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Heats of Formation of $GaCl_3$ and Its Fragments

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The heats of formation of $GaCl_3$ and its fragments are computed. The geometries and frequencies are obtained at the B3LYP level. The CCSD(T) approach is used to solve the correlation problem. The effect of Ga 3*d* correlation is studied and found to affect the bond energies by up to 1 kcal/mol. Both basis set extrapolation and bond functions are considered as ways to approach the basis set limit. Spin−orbit and scalar relativistic effects are also considered.

1. Introduction

The calculation of accurate bond energies for compounds containing third-row elements has received considerably less attention than similar calculations for compounds containing only first- and second-row atoms. Recently, Curtiss and co-workers[1] published an extension of the G2 theory[2] for the third row. Their agreement with experiment was very good for their 40 test cases.

The ability to compute accurate bond energies for compounds containing third-row atoms is important for many applications; for example, $GaCl_n$ heats of formation are required for the modeling of some processes related to the fabrication of semiconductor devices. However, some of the success of the G2 approach for the third-row systems must have come from a cancelation of errors; for example, Curtiss and co-workers included spin−orbit effects but neglected scalar relativistic effects. Recently, Collins and Grev[3] showed that the scalar relativistic effects reduced the atomization energy of SiH_4 by 0.7 kcal/mol, and it is expected that the magnitude of this effect will be significantly larger for the third row. In addition to the neglect of the scalar relativistic effects, the G2 approach does not correlate the Ga 3d orbital, which could be important for some systems.

We should note that Balasubramanian and co-workers[4] have studied the $GaCl_n$ systems. They studied the excited states as well as the ground states. While these studies give insight into the $GaCl_n$ sytems, the level of theory is not sufficient to obtain highly accurate atomization energies, which is the goal of our work.

2. Methods

The geometries are optimized using the hybrid[5] B3LYP[6] approach in conjunction with the 6-31G* basis set.[7] The harmonic frequencies confirm that the stationary points correspond to minima and are used to compute the zero-point energies.

The energetics are computed using the restricted coupled cluster singles and doubles approach[8,9] including the effect of connected triples determined using perturbation theory,[10,11] RCCSD(T). In the valence RCCSD(T) calculations, the Ga 4s and 4p and the chlorine 3s and 3p electrons are correlated. Because the Ga 3d orbital is relatively close to the 4s and 4p orbitals, 13 Ga electrons are correlated in most calculations, which are denoted as val+3d. The RCCSD(T) calculations are performed using Molpro 96,[12] while the B3LYP calculations are performed using Gaussian94.[13]

We also compute the energetics using our G2(MP2/B3LYP/cc) modification[14] to the G2(MP2) approach,[15] which we denoted as G2(MP2)′. We use the basis sets suggested by Curtiss and co-workers.[1] These results should be similar to those obtained using the third-row G2 approach proposed by Curtiss and co-workers. In addition, we report atomization energies using the B3LYP approach in conjunction with the 6-31G* and 6-311+G(3df,2p) basis sets;[7] the latter calculations are denoted B3LYP(big). In all calculations, unless otherwise noted, the geometries and zero-point energies come from the B3LYP/6-31G* calculations.

The Cl basis sets are the augmented-correlation-consistent polarized valence (aug-cc-pV) sets developed by Dunning and co-workers;[16−19] the triple-ζ (TZ), quadruple-ζ (QZ), and quintuple-ζ (5Z) sets are used. For Ga, cc-pV sets are developed for both 3 and 13 electron correlation treatments. The Ga basis sets are derived from the (21s16p10d) set optimized by Partridge.[20] Using a general contraction, this primitive set is contracted to 4s3p1d. Flexibility is introduced into the valence set by uncontracting the two functions with largest coefficients in the atomic 4s, 4p, and 3d orbitals, thus yielding our 6s5p3d valence basis set. We should note that for the 4s and 4p orbitals the uncontracted functions are the most diffuse, while for the 3d orbital those with the largest coefficients are not the most diffuse functions; see Table 1. Three even-tempered polarization sets are optimized at the CCSD(T) level for a 3 electron correlation treatment: TZ 2d1f, QZ 3d2f1g, and 5Z 4d3f2g1h−see Table 2. We should note that the d polarization functions have some overlap with the most diffuse valence functions. However, there is not a linear dependence problem since the diffuse valence functions are only included in the general contraction of the 3d orbital. This suggests that it might be possible to reduce the number of d primitives by uncontracting additional valence functions and not adding as many polarization functions, but this was not studied.

Extra flexibility in the valence set and additional tight polarization functions are needed to correlate the Ga 3d orbital. Starting from these valence cc-pV sets, the cc-pV(3d) basis sets were developed. The first 12 s primitives were contracted to two functions and the remaining s functions were uncontracted. The first 6 p primitives were contracted to one function and

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TABLE 1: Ga Valence Basis Set

exponent	coefficients					
	21 s Primitives Contracted to 6 Functions[a]					
11280660.000000	0.000004	−0.000001	0.000000	0.000000	0.0	0.0
1689168.000000	0.000032	−0.000010	0.000004	−0.000001	0.0	0.0
384417.200000	0.000166	−0.000051	0.000020	−0.000005	0.0	0.0
108888.000000	0.000701	−0.000217	0.000083	−0.000019	0.0	0.0
35524.670000	0.002548	−0.000792	0.000303	−0.000070	0.0	0.0
12825.110000	0.008257	−0.002580	0.000984	−0.000229	0.0	0.0
5002.055000	0.024172	−0.007658	0.002931	−0.000683	0.0	0.0
2074.448000	0.063608	−0.020740	0.007951	−0.001849	0.0	0.0
904.341300	0.145693	−0.050747	0.019665	−0.004590	0.0	0.0
410.659200	0.270285	−0.107348	0.042165	−0.009831	0.0	0.0
192.682400	0.349210	−0.180646	0.073860	−0.017384	0.0	0.0
92.076100	0.237554	−0.173739	0.074780	−0.017581	0.0	0.0
42.057700	0.048122	0.110693	−0.053340	0.012508	0.0	0.0
21.072620	−0.002297	0.541834	−0.357364	0.090332	0.0	0.0
10.448810	0.001791	0.446892	−0.425141	0.110489	0.0	0.0
4.777393	−0.000828	0.076222	0.201113	−0.061215	0.0	0.0
2.282456	0.000355	−0.000944	0.714611	−0.256188	0.0	0.0
1.035248	−0.000141	0.001782	0.368773	−0.260360	0.0	0.0
0.257674	0.000050	−0.000348	0.015377	0.349329	0.0	0.0
0.119166	0.000000	0.000000	0.000000	0.000000	1.0	0.0
0.051285	0.000000	0.000000	0.000000	0.000000	0.0	1.0
	16 p Primitives Contracted to 5 Functions[b]					
22071.040000	0.000055	−0.000021	0.000003	0.0	0.0	
5225.112000	0.000486	−0.000184	0.000030	0.0	0.0	
1697.065000	0.002796	−0.001063	0.000175	0.0	0.0	
649.185700	0.012226	−0.004689	0.000763	0.0	0.0	
275.279900	0.042709	−0.016633	0.002743	0.0	0.0	
125.413600	0.118663	−0.047788	0.007810	0.0	0.0	
60.075240	0.248580	−0.104526	0.017420	0.0	0.0	
29.728220	0.360243	−0.161332	0.026491	0.0	0.0	
15.039750	0.295072	−0.114334	0.019397	0.0	0.0	
7.571398	0.098466	0.145968	−0.031324	0.0	0.0	
3.738135	0.008759	0.427236	−0.080169	0.0	0.0	
1.796543	0.001397	0.423991	−0.100165	0.0	0.0	
0.829826	0.000077	0.159899	−0.010567	0.0	0.0	
0.272860	0.000069	0.009504	0.284317	0.0	0.0	
0.101539	0.000000	0.000000	0.000000	1.0	0.0	
0.037656	0.000000	0.000000	0.000000	0.0	1.0	
	10 d Primitives Contracted to 3 Functions[c]					
530.681300	0.000388	0.0	0.0			
159.522200	0.003570	0.0	0.0			
61.797800	0.018583	0.0	0.0			
26.863720	0.063777	0.0	0.0			
12.462250	0.157300	0.0	0.0			
5.980455	0.268197	0.0	0.0			
2.860390	0.325369	1.0	0.0			
1.336497	0.291513	0.0	1.0			
0.599223	0.172085	0.0	0.0			
0.244454	0.044142	0.0	0.0			

[a] In the cc-pV(3d) basis set the first 12 primitives are contracted to two functions using the same contraction coefficients. The nine most diffuse s functions are uncontracted. Thus the cc-pV(3d) basis set is (21s/11s). [b] In the cc-pV(3d) basis set the first 6 primitives are contracted to one function using the same contraction coefficients. The 10 most diffuse p functions are uncontracted. Thus the cc-pV(3d) basis set is (16p/11p). [c] In the cc-pV(3d) basis set the function with an exponent of 5.980455 is also uncontracted, yielding a cc-pV(3d) basis set of the form (10d/4d).

the remaining functions were uncontracted. The function with the third largest coefficient in the 3d orbital was uncontracted. Three sets of tight functions were optimized at the CCSD(T) level correlating 13 electrons. These tight polarization functions are tabulated in Table 2. The tight polarization sets are TZ 2f1g, QZ 3f2g1h, and 5Z 4f3g2h1i. Thus, the cc-pV5Z(3d) basis set would have a 11s11p4d valence set, a 4d3f2g1h valence polarization set, and a 4f3g2h1i tight polarization set, yielding a basis set of the form (21s16p14d7f5g3hi1)/[11s11p8d7f5 g3h1i]. Only the pure spherical harmonic components are used.

To improve the accuracy of the results, several extrapolation techniques are used. We use the two-point n^{-3} scheme described by Helgaker et al.[21] We also use the two-point n^{-4}, three-point ($n^{-4} + n^{-6}$), and variable α ($n^{-\alpha}$) schemes described by Martin.[22]

Bond functions are an alternative approach to saturate the basis set and we tried this for $GaCl_n$. Starting from the cc-pVTZ-(3d) set, bond functions are added at the midpoints of all bonds. The bond functions consist of an sp set with exponents 1.8, 0.6, and 0.2, a d set with exponents 1.2 and 0.4, and f and g functions with exponents of 0.8 and 0.9, respectively. The sets with bond functions added are denoted as +bf.

The scalar relativistic contribution is computed in two ways: (1) using perturbation theory (+R) including only the mass−velocity and Darwin terms and (2) using the Douglas−Kroll (DK) approach[23] with only the one electron terms. Since the

TABLE 2: Exponents for the Polarization Sets

Valence Polarization Functions

	cc-pVTZ	cc-pVQZ	cc-pV5Z
	Exponent	Exponent	Exponent
d	0.309481	0.406196	0.526042
	0.108210	0.178000	0.268663
		0.078002	0.137213
			0.070078
f	0.283000	0.476367	0.690800
		0.183925	0.314000
			0.142727
g		0.420000	0.710878
			0.291224
h			0.482000

Additional Tight Functions for the cc-pV(3d) Sets

	cc-pVTZ(3d)	cc-pVQZ(3d)	cc-pV5Z(3d)
f	6.854555	12.822600	22.146651
	1.869764	4.515000	9.472477
		1.589789	4.051530
			1.732904
g	4.920000	8.093748	13.561575
		2.501931	5.475000
			2.210335
h		5.477000	8.834931
			2.943996
i			6.728000

+R approach is sensitive to the flexibility of the inner shell functions and the DK integral program that we use is limited to segmented basis sets and up to f functions, we use a modified cc-pVTZ(3d) basis set in these calculations. The *s* spaces of both Ga and Cl are uncontracted. The inner six Ga and inner four Cl p functions are contracted to one function using the SCF coefficients for the atomic 2p orbital, while the remaining p functions are uncontracted. The inner five Ga d functions are contracted to one function, with the rest of the functions free. The more diffuse of the d polarization functions is added; the tighter d polarization function overlaps with the existing valence functions and is therefore not included. The Ga f and the Cl d and f polarization functions are uncontracted. The Ga g function is not included. We denote this basis set as cc-pVTZ(3d)′. Since these DK integrals are not interfaced to Molpro, we perform modified coupled pair functional[24] (MCPF) calculations instead of CCSD(T) calculations. These calculations are performed using Molecule-Sweden,[25] which has been interfaced to the DK integral program of Hess. There is no spin−orbit splitting for GaCl and $GaCl_3$, as they have closed shell ground states. The spin−orbit splitting is expected to be very small for the X^2A_1 state of $GaCl_2$ and is therefore ignored. Thus only the atomic spin−orbit splitting contributes to the dissociation energy; this is computed using experiment[26] as the difference between the lowest m_j component and the m_j weighted average energy.

The heat capacity, entropy, and temperature dependence of the heat of formation are computed for 300−4000 K using a rigid rotor/harmonic oscillator approximation. The B3LYP/6-31G* frequencies are used in these calculations. These results are fit in two temperature ranges, 300−1000 and 1000−4000 K using the Chemkin[27] fitting program and following their constrained three-step procedure.

3. Results and Discussion

The computed spectroscopic constants for GaCl are summarized in Table 3. The B3LYP/6-31G* and experimental[28] values are given at the bottom of the table. An inspection of

TABLE 3: GaCl Spectroscopic Constants as a Function of Level of Theory

	r_e (Å)			D_e (kcal/mol)			ω_e (cm^{-1})		
	TZ(3d)	QZ(3d)	5Z(3d)	TZ(3d)	QZ(3d)	5Z(3d)	TZ(3d)	QZ(3d)	5Z(3d)
SCF	2.231	2.228	2.227	89.05	89.18	89.27	359	358	358
SCF−BSSE	2.232	2.229	2.227	88.98	89.17	89.26	359	358	358
CCSD	2.255	2.254	2.253	106.15	108.27	108.97	371	377	378
CCSD−BSSE	2.258	2.255	2.254	105.62	108.06	108.82	371	373	378
CCSD(T)	2.259	2.257	2.256	108.84	111.12	111.90	371	373	375
CCSD(T)−BSSE	2.262	2.258	2.257	108.26	110.89	111.74	371	373	375
CCSD+3d	2.218	2.207	2.203	107.39	109.40	110.14	366	367	371
CCSD+3d−BSSE	2.224	2.210	2.204	106.06	108.94	109.88	363	367	370
CCSD(T)+3d	2.219	2.208	2.204	110.31	112.48	113.33	365	367	370
CCSD(T)+3d−BSSE	2.226	2.211	2.205	108.85	111.97	113.04	360	366	367

	r_e (Å) TZ(3d)′	D_e (kcal/mol) TZ(3d)′	ω_e (cm^{-1}) TZ(3d)′
SCF	2.231	88.98	358
SCF+R	2.232	88.20	354
SCF(DK)	2.233	88.28	354
SCF−BSSE	2.232	88.98	358
SCF+R−BSSE	2.232	88.17	354
SCF(DK)−BSSE	2.233	88.17	354
MCPF	2.255	106.42	376
MCPF+R	2.255	105.92	373
MCPF(DK)	2.266	105.60	377
MCPF−BSSE	2.258	105.92	370
MCPF+R−BSSE	2.258	105.45	367
MCPF(DK)−BSSE	2.269	105.06	376
MCPF(3d)	2.218	107.41	365
MCPF(3d)+R	2.218	106.92	362
MCPF(3d,DK)	2.219	106.95	362
MCPF(3d)−BSSE	2.223	106.56	364
MCPF(3d)+R−BSSE	2.223	106.11	361
MCPF(3d,DK)-BSS	2.223	106.04	361
B3LYP/6-31G*	2.249		352
expt[28]	2.2017		365.3

TABLE 4: Summary of the CCSD(T) Atomization Energies as a Function of Basis Set, in kcal/mol

	correlation treatment			
	valence		valence + Ga 3d	
basis (Ga/Cl)		−BSSE		−BSSE
	$GaCl$			
cc-pVTZ/aug-cc-pVTZ	108.57			
cc-pVQZ/aug-cc-pVQZ	111.07			
cc-pV5Z/aug-cc-pV5Z	112.02			
cc-pVTZ(3d)/aug-cc-pVTZ	108.83	108.24	110.20	108.78
cc-pVQZ(3d)/aug-cc-pVQZ	111.11	110.87	112.27	111.79
cc-pV5Z(3d)/aug-cc-pV5Z	111.90	111.73	113.07	112.80
cc-pVTZ(3d)/aug-cc-pVTZ+bf	115.06	111.34	120.38	112.36
	$GaCl_2$			
cc-pVTZ(3d)/aug-cc-pVTZ	157.96	156.41	157.90	154.68
cc-pVQZ(3d)/aug-cc-pVQZ	162.29	161.66	161.61	160.50
cc-pVTZ(3d)/aug-cc-pVTZ+bf	170.66	163.04	178.32	162.58
	$GaCl_3$			
cc-pVTZ(3d)/aug-cc-pVTZ	254.94	252.68	256.18	251.34
cc-pVQZ(3d)/aug-cc-pVQZ	261.53	260.60	262.21	260.53
cc-pVTZ(3d)/aug-cc-pVTZ+bf	274.83	262.54	287.47	263.28

the upper half of the table shows that the bond length increases with valence correlation and decreases when the Ga 3d is also correlated. As expected, the bond length decreases with basis set improvement. The value obtained using the cc-pV5Z(3d) basis set at the CCSD(T) level of theory, including Ga 3d correlation, is in good agreement with experiment. The dissociation energy increases with electron correlation and basis set improvement. The value obtained with the correlation treatment including the Ga 3d orbital is slightly larger than that computed using the valence treatment. We discuss the dissociation energy in more detail below. The harmonic frequency is not very sensitive to the level of theory, and the values computed at the CCSD(T) val+3d level are in good agreement with experiment.

At the SCF level, the cc-pVTZ(3d) and cc-pVTZ(3d)′ basis sets yield very similar results. The MCPF results using the cc-pVTZ(3d)′ basis set are very similar to the CCSD results using the cc-pVTZ(3d) basis; thus we conclude that we can use the cc-pVTZ′ basis set and the MCPF approach to investigate the scalar relativistic effects. Overall the results obtained using perturbation theory and the DK approach are very similar. There is a very small scalar relativistic effect on the spectroscopic constants. The bond length is essentially unchanged and the D_0 and ω_e values are reduced slightly. The small scalar relativistic effect arises because the bonding involves the Ga 4p and Cl 3p orbitals, and relativity mostly affects the s orbitals. As we show below, there is a larger scalar relativistic effect on the atomization energies of $GaCl_2$ and $GaCl_3$ because the Ga sp hybridizes in the larger systems. Finally, we note that the B3LYP/6-31G* results are in reasonable agreement with the higher levels of theory and experiment, and therefore this is the level we use to determine the geometries and zero-point energies of the $GaCl_n$ systems.

The results of the CCSD(T) calculations, using the cc-pV basis sets, are summarized in Table 4. The first three GaCl calculations use the valence cc-pV basis sets. As expected, the dissociation energy increases as the basis set is improved from TZ to 5Z. The next three lines correspond to using the cc-pV(3d) basis sets. The results obtained with these basis sets correlating only the valence electrons are only slightly larger than those obtained using the valence cc-pV basis sets. This is not unexpected, as the tight functions needed to correlate the Ga 3d orbital do not affect the valence treatment. The BSSE correction at this level is small. When the Ga 3d correlation is added, the computed dissociation energies, without the BSSE correction, increase by up to 1.37 kcal/mol, with the size of the effect decreasing with basis set improvement. After correcting for BSSE, the effect of Ga 3d correlation increases with basis set improvement. For the cc-pV5Z(3d) basis set, the effect of Ga 3d correlation is virtually identical with and without BSSE, being slightly more than 1 kcal/mol. Comparing the CCSD(T) results using the cc-pV5Z(3d) basis set in Tables 3 and 4 shows that optimizing the geometry at the CCSD(T) level increases the D_e by only 0.26 kcal/mol compared with using the B3LYP/6-31G* geometry. Thus, using the B3LYP geometry should not introduce a significant error in the computed atomization energies.

The results obtained using the cc-pVTZ(3d)+bf set are significantly larger than those obtained using the atomic centered basis sets if the BSSE is not accounted for. However, after correcting for BSSE, the cc-pVTZ(3d)+bf basis set yields a binding energy that falls between the cc-pVQZ(3d) and cc-pV5Z(3d) sets.

The results for $GaCl_2$ and $GaCl_3$ are consistent with those for GaCl. For $GaCl_2$ and $GaCl_3$, the increase in the BSSE when the Ga 3d is correlated is larger than found for GaCl, but the BSSE for the cc-pVQZ(3d) basis set is still acceptable. The results with bond functions are slightly larger than those obtained with the cc-pVQZ(3d) set, as found for GaCl.

For $GaCl_2$ all of the basis sets suggest that Ga 3d correlation decreases the atomization energy, which is the opposite effect found for GaCl. For $GaCl_3$, the results obtained using the cc-pVTZ(3d)+bf set suggest an increase in atomization energy with Ga 3d correlation, while the other two sets suggest a decrease. It should be noted that the decrease in the atomization energy with the cc-pVQZ(3d) set is very small.

To achieve highly accurate results, some correction for remaining basis set incompleteness must be made. This is true of the results obtained using the atomic centered basis set and those using bond functions. In Table 5 we consider extrapolation of the CCSD(T) results for the atom centered basis sets. We first note that the valence correlation treatment yields similar results for all extrapolation methods and for both the cc-pV and cc-pV(3d) basis sets. Correcting for the BSSE does not significantly affect the extrapolated values. The same observation holds for the treatment including Ga 3d correlation. The extrapolated values also support a 3d correlation effect of about 1 kcal/mol.

The extrapolated results for $GaCl_2$ and $GaCl_3$ are also given in Table 5. The difference between the n^{-3} and n^{-4} extrapolations increases as the total atomization energy increases, however the difference between the two extrapolation methods is still relatively small. The BSSE correction has a slightly larger effect than for GaCl. It is interesting to note that for $GaCl_3$, after extrapolation, the correlation of the Ga 3d increases the atomization energy slightly, as found for the cc-pVTZ(3d)+bf basis set, but not for the cc-pVTZ(3d) and cc-pVQZ(3d) basis sets.

We summarize our atomization energies in Table 6. The first two lines are the B3LYP results. Increasing the size of the basis set has a relatively small effect on the B3LYP results. The results on the third line are obtained from the G2(MP2)′ approach, but without including the zero-point energy. These results are significantly larger than those obtained using the B3LYP approach.

The remaining results in the table are the extrapolated CCSD(T) results that include Ga 3d correlation and the BSSE correction. The three-point $n^{-4}+n^{-6}$ extrapolation is possible

TABLE 5: Summary of the Basis Set Extrapolation for the CCSD(T) Atomization Energies, in kcal/mol

	method^a					
	3	3	4	4	4 + 6	α^b
correlation/basis	TZ,QZ	QZ,5Z	TZ,QZ	QZ,5Z	TZ,QZ,5Z	TZ,QZ,5Z
			GaCl			
Valence/cc-pV	112.89	113.02	112.51	112.79	112.89	113.06 (3.242)
Valence/cc-pV(3d)	112.77	112.72	112.43	112.54	112.58	112.63 (3.654)
Valence−BSSE/cc-pV(3d)	112.80	112.63	112.39	112.43	112.44	112.46 (3.901)
Val+3d/cc-pV(3d)	113.78	113.91	113.46	113.72	113.81	113.97 (3.171)
Val+3d−BSSE/cc-pV(3d)	113.99	113.85	113.53	113.61	113.64	113.67 (3.812)
			$GaCl_2$			
Valence/cc-pV(3d)	165.45	164.79				
Valence−BSSE/cc-pV(3d)	165.49	164.69				
Val+3d/cc-pV(3d)	164.33	163.76				
Val+3d−BSSE/cc-pV(3d)	164.75	163.86				
			$GaCl_3$			
Valence/cc-pV(3d)	266.34	265.33				
Valence−BSSE/cc-pV(3d)	266.38	265.17				
Val+3d/cc-pV(3d)	266.61	265.69				
Val+3d−BSSE/cc-pV(3d)	267.24	265.83				

[a] The value signifies the type extrapolation, for example "3" indicates an n^{-3} extrapolation and "4 + 6" indicates an $n^{-4} + n^{-6}$ extrapolation. The second line shows which basis sets are used in the extrapolation. [b] The optimized α value is given in parentheses.

TABLE 6: Summary of the Atomization Energies, without Zero-Point Energy, as a Function of Level of Theory, in kcal/mol

method	GaCl	$GaCl_2$	$GaCl_3$
B3LYP	108.79	154.78	246.49
B3LYP(big)	109.88	155.84	247.68
G2(MP2)′ (no ZPE)	113.08	164.02	265.74
3-point extrapolation of CCSD(T)−BSSE	113.64		
av 2-point extrapolation of CCSD(T)−BSSE^a	113.76	164.31	266.54
BFs with additive correction	(113.64)	165.14	267.12
BFs with multiplicative correction	(113.64)	164.43	266.28

[a] The cc-pVTZ(3d) and cc-pVQZ(3d) sets are used.

TABLE 7: Summary of the Scalar Relativistic Effect on the Atomization Energy, in kcal/mol^a

	SCF	MCPF	MCPF(3d)
	GaCl		
nonrelativistic	89.000	106.418	107.296
perturbation theory(+R)	88.189	105.939	106.834
Douglas−Kroll(DK)	88.246	105.556	106.836
+R−nonrelativistic	−0.810	−0.479	−0.462
DK−nonrelativistic	−0.753	−0.862	−0.460
	$GaCl_2$		
nonrelativistic	131.195	153.054	152.350
+R	126.396	149.519	148.671
DK	126.415	148.826	148.701
+R−nonrelativistic	−4.799	−3.535	−3.679
DK−nonrelativistic	−4.780	−4.228	−3.649
	$GaCl_3$		
nonrelativistic	210.625	247.707	247.680
+R	203.980	242.357	241.983
DK	203.983	241.084	241.863
+R−nonrelativistic	−6.645	−5.351	−5.697
DK−nonrelativistic	−6.643	−6.624	−5.817

[a] The cc-pVTZ(3d)′ set is used.

only for GaCl, but a comparison of lines 4 and 5 shows that the average of the two-point n^{-3} and n^{-4} extrapolations using the TZ and QZ basis sets is very similar to the result obtained using the three-point extrapolation. Therefore we report the average of the two-point extrapolation values for $GaCl_2$ and $GaCl_3$. The correction for the bond functions results is not as straightforward and we use two different approaches. In the first, we assume an equal error in each bond. We compute the error for one bond in the +bf treatment as the difference between the GaCl bond function result (112.36 kcal/mol) and the 3-point extrapolated result corrected for BSSE (113.64 kcal/mol). We therefore add two and three times 1.28 kcal/mol to the $GaCl_2$ and $GaCl_3$ bond function results, respectively. In the second approach we assume that the error scales like the atomization energy; the scale factor is computed as the GaCl three-point atomization energy divided by the bond function result (113.64/112.36 = 1.011). The corrected $GaCl_2$ and $GaCl_3$ values are obtained by multipling the $GaCl_2$ and $GaCl_3$ +bf results by this scale factor. An inspection of Table 6 shows that the two bond function correction methods and the average of the two-point extrapolations vary by less than 1 kcal/mol. The G2(MP2)′ results also agree well with the other approaches to estimate the atomization energy. We should note that this agreement is not always the case; for example, the G2 and G2(MP2)′ approaches do not work well for GaF_n.[29]

The calculation of the scalar relativistic effect on the atomization energy is summarized in Table 7. We first note that the nonrelativistic MCPF results are in reasonable agreement with the CCSD(T) results given in Table 4 using the cc-pVTZ(3d) basis set. The scalar relativistic effect at the SCF level computed using perturbation theory (+R) is very similar to that obtained using the Douglas−Kroll (DK) approach. However, the two approaches differ for the MCPF treatment that only correlates the valence electrons. There is a small mixing of the Ga 3d and Cl orbitals, which is different in the nonrelativistic and DK calculations because of the change in the orbital energies. If both sets of orbitals are correlated, such a mixing has no effect and now the +R and DK results agree. Thus we feel that the MCPF(3d) results are the most reliable. While the scalar relativistic effect is small for GaCl, it becomes about 8 times larger for $GaCl_2$. This arises from the Ga sp hybridization. The effect is even larger for $GaCl_3$ as the sp hybridization becomes more complete as three bonds are formed.

In Table 8 we summarize our best estimate for the atomization energies, along with experiment. The best nonrelativistic values, without zero-point energy, are taken from Table 6. The zero-point energies are taken from the B3LYP/6-31G* calculations. The spin−orbit effect is taken from experiment, as described above. The scalar relativistic result is computed as the average of the MCPF(3d) Douglas−Kroll and perturbation theory results. The contribution from the scalar relativistic effect is larger than the spin−orbit effect for $GaCl_2$ and $GaCl_3$. It would therefore

TABLE 8: Summary of Results, in kcal/mol

method	GaCl	$GaCl_2$	$GaCl_3$
best D_e	113.64	164.31	266.54
ZPE (B3LYP)	−0.50	−1.24	−2.42
spin−orbit (Expt)	−2.42	−3.26	−4.10
scalar rel	−0.46	−3.66	−5.76
spin orbit + scalar rel	−2.88	−6.92	−9.86
best atomization energy at 0 K	110.26	156.15	254.26
correction to 298 K	0.77	1.33	1.88
best atomization energy at 298 K	111.03	157.48	256.15
experiment, 298 K	110.94[31]	180.82[31]	255.40[31]
	114.38[30]		260.45[30]
experiment 0 K	113.46[28]		
experiment 298 K + theory[a] (298→ 0)	110.18[31]	179.50[31]	253.51[31]
	113.53[30]		258.57[30]

[a] The B3LYP frequencies are used in conjunction with the rigid rotor/harmonic oscillator approximation to convert the experimental values at 298 K to 0 K.

appear that this contribution to the binding should be added to the G2 procedures for molecules containing third- and fourth-row atoms. We should also note that our values are larger than those reported by Balasubramaianian[4] (105, 143, and 233 kcal/mol for GaCl, $GaCl_2$, and $GaCl_3$, respectively), as expected.

The available experimental data[28,30,31] are summarized at the bottom of the table. Our best estimate for the atomization energies of GaCl and $GaCl_3$ are in good agreement with the values reported by Pankratz.[31] Our value for $GaCl_2$ is significantly smaller than that given by Pankratz. Since theory is expected to be equally accurate for all systems, the computed value for $GaCl_2$ is to be preferred to the experimental value.

Using our best atomization energies, our computed changes in the heat of formation with temperature, and the experimental heats of formation of Ga (271.96 kcal/mol at 298 K[32]) and Cl (121.679 kcal/mol at 298 K[30]), we deduce the following heats of formation at 298 K: −16.95, −34.32, and −103.90 kcal/mol for GaCl, $GaCl_2$, and $GaCl_3$, respectively. Using our heats of formation at 298 K and the B3LYP frequencies and geometries, we evaluate the heat capacity, entropy, and heat of formation from 300 to 4000 K. The parameters obtained from the resulting fits can be found on the web.[33]

4. Conclusions

The bond energies of $GaCl_n$, for $n = 1-3$, are computed using the CCSD(T) approach correlating the valence and Ga 3d electrons. For GaCl it is possible to perform calculations using the cc-pV5Z(3d) basis and therefore the extrapolation to the complete basis set limit is expected to be accurate. For $GaCl_2$ and $GaCl_3$ the cc-pVTZ(3d) and cc-pVQZ(3d) basis sets are used to extrapolate the results to the complete basis set limit. These extrapolated values are supported by results obtained using a basis set with bond functions. The spin−orbit effect is taken from experiment while the scalar relativistic effect is computed using perturbation theory and using the Douglas−Kroll approach. Our best heats of formation formation at 298 K are −16.95, −34.32, and −103.90 kcal/mol for GaCl, $GaCl_2$, and $GaCl_3$, respectively. The temperature dependence of the heat of formation, the heat capacity, and entropy are computed and fit to the standard 14 coefficients,[27] which are available on the Web.[33]

References and Notes

(1) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning, R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.

(2) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(3) Collins, C. L.; Grev, R. S. *J. Chem. Phys.* **1998**, *108*, 5465.

(4) Dai, D.; Balasubramanian, K. *J. Chem. Phys.* **1993**, *99*, 293. Kim, G.; Balasubramanian, K. *Chem. Phys. Lett.* **1992**, *193*, 109.

(5) Becke, A. D. *J. Chem. Phys.* **1993,** *98*, 5648.

(6) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994,** *98*, 11623.

(7) Frisch, M. J.; Pople, J. A.; Binkley, J. S., *J. Chem. Phys.* **1984,** *80*, 3265 and references therein.

(8) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

(9) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993,** *99*, 5219.

(10) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989,** *157*, 479.

(11) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993,** *98*, 8718.

(12) MOLPRO 96 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, and P. R. Taylor. The closed-shell CCSD program is described in: Hampel, C.; Peterson, K.; Werner, H.-J. *Chem. Phys. Lett*. **1992**, *190*, 1.

(13) Gaussian 94, Revision D.1; M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople; Gaussian, Inc., Pittsburgh, PA, 1995.

(14) Bauschlicher, C. W.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.

(15) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(16) Dunning, T. H. *J. Chem. Phys.* **1989,** *90*, 1007.

(17) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992,** *96*, 6796.

(18) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993,** *98*, 1358.

(19) Woon, D. E.; Peterson, K. A.; Dunning, T. H. Unpublished.

(20) Partridge, H. *J. Chem. Phys.* **1989,** *90*, 1043.

(21) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997,** *106*, 9639.

(22) Martin, J. M. L. *Chem. Phys. Lett.* **1996,** *259*, 669.

(23) Hess, B. A. *Phys. Rev. A* **1985,** *32*, 756.

(24) Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *84*, 5606.

(25) MOLECULE-Sweden is an electronic structure program written by J. Almlöf, C. W. Bauschlicher, M. R. A. Blomberg, D. P. Chong, A. Heiberg, S. R. Langhoff, P.-Å. Malmqvist, A. P. Rendell, B. O. Roos, P. E. M. Siegbahn, and P. R. Taylor.

(26) Moore, C. E. Atomic energy levels. *Natl. Bur. Stand.* (US) circ. **1949**, *467*.

(27) Kee, R. J.; Rupley, F. M.; Miller, J. A. SAND87−8215B, Sandia National Laboratories, 1991.

(28) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(29) Bauschlicher, C. W.; Melius, C. F.; Allendorf, M. D. *J. Chem. Phys.*, in press.

(30) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. J. *J. Phys. Chem. Ref. Data* **1982,** *11* Suppl. 2.

(31) Pankratz, L. B. Thermodynamic Properties of Halides. U.S. Bureau of Mines, Bulletin 674, Supt. of Docs., Washington, DC, 1984.

(32) Hultgren, R.; Desai, P. R.; Hawkins, D. T.; Gleiser, M.; Kelly, K. K.; Wagman, D. D. *Selected Values of the Thermodynamic Properties of the Elements*; American Society for Metals: Metals Park, OH, 1973.

(33) The values can be found at http://www.ipt.arc.nasa.gov.