vs	
MP2/BC6-31G(d,p)	16.4	MP2/BC6-31G(d,p)	15.3
B3LYP/6-31G(d,p)	58.9	B3LYP/6-31G(d,p)	22.7
B3LYP/BC6-31G(d,p) vs		B3LYP/BC6-31G(d,p) vs	
B3LYP/6-31G(d,p)	20.3	B3LYP/6-31G(d,p)	19.5
MP2/BC6-31G(d,p)	51.8	MP2/BC6-31G(d,p)	18.9

^a A total of 73 frequencies were used to calculate the MAD between experimental and calculated frequencies, and 145 frequencies were used to calculate the MAD between the calculated frequencies.

It is interesting to note that after scaling the MAD are now similar for all levels of theory and basis sets.

The frequency scaling factors for first and second row elements are 0.9608 and 0.9370 at B3LYP/6-31G(d,p) and MP2/6-31G(d,p), respectively.^{12,13} Using the 73 experimental frequencies available for compounds containing third row elements scaling factors were calculated by dividing the experimental frequencies with the corresponding calculated

frequencies and then taking their average. The scale factors were found to be 0.9408 and 0.9246 at B3LYP/6-31G(d,p) and B3LYP/BC6-31G(d,p), respectively, and 0.8982 and 0.8926 at MP2/6-31G(d,p) and MP2/BC6-31G(d,p), respectively. These scaling factors indicate that in general frequencies calculated for compounds involving third row elements tend to be generally higher than those calculated for compounds containing first and second row elements.

3.3. Thermodynamic Properties for the Isogyric Reactions Involving Third Row Elements. The thermodynamic properties for reactions 1 and 2 are listed in Table 5.

For all X, X = Ga, Ge, As, Se, and Br, reaction 1 is exothermic with G3MP2 enthalpies of -2.3, -9.2, -29.6, -46.7, and -56.0 kJ mol⁻¹, respectively. From Figure 1, it is interesting to note that all levels predict that the enthalpy of reaction becomes more exothermic in going from Ga to Br. The G3MP2 free energies of reaction for X = Ge, As, Se and Br are exergonic with values of -9.2, -29.9, -44.5, and -54.3 kJ mol⁻¹, while for X = Ga the reaction is slightly endergonic with a G3MP2 free energy of 5.0 kJ mol⁻¹. For X = Ga, Ge, and As, reaction 2 is exothermic with G3MP2 enthalpies of -23.8, -25.3, and -14.2 kJ mol⁻¹, respectively, while for X = Se and Br, reaction 2 is endothermic with ΔH of 13.0 and 43.6 kJ mol⁻¹, respectively. From Figure 2, we see that in this case the enthalpy of reaction becomes more endothermic in going from Ga to Br for all

Table 5. Thermodynamic Properties for the Reactions 1 and 2 (in kJ mol⁻¹) at 298.15 K

CH ₃ GaH ₂ + HCN → CH ₃ CN + GaH ₃								SiH ₃ GaH ₂ + HCN → SiH ₃ CN + GaH ₃						
	6-31G(d)			BC6-31G(d)				6-31G(d)			BC6-31G(d)			
level	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a
HF	−22.0	−25.5	−18.6	−11.5	−14.7	−8.3	−10.8	−29.0	−36.4	−29.5	−24.4	−31.6	−24.6	−4.8
MP2(P) ^b	−4.1	−6.8	−0.9	0.2	−2.3	2.7	−4.5	−22.6	−28.4	−21.5	−22.4	−25.6	−28.4	−2.8
B3LYP(P) ^b	−14.5	−17.9	−11.8	−8.1	−8.7	−11.1	−9.2	−17.9	−24.3	−18.9	−16.1	−22.3	−17.5	−2.0
G3MP2	−0.8	−2.3	5.0					−22.3	−23.8	−19.3				
CH ₃ GeH ₃ + HCN → CH ₃ CN + GeH ₄								SiH ₃ GeH ₃ + HCN → SiH ₃ CN + GeH ₄						
	6-31G(d)			BC6-31G(d)				6-31G(d)			BC6-31G(d)			
level	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a
HF	−24.3	−27.4	−27.8	−5.3	−8.7	−9.3	−18.7	−31.1	−36.5	−36.4	−14.7	−19.7	−19.6	−16.8
MP2(P) ^b	−11.1	−13.4	−14.1	1.4	−0.4	−1.3	−13.0	−24.6	−28.5	−28.6	−16.7	−19.7	−19.7	−8.8
B3LYP(P) ^b	−22.2	−25.6	−25.6	−10.2	−13.0	−13.5	−12.6	−21.6	−26.4	−26.0	−14.1	−18.0	−17.7	−8.4
G3MP2	−8.6	−9.2	−9.2					−24.4	−25.3	−27.5				
CH ₃ AsH ₂ + HCN → CH ₃ CN + AsH ₃								SiH ₃ AsH ₂ + HCN → SiH ₃ CN + AsH ₃						
	6-31G(d)			BC6-31G(d)				6-31G(d)			BC6-31G(d)			
level	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a
HF	−41.2	−45.4	−46.0	−25.5	−30.3	−31.3	−15.1	−19.4	−24.9	−25.6	12.0	5.2	4.3	−30.1
HF(P) ^b	−40.6	−44.6	−45.2	−30.8	−34.7	−35.7	−9.9	−37.7	−24.8	−25.4	3.7	−1.8	−2.4	−23.0
MP2	−29.8	−33.2	−34.0	−15.9	−19.9	−21.1	−13.3	−9.7	−14.0	−14.9	19.2	13.7	12.5	−27.7
MP2(P) ^b	−29.2	−32.3	−33.0	−20.0	−23.0	−24.2	−9.3	−11.8	−15.8	−16.7	10.0	5.8	4.9	−21.6
B3LYP	−41.8	−45.7	−46.1	−27.0	−31.4	−32.2	−14.3	−14.3	−19.2	−19.3	14.1	7.9	7.3	−27.1
B3LYP(P) ^b	−39.1	−43.2	−43.6	−30.0	−33.8	−34.6	−9.4	−12.3	−17.3	−17.3	8.3	3.1	2.7	−20.4
G3MP2	−29.6	−29.6	−29.9					−14.1	−14.2	−17.3				
CH ₃ SeH + HCN → CH ₃ CN + SeH ₂								SiH ₃ SeH + HCN → SiH ₃ CN + SeH ₂						
	6-31G(d)			BC6-31G(d)				6-31G(d)			BC6-31G(d)			
level	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a
HF	−50.9	−56.6	−54.5	−41.5	−47.3	−45.4	−9.3	15.9	8.8	10.1	46.9	39.2	40.3	−30.4
HF(P) ^b	−53.5	−59.0	−56.9	−49.1	−54.2	−52.3	−4.8	12.9	6.0	7.3	37.1	30.4	31.6	−24.4
MP2	−39.8	−44.5	−42.7	−33.1	−37.7	−36.0	−6.8	22.7	16.8	17.7	50.7	44.2	45.0	−27.4
MP2(P) ^b	−42.9	−47.3	−45.4	−39.9	−43.9	−42.2	−3.4	17.8	12.2	13.1	40.4	34.9	35.9	−22.7
B3LYP	−49.4	−54.6	−52.4	−40.6	−45.5	−43.3	−9.1	15.6	9.1	10.5	43.4	36.7	38.2	−27.6
B3LYP(P) ^b	−49.6	−55.0	−52.7	−45.6	−50.5	−47.9	−4.5	14.9	8.3	9.8	36.3	30.2	32.7	−21.9
G3MP2	−47.1	−46.7	−44.5					12.3	13.0	11.7				
CH ₃ Br + HCN → CH ₃ CN + HBr								SiH ₃ Br + HCN → SiH ₃ CN + HBr ^e						
	6-31G(d)			BC6-31G(d)				6-31G(d)			BC6-31G(d)			
level	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	Δ(ΔH) ^a
HF	−49.3	−55.4	−53.6	−45.2	−51.4	−49.6	−4.0	58.2	50.1	50.6	82.0	73.5	73.9	−23.4
HF(P) ^b	−56.2	−62.0	−60.1	−55.6	−61.2	−59.3	−0.8	51.0	43.3	43.9	71.0	63.2	63.6	−19.9
MP2	−42.4	−47.3	−45.8	−41.0	−45.8	−44.3	−1.5	58.4	51.8	51.9	79.6	72.6	72.6	−20.8
MP2(P) ^b	−50.5	−55.1	−53.5	−51.0	−55.4	−53.8	0.3	49.5	43.1	43.3	68.7	62.1	62.2	−19.0
B3LYP	−48.8	−54.1	−52.2	−44.5	−49.9	−48.0	−4.2	50.7	43.6	44.1	72.1	64.6	64.9	−21.0
B3LYP(P) ^b	−52.9	−58.1	−56.2	−52.2	−57.2	−55.3	−0.9	46.2	39.3	39.8	63.8	56.8	57.2	−17.5
G3MP2	−56.9	−56.0	−54.3	−57.1	−56.1	−54.5	0.1	42.0	43.6	43.8	40.4	42.0	42.1	1.6
exptl		−63.2 ^c												
									29.6 ^d					

^a $\Delta(\Delta H)$ represents the difference between enthalpies of reaction calculated with the standard 6-31G and the BC6-31G basis sets. ^b Represents 6-31G(d,p) basis set. ^c The value is calculated from experimental ΔH_f of CH_3Br , HCN , CH_3CN , and HBr given in Table 9. ^d The value is calculated from experimental ΔH_f of SiH_3Br , HCN , SiH_3CN , and HBr given in Table 9. ^e The thermodynamic properties are taken from ref 7.

levels of theory. Similarly, the free energies are exergonic for X = Ga, Ge, and As, with values of -19.3 , -27.5 , and -17.3 kJ mol $^{-1}$, respectively, and endergonic for X = Se and Br, with values of 11.7 and 43.8 kJ mol $^{-1}$ at G3MP2.

For the reactions with CH_3Br and SiH_3Br , the G3MP2 enthalpies and free energies are calculated using both the standard 6-31G(d) and BC6-31G(d) basis sets. The G3MP2 energies calculated using the standard 6-31G(d)

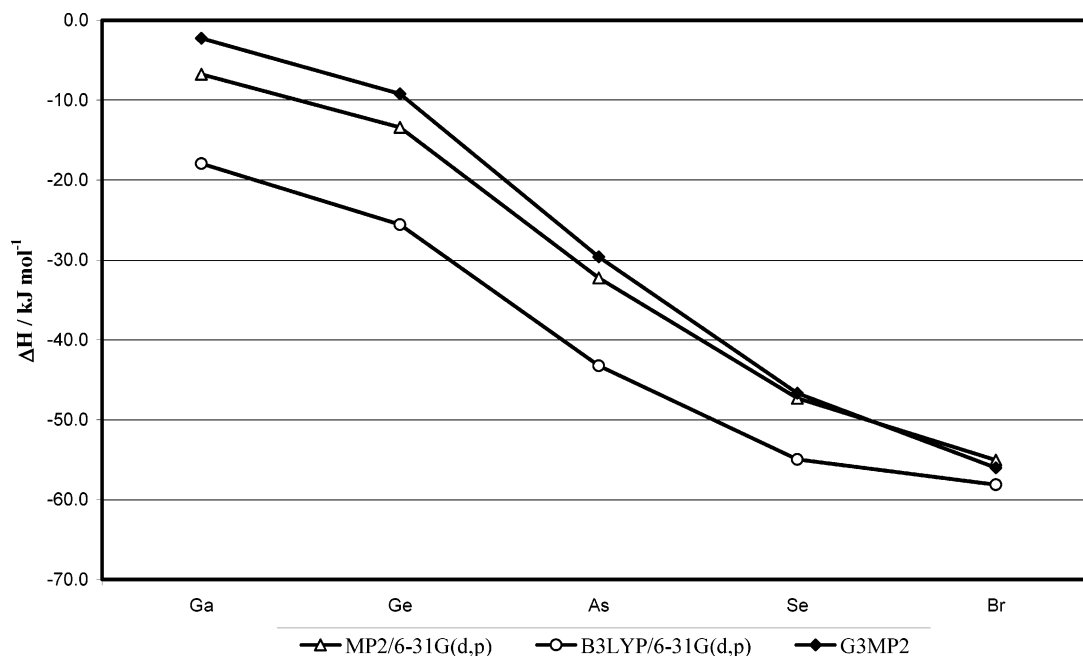


Figure 1. Enthalpies of reaction 1 calculated at different levels of theory with the standard 6-31G(d,p) basis set.

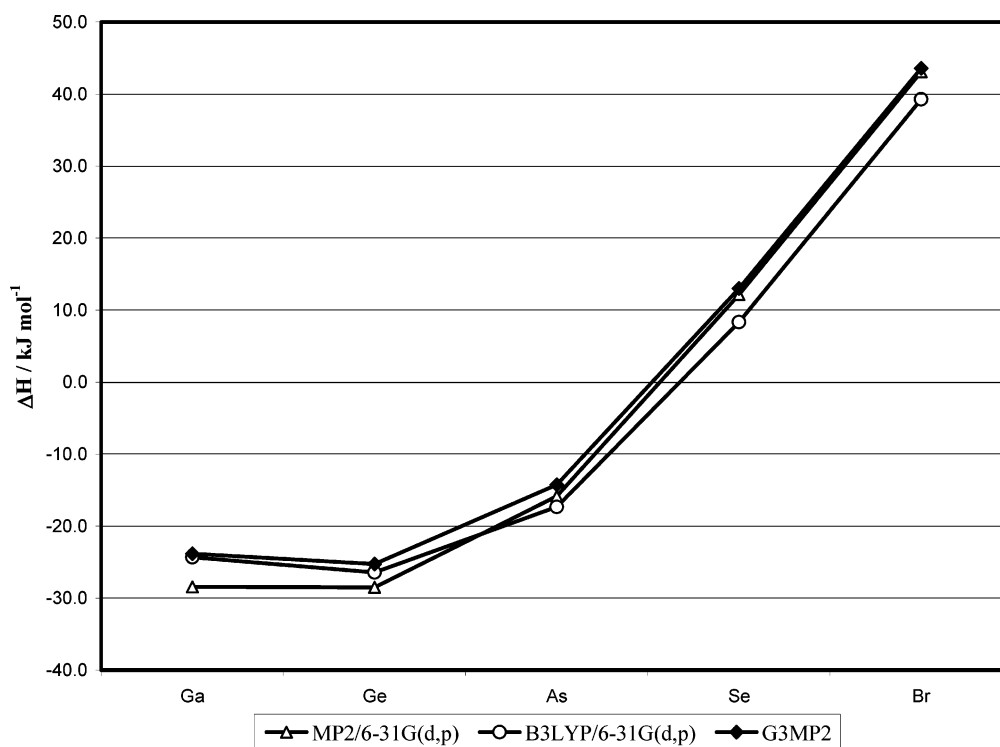


Figure 2. Enthalpies of reaction 2 calculated at different levels of theory with the standard 6-31G(d,p) basis set.

and the BC6-31G(d) basis set differ by only 0.2 kJ mol⁻¹ for the reaction with CH₃Br and 1.6 kJ mol⁻¹ with SiH₃Br (Table 5). Experimental enthalpies of reaction estimated from the heats of formation of the individual species (Table 9, to be discussed) are only available for the reaction with CH₃-Br and SiH₃Br. The G3MP2 enthalpies for both these two reactions agree reasonably well with experiment deviating by 7 kJ mol⁻¹ and 14 kJ mol⁻¹, respectively. Although in some reactions addition of p-polarization functions to hydrogen gives better thermodynamic values, overall polarization functions have little effect on the thermodynamics.

Figures 3 (reaction 1) and 4 (reaction 2) represent the differences between the G3MP2 enthalpies from the enthalpies calculated at the MP2 and B3LYP levels of theory using both the standard 6-31G(d,p) and BC6-31G(d,p) basis sets. From Figure 3, it is clear that when X = Br, the error in the enthalpies calculated at the MP2 and B3LYP levels of theory is small for both the basis sets. This is similar to our previous investigation on the bromination of alkenes.⁸ However, the errors in enthalpies calculated at B3LYP/6-31G(d,p) are slightly larger for X = Ga, Ge, As, and Se. For all X in reaction 2, the enthalpies of reaction calculated at both the

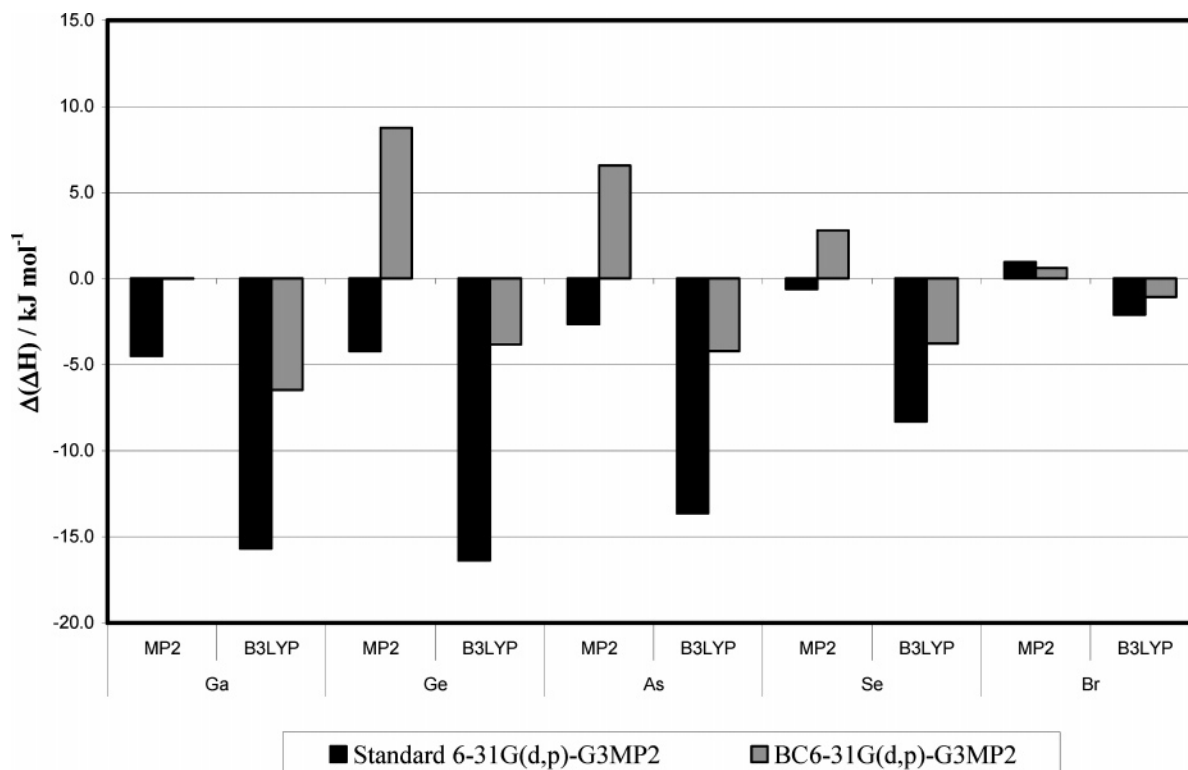


Figure 3. Difference between enthalpies of reaction 1 calculated at the MP2 and B3LYP levels of theory with G3MP2.

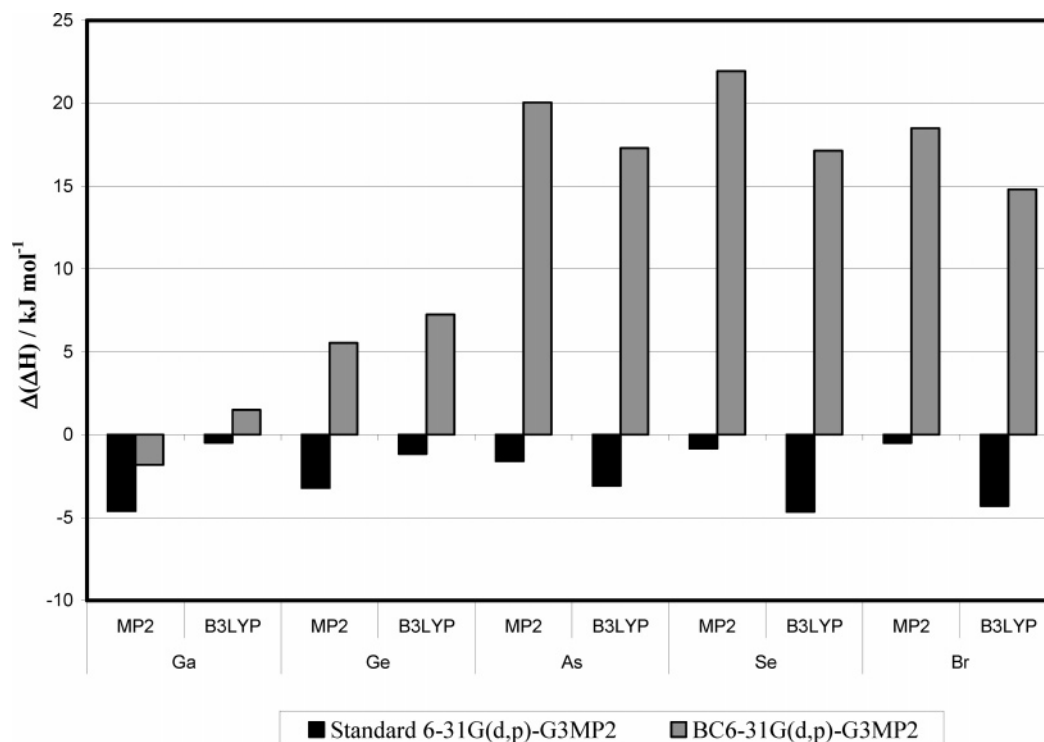


Figure 4. Difference between enthalpies of reaction 2 calculated at the MP2 and B3LYP levels of theory with G3MP2.

MP2 and B3LYP levels of theory using the standard 6-31G-(d,p) basis set are in excellent agreement with the G3MP2 enthalpies (all within 5 kJ mol⁻¹), while the BC6-31G(d) basis set performs especially poorly for X = Ge, As, Se, and Br. It is important to mention here that for the reaction of HCN with SiH₃AsH₂ the enthalpy calculated by the BC6-31G basis set is found to be endothermic, while with standard

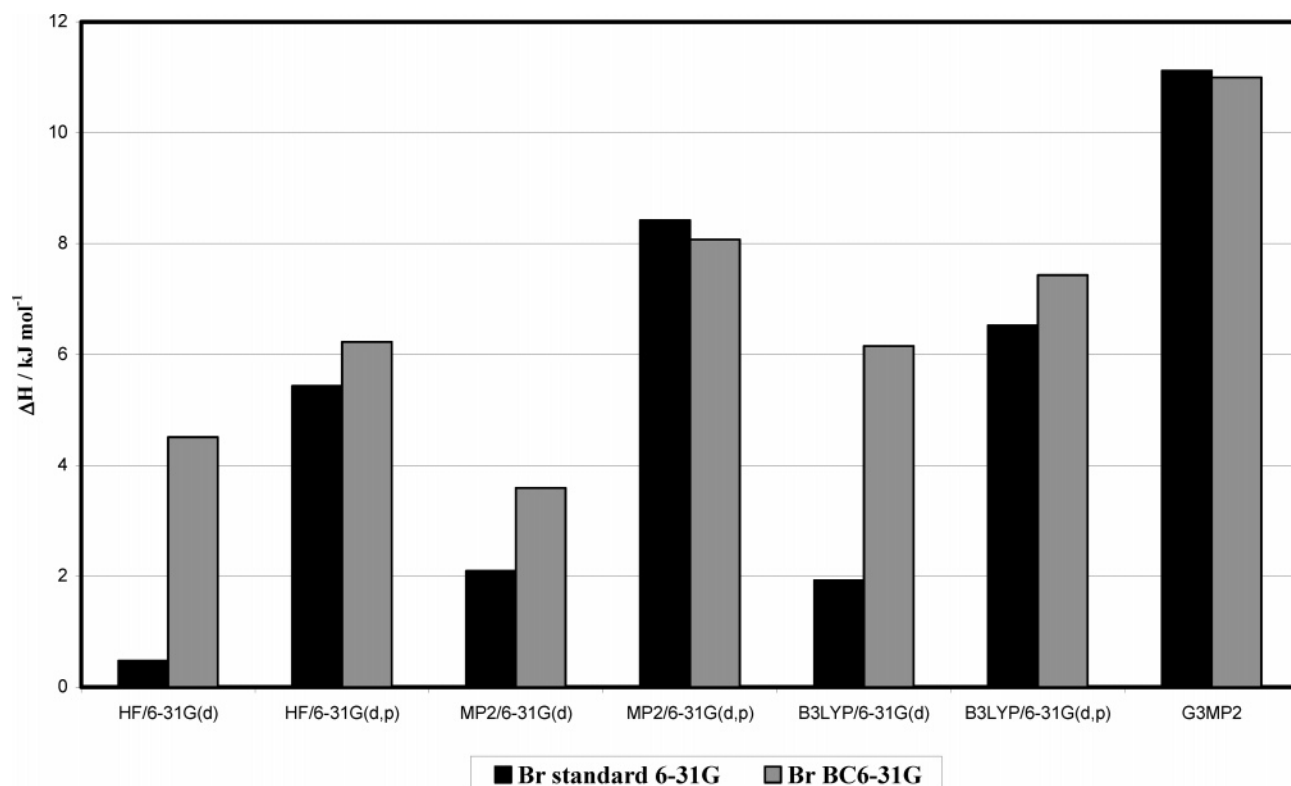
6-31G, it is found to be exothermic in agreement with the G3MP2 level of theory (Table 5).

Both reactions 1 and 2 involved HCN as one of the reactants. To see the effect of second row elements on reaction thermodynamics, two more reactions, reaction 3 (CH₃Br + HCl → CH₃Cl + HBr) and reaction 4 (SiH₃Br + HCl → SiH₃Cl + HBr) are considered. The thermodynamic

Table 6. Thermodynamic Properties for the Reactions 3 and 4 (in kJ mol^{-1}) at 298.15 K

level	$\text{CH}_3\text{Br} + \text{HCl} \rightarrow \text{CH}_3\text{Cl} + \text{HBr}$							$\text{SiH}_3\text{Br} + \text{HCl} \rightarrow \text{SiH}_3\text{Cl} + \text{HBr}$						
	6-31G(d)			BC6-31G(d)			$\Delta(\Delta H)^a$	6-31G(d)			BC6-31G(d)			$\Delta(\Delta H)^a$
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG		ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	
HF	1.0	0.5	-2.4	5.1	4.5	1.7	-4.0	-5.4	-6.7	-6.8	18.4	16.7	16.5	-23.4
HF(P) ^b	6.0	5.4	2.6	6.6	6.2	3.4	-0.8	-1.2	-2.4	-2.4	18.7	17.5	17.4	-19.9
MP2	2.5	2.1	-0.7	3.9	3.6	0.8	-1.5	-1.7	-2.9	-2.9	19.5	17.9	17.8	-20.8
MP2(P) ^b	8.9	8.4	5.6	8.4	8.1	5.3	0.3	4.0	2.9	2.9	23.2	21.8	21.8	-18.9
B3LYP	2.3	1.9	-0.9	6.6	6.2	3.3	-4.3	-5.2	-6.1	-6.1	16.2	14.9	14.7	-21.0
B3LYP(P) ^b	7.0	6.5	3.7	7.7	7.4	4.7	-0.9	-1.3	-2.3	-2.3	16.3	15.2	15.1	-17.5
G3MP2	11.3	11.1	8.3	11.2	11.0	8.2	0.1	-2.4	-2.7	-2.7	-4.0	-4.3	-1.7	-1.6
exptl	6.5 ^c							-7.7 ^d						

^a $\Delta(\Delta H)$ represents the difference between enthalpies of reaction calculated with the standard 6-31G and the BC6-31G basis sets. ^b Represents 6-31G(d,p) basis set. ^c The value is calculated from the experimental ΔH_f° of CH_3Br , HCl , CH_3Cl , and HBr given in Table 9. ^d The value is calculated from the experimental ΔH_f° of SiH_3Br , HCl , SiH_3Cl , and HBr given in Table 9.

**Figure 5.** Enthalpy of reaction for $\text{CH}_3\text{Br} + \text{HCl} \rightarrow \text{CH}_3\text{Cl} + \text{HBr}$ calculated at different levels of theory and basis sets.

properties for reactions 3 and 4 are listed in Table 6, and the plots of reaction enthalpies vs theory/basis set are given in Figure 5 for reaction 3 and Figure 6 for reaction 4. G3MP2 enthalpies calculated with the standard 6-31G(d) basis set are in excellent agreement with the G3MP2 enthalpies calculated with the BC6-31G(d) basis set, differing by only 0.1 kJ mol^{-1} for reaction 3 and 1.6 kJ mol^{-1} for reaction 4. The G3MP2 enthalpies were also found to agree well with experiment differing by no more than 5 kJ mol^{-1} . The G3MP2 enthalpies calculated with both the standard 6-31G(d) and BC6-31G(d) basis set are found to be endothermic for reaction 3 and exothermic for reaction 4. For reaction 3, the HF, MP2, and B3LYP enthalpies calculated using the standard 6-31G and the BC6-31G basis set are in excellent agreement, differing by no more than 4.3 kJ mol^{-1} . In this case, all enthalpies of reaction are in good agreement with both the G3MP2 and experimental values. However, for

reaction 4, the differences between the enthalpies of reaction calculated with the standard 6-31G and the BC6-31G basis set are large, ranging from 17.5 to 23.4 kJ mol^{-1} . The reaction enthalpies calculated with the standard 6-31G basis set are found to be exothermic (except for MP2/6-31G(d,p)), while the reaction enthalpies obtained by BC6-31G are endothermic for all levels of theory and basis sets investigated (Table 6 and Figure 6). In this case, the enthalpies calculated with the BC6-31G basis set are in poor agreement with both the G3MP2 and the experimental values. Therefore, the choice of basis set is extremely important for reactions involving both second and third row elements.

For reactions 2 and 4, both involving Si, the standard 6-31G basis set predicts better reaction enthalpies and free energies than the BC6-31G basis set. It would be interesting to see if the same result is found for other second row elements. Therefore, thermodynamic properties for reaction

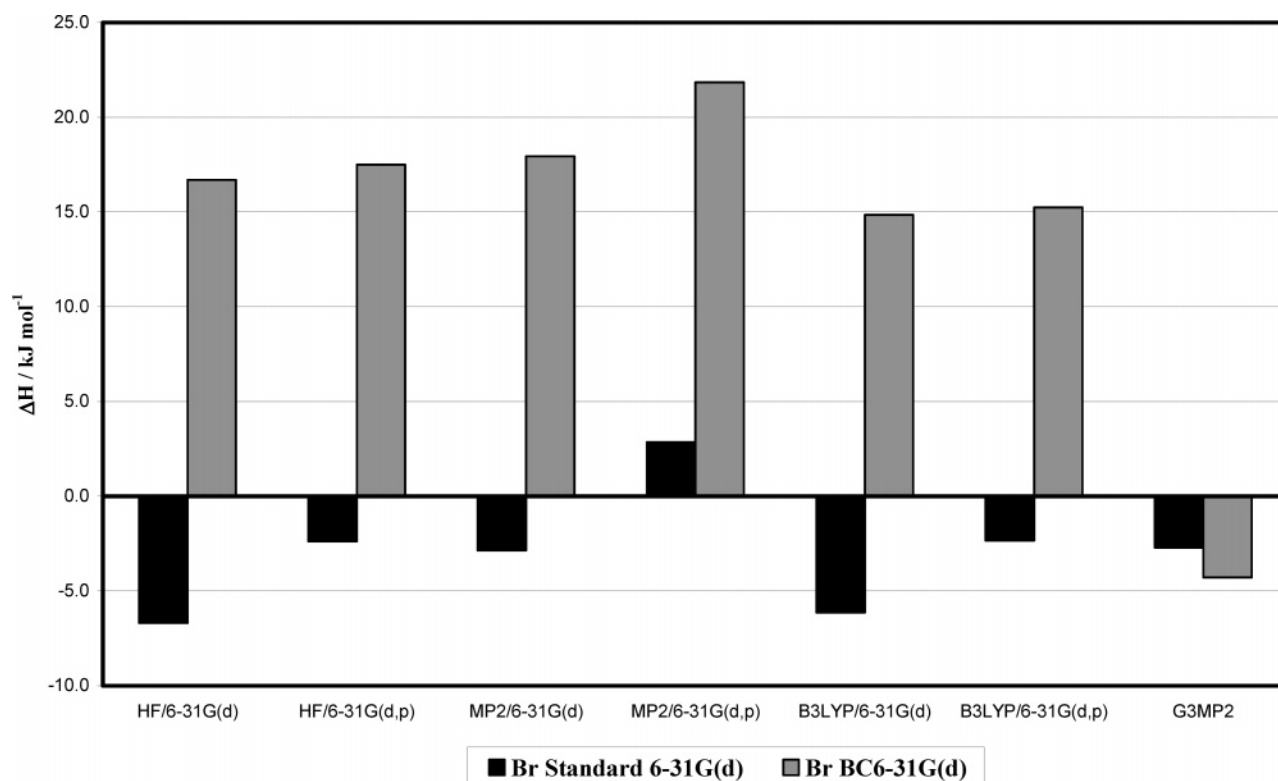


Figure 6. Enthalpy of reaction for $\text{SiH}_3\text{Br} + \text{HCl} \rightarrow \text{SiH}_3\text{Cl} + \text{HBr}$ calculated at different levels of theory and basis sets.

Table 7. Thermodynamic Properties for the Reaction 5 (in kJ mol^{-1}) at 298.15 K

level	6-31G(d)			BC6-31G(d)			$\Delta(\Delta H)^a$
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	
HF	18.8	11.4	12.8	34.4	26.8	28.0	-15.4
HF(P) ^b	11.9	4.9	6.3	23.7	16.7	18.0	-11.8
MP2	15.0	9.0	10.0	29.4	23.1	24.0	-14.1
MP2(P) ^b	6.3	0.6	1.6	18.6	12.8	13.8	-12.2
B3LYP	17.1	10.7	12.0	30.2	23.5	24.7	-12.8
B3LYP(P) ^b	12.9	6.5	7.9	22.1	15.8	17.1	-9.3
G3MP2	4.5	5.6	6.8				

^a $\Delta(\Delta H)$ represents the difference between enthalpies of reaction calculated with the standard 6-31G and the BC6-31G basis sets.

^b Represents the 6-31G(d,p) basis set.

5, $\text{PH}_2\text{Br} + \text{HCN} \rightarrow \text{PH}_2\text{CN} + \text{HBr}$, are calculated using both the standard 6-31G and the BC6-31G basis sets, and the values are given in Table 7. The plot of reaction enthalpies vs level of theory/basis set is shown in Figure 7. Differences in enthalpies calculated with the standard 6-31G and the BC6-31G basis sets range from 9.3 to 15.4 kJ mol^{-1} depending on the level of theory. Like reaction 4, SiH_3Br , the reaction enthalpies and free energies calculated with the standard 6-31G basis set is in better agreement with G3MP2 values (Table 7 and Figure 7).

Mean Absolute Deviations (MAD) of the Reaction Enthalpies. The mean absolute deviations for the reaction enthalpies involving first and third row elements, reaction 1, and for reactions involving first, second, and third row elements, reactions 2 and 5, are calculated at different levels of theory and basis sets from G3MP2 enthalpies, and the values are given in Table 8. The MAD for enthalpies of reactions involving first and third row elements are not

significantly affected by the change of basis set, ranging from 2.6 to 13.5 kJ mol^{-1} for the standard 6-31G basis set and 1.8 to 5.8 kJ mol^{-1} for the BC6-31G basis set. The MAD are slightly higher at B3LYP/6-31G(d,p) and HF/6-31G(d). On the other hand, the MAD for the reaction enthalpies involving first, second, and third row elements (reactions 2 and 5) are significantly larger for the BC6-31G basis set at all levels of theory investigated, ranging from 10.1 to 18.4 kJ mol^{-1} . The MAD for the standard 6-31G basis set range from only 2.3 to 8.5 kJ mol^{-1} depending on the level of theory. Therefore, although the Binning-Curtiss and standard basis sets perform almost identically for reactions involving only first and third row elements, the standard basis set performs much better for reactions involving first, second, and third row elements. These results indicate that the BC6-31G basis set for third row elements is improperly balanced relative to the standard 6-31G basis set used for first and second row elements. The imbalance would result in basis set superposition error and basis set incompleteness error. The extra basis functions (3d) for the standard basis set are evidently playing a significant role, especially when bonding between second and third row elements is present.

3.4. Exploring Heats of Formation (ΔH_f). No experimental or theoretical heats of formation (ΔH_f) have been reported for CH_3SeH , SiH_3SeH , CH_3AsH_2 , SiH_3AsH_2 , $\text{CH}_3\text{-GeH}_3$, and SiH_3GeH_3 . In this study, the enthalpies for reactions 1 and 2 for all X, X = Ga, Ge, As, Se, and Br, have been obtained. The ΔH_f values obtained in this study are given in Table 9. From the G3MP2 enthalpies of reaction and the most recent and reliable experimental heats of formation for CH_3CN , SiH_3CN , SeH_2 , AsH_3 , GeH_4 , HCN , ΔH_f for CH_3SeH , SiH_3SeH , CH_3AsH_2 , SiH_3AsH_2 , CH_3GeH_3 , and SiH_3GeH_3 are calculated to be 18.3, 18.0, 38.4, 82.4,

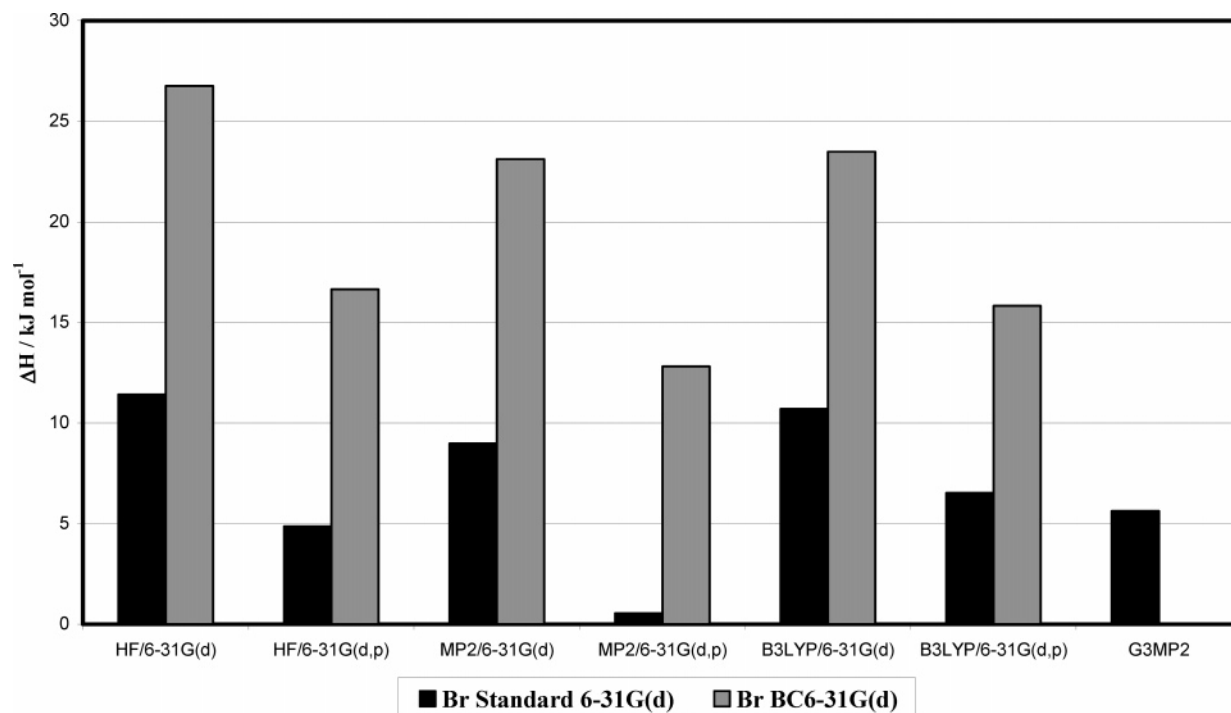


Figure 7. Enthalpy of reaction for $\text{PH}_2\text{Br} + \text{HCN} \rightarrow \text{PH}_2\text{CN} + \text{HBr}$ calculated at different levels of theory and basis sets.

Table 8. Mean Absolute Deviations for the Enthalpies of Reaction Involving First and Third Row Elements, Reaction 1, and First, Second, and Third Row Elements, Reactions 2 and 5 (in kJ mol^{-1})

theory	reaction 1		reactions 2 and 5	
	6-31G(d)	BC6-31G(d)	6-31G(d)	BC6-31G(d)
HF	13.5	3.8	8.5	18.4
HF(P) ^b	6.7	3.6	3.1	10.1
MP2	2.9	5.8	2.6	17.6
MP2(P) ^b	2.6	3.8	2.6	12.5
B3LYP	5.2	1.8	2.3	14.1
B3LYP(P) ^b	11.2	3.9	2.4	11.1

^a MAD is calculated from G3MP2 enthalpies. ^b Represents the 6-31G(d,p) basis set.

41.9, and 117.4 kJ mol^{-1} , respectively. Heats of formation were also calculated for HCN, CH_3CN , SiH_3CN , HBr, CH_3Br , SiH_3Br , CH_3Cl , HCl and SiH_3Cl , for which reliable ΔH_f values are available for comparison. The ΔH_f for CH_3Br , HCN, CH_3CN , and HBr are calculated using the G3MP2 enthalpy of reaction for $\text{CH}_3\text{Br} + \text{HCN} \rightarrow \text{CH}_3\text{CN} + \text{HBr}$ ($\Delta H = -56.0 \text{ kJ mol}^{-1}$ at G3MP2) and the most recent experimental heats of formation for CH_3Br , HCN, CH_3CN , and HBr (given in Table 9). The resulting ΔH_f values are -37.8 , 131.8 , 73.9 , and $-36.4 \text{ kJ mol}^{-1}$, respectively, all values being in excellent agreement with experiment. Similarly, heats of formation for HCN, SiH_3Br , SiH_3CN , and HBr are calculated using the enthalpy of reaction for $\text{SiH}_3\text{Br} + \text{HCN} \rightarrow \text{SiH}_3\text{CN} + \text{HBr}$ (43.6 kJ mol^{-1} at G3MP2), along with experimental heats of formation for HCN, SiH_3Br , HBr, and SiH_3CN . The ΔH_f values are again in excellent agreement with experiment. Heats of formation of CH_3Br , HBr, SiH_3Br , CH_3Cl , HCl, and SiH_3Cl are also calculated using the enthalpy of reaction 3, $\text{CH}_3\text{Br} + \text{HCl} \rightarrow \text{CH}_3\text{Cl} + \text{HBr}$ (11.1 kJ mol^{-1} at G3MP2), and reaction 4, $\text{SiH}_3\text{Br} + \text{HCl}$

Table 9. Heats of Formation (ΔH_f) (in kJ mol^{-1}) at 298.15 K^a

molecules	experiment	present work	molecules	present work ^a
CH_3Br	-38.0 ± 1.3^b	$-37.8,^n -38.7^p$	CH_3SeH	18.3
HCN	131.67^c	$131.8,^n 131.9^o$	SiH_3SeH	18.0
CH_3CN	74.04 ± 0.37^d	73.9^n	CH_3AsH_2	38.4
HBr	$-36.2^{e,f}$	$-36.4,^n -36.5,^o$	SiH_3AsH_2	82.4
		$-35.5,^p -31.4^q$		
SiH_3Br	-78.24^g	$-78.0,^o -83.0^q$	CH_3GeH_3	41.9
SiH_3CN	133.5^h	130.1^o	SiH_3GeH_3	117.4
SeH_2	29.2 ± 0.8^i			
AsH_3	$66.4 \pm 1^{j,k}$			
GeH_4	$90.3 \pm 2^{l,m}$			
CH_3Cl	-83.68^g	-83.01^p		
HCl	-92.31^g	$-93.0,^p -97.1^q$		
SiH_3Cl	-141.84^g	-137.1^q		

^a See text for explanation. ^b Reference 41. ^c Reference 42. ^d Reference 43. ^e Reference 44. ^f Reference 45. ^g Reference 46. ^h Reference 7 (obtained from experimental heats of formation and calculated heat of reaction). ⁱ Reference 47. ^j Reference 48. ^k Reference 49. ^l Reference 50. ^m Reference 51. ⁿ Calculated using the enthalpy of reaction for $\text{CH}_3\text{Br} + \text{HCN} \rightarrow \text{CH}_3\text{CN} + \text{HBr}$ and experimental ΔH_f values for CH_3Br , HCN, CH_3CN , and HBr. ^o Calculated using the enthalpy of reaction for $\text{SiH}_3\text{Br} + \text{HCN} \rightarrow \text{SiH}_3\text{CN} + \text{HBr}$ and experimental ΔH_f values for SiH_3Br , HCN, HBr, and SiH_3CN . ^p Calculated using the enthalpy of reaction for $\text{CH}_3\text{Br} + \text{HCl} \rightarrow \text{CH}_3\text{Cl} + \text{HBr}$ and experimental ΔH_f values for CH_3Br , HCl, CH_3Cl , and HBr. ^q Calculated using the enthalpy of reaction for $\text{SiH}_3\text{Br} + \text{HCl} \rightarrow \text{SiH}_3\text{Cl} + \text{HBr}$ and experimental ΔH_f values for SiH_3Br , HCl, SiH_3Cl , and HBr.

$\rightarrow \text{SiH}_3\text{Cl} + \text{HBr}$ (-2.7 kJ mol^{-1} at G3MP2) and by using the experimental heats of formation of CH_3Br , HCl, CH_3Cl , HBr, SiH_3Br , and SiH_3Cl . The ΔH_f values obtained by reaction 3 is in excellent agreement with experiment, while the values obtained by using reaction 4 is also in reasonable agreement with experiment differing by no more than 4.8 kJ mol^{-1} from experiment. Therefore, these results provide

further evidence that the G3MP2 enthalpies are very reliable for the reactions studied and proved to be useful in predicting the performance of the standard 6-31G and BC6-31G basis sets.

4. Conclusions

Computations were carried out in order to compare the standard and BC6-31G basis sets for thermodynamic properties, geometries, and frequencies. The performance of the standard 6-31G basis set compared to the BC6-31G basis set for a series of isogyric reactions containing third row elements, Ga, Ge, As, Se, and Br, was evaluated using G3MP2 theory. A comparison of the thermodynamic properties calculated with the standard 6-31G and the BC6-31G basis set with the G3MP2 energies revealed that for compounds with first row elements and third row elements, both basis sets perform equally well, while compounds with second and third row elements or with first, second, and third row, elements, the standard 6-31G basis set showed the best performance. Optimized geometries were also tabulated and compared for the standard 6-31G(d,p) and BC6-31G(d,p) basis sets. Geometric parameters calculated with both the basis sets were found to agree well with experiment, with errors similar to those found for compounds containing first and second row elements. Frequencies were also compared to experiment, and the unscaled B3LYP/6-31G(d,p) frequencies were found to be in better agreement with experiment (Table 4). MP2/6-31G(d,p) were also found to predict better frequencies than MP2/BC6-31G(d,p). Scaling the frequencies with standard scale factors lowers the MAD for all levels and basis sets studied suggesting that the standard scale factors for first and second row elements may also be used for third row elements. Calculations using the G3MP2 theory proved useful in determining the accuracy of the levels of theory and basis sets. When studying reactions involving heavy atoms, the choice of the basis set is crucial. As illustrated in this study, enthalpies of reaction can vary up to 30.4 kJ mol⁻¹ at the B3LYP and MP2 levels of theory which in several cases may lead to predicting a reaction is endothermic when it is actually exothermic and vice versa. Since the standard 6-31G basis set performs very well with all the reactions, we recommend that the standard 6-31G basis set be used for calculations involving third row elements. It has also been shown that reaction enthalpies calculated at G3MP2, along with existing experimental data, can be used to calculate reliable heats of formation.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Council of Canada (NSERC) for financial support and the Atlantic Computational Excellence Network (ACEnet) for computer time.

Supporting Information Available: Full geometries and energies of all structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Curtiss, L. A.; Redfern, P. C. *J. Chem. Phys.* **2001**, *114*, 9287–9295.

- (2) Binning, Jr., R. C.; Curtiss, L. A. *J. Comput. Chem.* **1990**, *11*, 1206.
- (3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.05*; Gaussian, Inc.: Wallingford, CT, 2004.
- (4) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363. GAMESS Version = Feb 22, 2006 (R5) from Iowa State University.
- (5) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, *22*, 976–984.
- (6) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764–7776.
- (7) Islam, S. M.; Hollett, J. W.; Poirier, R. A. *J. Phys. Chem. A* **2007**, *111*, 526–540.
- (8) Islam, S. M.; Poirier, R. A. *J. Phys. Chem. A* In press.
- (9) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703–4709.
- (10) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650–7657.
- (11) Curtiss, L. *Computational Thermochemistry on the Web*. <http://chemistry.anl.gov/compmat/comptherm.htm> (accessed Sept 24, 2007).
- (12) National Institute of Standards and Technology. *Vibrational Frequency Scaling Factors on the Web*. <http://srdata.nist.gov/cccbdb/vsf.asp> (accessed Sept 24, 2007).
- (13) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.
- (14) Bartmess, J. E.; Hinde, R. J. *Can. J. Chem.* **2005**, *83*, 2005–2012.
- (15) Inorganic (non carbon-containing) compounds. In *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Spec. Publ. 18; Sutton, L. E., Ed.; The Chemical Society: London, U.K.; 1956–1959; pp M 1s–M 58s.
- (16) Stevenson, D. P. *J. Chem. Phys.* **1940**, *8*, 285–287.
- (17) Ohno, K.; Matsumura, H.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *118*, 1–17.
- (18) Stevenson, P. E.; Lipscomb, W. N. *J. Chem. Phys.* **1970**, *52*, 5343–5353.

- (19) Breidung, J.; Thiel, W.; Demaison, J. *Chem. Phys. Lett.* **1997**, *266*, 515–520.
- (20) Harjanto, H.; Harper, W. W.; Clouthier, D. J. *J. Chem. Phys.* **1996**, *105*, 10189–10200.
- (21) Herzberg, G.; Verma, R. D. *Can. J. Phys.* **1964**, *42*, 395–432.
- (22) Herzberg, G. *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; D. Van Nostrand: Princeton, NJ, 1967.
- (23) Graner, G. *J. Mol. Spectrosc.* **1981**, *90*, 394–438.
- (24) Duncan, J. L. *J. Mol. Struct.* **1970**, *6*, 447–456.
- (25) Duncan, J. L.; Harvie, J. L.; McKean, D. C.; Cradock, S. J. *Mol. Struct.* **1986**, *145*, 225–242.
- (26) Chadwick, D.; Millen, D. J. *J. Mol. Struct.* **1975**, *25*, 216–218.
- (27) Harvey, A. B.; Wilson, M. K. *J. Chem. Phys.* **1966**, *45*, 678–688.
- (28) Harvey, A. B.; Wilson, M. K. *J. Chem. Phys.* **1966**, *44*, 3535–3546.
- (29) Mathews, S.; Duncan, J. L.; McKean, D. C.; Smart, B. A. *J. Mol. Struct.* **1997**, *413*, 553–573.
- (30) Laurie, V. W. *J. Chem. Phys.* **1959**, *30*, 1210–1214.
- (31) (a) Obenhammer, H.; Lobreyer, T.; Sundermeyer, W. *J. Mol. Struct.* **1994**, *323*, 125–128. (b) Jensen, J. O. *Spectrochim. Acta, Part A* **2003**, *59*, 3093–3102.
- (32) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
- (33) Shimanouchi, T. Molecular Vibrational Frequencies. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J. Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD 20899, June 2005. <http://webbook.nist.gov> (accessed Oct 31, 2007).
- (34) Straley, J. W.; Tindal, C. H.; Nielsen, H. H. *Phys. Rev.* **1942**, *62*, 161–165.
- (35) Pullumbi, P.; Bouteiller, Y.; Manceron, L.; Mijoule, C. *Chem. Phys.* **1994**, *185*, 25–37.
- (36) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2003**, *107*, 11371–11379.
- (37) Muller, J.; Sternkicker, H.; Bergmann, U.; Atakan, B. *J. Phys. Chem. A* **2000**, *104*, 3627–3634.
- (38) Paplewski, P.; Beckers, H.; Burger, H. *J. Mol. Spectrosc.* **2002**, *213*, 69–78.
- (39) Duncan, J. L.; Allan, A.; McKean, D. C. *Mol. Phys.* **1970**, *18*, 289–303.
- (40) Lannon, J. A.; Weiss, G. S.; Nixon, E. R. *Spectrochim. Acta, Part A* **1970**, *26*, 221–233.
- (41) Adams, G. P.; Carson, A. S.; Laye, P. G. *Trans. Faraday Soc.* **1966**, *62*, 1447–1449.
- (42) Hansel, A.; Scheiring, C.; Glantschnig, M.; Lindinger, W.; Ferguson, E. E. *J. Chem. Phys.* **1998**, *109*, 1748–1750.
- (43) An, X.; Mansson, M. *J. Chem. Thermodyn.* **1983**, *15*, 287–293.
- (44) *CRC Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1977–1978; Vol. 58, p D69.
- (45) McBride, B. J.; Zehe, M. J.; Gordon, S. *NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species*; Glenn Research Center: Cleveland, OH, 2002; p 20.
- (46) Chase, M. W. *NIST-JANAF Thermochemical Tables*, 4th ed.; Monograph 9. *J. Phys. Chem. Ref. Data* 1998; pp 1–1951.
- (47) Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1986**, *85*, 4815–4824.
- (48) Berkowitz, J. *J. Chem. Phys.* **1988**, *89*, 7065–7076.
- (49) Gunn, S. R.; Jolly, W. L.; Green, L. G. *J. Phys. Chem.* **1960**, *64*, 1334–1335.
- (50) Ruscic, B.; Schwarz, M.; Berkowitz, J. *J. Chem. Phys.* **1990**, *92*, 1865–1875.
- (51) Gunn, S. R.; Green, L. G. *J. Phys. Chem.* **1961**, *65*, 779–783. CT700224J