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The scalar relativistic contribution to gallium halide bond energies

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Abstract. The one-electron Douglas–Kroll (DK) and perturbation theory ($+R$) approaches are used to compute the scalar relativistic contribution to the atomization energies of GaF_n. These results are compared with previous $GaCl_n$ results. While the $+R$ and DK results agree well for the $GaCl_n$ atomization energies, they differ for GaF_n. The present work suggests that the DK approach is more accurate than the $+R$ approach. In addition, the DK approach is less sensitive to the choice of basis set. The computed atomization energies of GaF_2 and GaF_3 are smaller than the atomization energies from the somewhat uncertain experiments. It is suggested that additional calibration calculations for the scalar relativistic effects in GaF_2 and GaF_3 would be valuable.

Key words: Bond energies – Relativistic effects – Scalar relativistic effects – Complete basis set limit

1 Introduction

The calculation of accurate atomization energies for small molecules containing only H-Ar has become almost routine [1]. It is important to extend such studies to systems containing heavier atoms [2]. For systems with very heavy atoms (heavier than Xe, for example) fully relativistic approaches might be required; however, for systems containing K-Xe it might be possible to perform conventional calculations and account for the spin-orbit and scalar relativistic effects in some approximate manner.

For systems containing H-Ar, it is important to account for the spin-orbit effect in atoms and in degenerate molecular states [2]. Higher-order effects are less important and are generally ignored. The atomic spin-orbit splittings are easily obtained from the tabulation of Moore [3] and many molecular splittings are known [4]. While experience is limited, it appears that the molecular spin-orbital splittings can be computed fairly accurately using low-level approximations. For systems containing K-Xe, a similar approach for the spin-orbit effect is possible and is expected to be reasonably accurate.

While the spin-orbit effects seem straightforward to include, it is less clear how to account accurately for the scalar relativistic effects. For H-Ar the scalar relativistic effect is commonly ignored, but, as the atoms become heavier, the scalar relativistic effects grow rapidly in size, so that by the third row of the periodic table it is impossible to ignore them. For example, Collins and Grev [5] found the scalar relativistic effect was 0.7 kcal/mol for SiH_4, while we found [6] the scalar relativistic effect reduced the atomization energy of $GaCl_3$ by almost 6 kcal/mol, which is even larger than the spin-orbit effect.

For $GaCl_n$, we computed the scalar relativistic effect using perturbation theory ($+R$) and using the one-electron Douglas–Kroll (DK) approach [7]; the values obtained using these two approaches were in very good agreement. More recently we applied the same approaches to the atomization energies of GaF_n, and the agreement between the DK and $+R$ approaches was not as good, differing by 0.5 kcal/mol for the GaF_3 atomization energy. While the $+R$ approach will fail for very heavy atoms [8], it is somewhat surprising that it does not work well for GaF_n, especially since it works for $GaCl_n$. While 0.5 kcal/mol is small, if the goal is to compute atomization energies accurate to 1–2 kcal/mol, it is important to reduce the errors in all components of the calculation to a minimum. In this manuscript, we report on the scalar relativistic contribution to the GaX_n atomization energies. We show that the larger charge transfer in the GaF_n systems requires the use of the DK approach; thus we suggest that the DK approach is to be favored over perturbation theory even for atoms as light as Ga.

2 Methods

The GaF_n calculations are performed in an analogous manner to the previously published [6] $GaCl_n$ study. To allow an easier comparison of GaF_n and $GaCl_n$, we also give some details of the $GaCl_n$ calculations.

The geometries are optimized using the hybrid [9] B3LYP [10] approach in conjunction with the 6-31G* basis set [11]. The harmonic frequencies confirm that the stationary points correspond to minima and are used to compute the zero-point energies.

The atomization energies are computed using the restricted coupled-cluster singles and doubles approach [12, 13], including

the effect of connected triples determined using perturbation theory [14, 15], RCCSD(T), and the modified coupled-pair functional (MCPF) approach [16]. In these calculations, the F $2s$ and $2p$ and the Cl $3s$ and $3p$ electrons are always correlated. In the CCSD(T) calculations, the Ga $3d$, $4s$, and $4p$ electrons are correlated. In the MCPF calculations, the number of Ga electrons correlated varies: "MCPF" signifies that only the Ga $4s$ and $4p$ electrons are correlated, "MCPF(3d)" indicates that the Ga $3d$ electrons are also correlated, while "MCPF(3s3p3d)" indicates that Ga $3s$, $3p$, and $3d$ correlation is included, as well as the $4s$ and $4p$ valence correlation.

In the nonrelativistic calculations, the F and Cl basis sets are the augmented correlation-consistent polarized valence (aug-cc-pV) sets developed by Dunning and coworkers [17–19]. For Ga, the recently developed [6] cc-pV(3d) sets are used. The triple zeta (TZ), quadruple zeta (QZ), and quintuple zeta (5Z) sets are used. We refer to these sets collectively as cc-pV(3d).

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. [20]. We also use the two-point n^{-4}, three-point $(n^{-4} + n^{-6})$, and variable α $(n^{-\alpha})$ schemes described byMartin [21]. In those cases where the different extrapolation approaches agree, we can be confident that we have extrapolated to the complete basis set (CBS) limit.

The scalar relativistic contribution is computed in two ways:

1. Using $+R$ including only the mass-velocity and Darwin terms.
2. Using the DK approach [7] with only the one-electron terms.

In the $+R$ approach, the Darwin integrals are very large for the s functions with large exponents, thus it is important to converge tightly the self-consistent-field (SCF) calculations. The $+R$ approach is more sensitive [22] to the basis set contraction than the nonrelativistic or DK approaches, and therefore we use a more flexible contraction of the basis sets. In this work, the Ga basis set is derived from the cc-pVTZ(3d) set. The s space is uncontracted. The inner six Ga p functions are contracted to one function using the SCF coefficients from 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 Ga d polarization functions is added; the tighter d polarization function overlaps with the existing valence functions and is therefore not included. The Ga g function is not included. For Cl and F, basis sets are derived from the aug-cc-pVTZ sets. The s spaces are uncontracted. The inner two(four) F(Cl) p functions are contracted to one function. The F and Cl d and f polarization functions are uncontracted. We denote these Ga, F, and Cl basis set as cc-pVTZ(3d)′.

The DK approach does not appear to be more sensitive to the basis set contraction than the analogous nonrelativistic calculations, provided the contraction coefficients are based on DK atomic calculations. This is demonstrated in one set of tests, where the cc-pVTZ′ primitive basis sets are contracted twice, once using nonrelativistic atomic calculations and the second time using DK atomic calculations. However, to simplify the comparison, we perform most of the DK calculations using the same lightly contracted basis set as used in the $+R$ calculations.

The effect of spin-orbit coupling on the dissociation energy is computed using experimental values. Since GaX and GaX$_3$ are closed shells, there are no first-order molecular spin-orbit effects. For iodine bonds, Kim et al. [23] found a second-order molecular spin-orbit effect of about 1 kcal/mol. This effect is expected to be much smaller for Ga bonds, and is therefore ignored. The spin-orbit splitting is expected to be very small for the X^2A_1 states of GaX$_2$ and is therefore ignored. Thus only the atomic spin-orbit splitting contributes to the dissociation energy; this is computed using experimental values [3] as the difference between the lowest m_j component and the m_j weighted average energy.

The RCCSD(T) calculations are performed using Molpro [24], the B3LYP calculations are performed using Gaussian94 [25], and the MCPF calculations are performed using Molecule-Sweden [26]. The DK integrals are computed using the program written by Hess [7].

3 Results and discussion

We first consider GaCl$_n$ which has been considered previously [6]. The GaCl$_n$ results are summarized in Table 1. For all three systems, the $+R$ and DK approaches yield a similar relativistic effect at the SCF and MCPF(3d) levels of theory: the biggest difference is 0.12 kcal/mol for GaCl$_3$ at the MCPF(3d) level. When the Ga $3d$ electrons are not correlated, denoted "MCPF" in the table, there are sizeable differences between the $+R$ and DK approaches. This might initially appear odd, as the non-relativistic atomization energies at the MCPF and MCPF(3d) levels are similar and the relativistic effect at the SCF and MCPF(3d) levels are similar. An inspection of the orbitals shows that the Ga $3d$ orbitals have mixed slightly with the Cl valence orbitals, and that the small mixing is slightly different for the DK and nonrelativistic SCF approaches, which probably arises from the differences in the orbital energies when the relativistic effects are included. By including the Ga $3d$ orbital in the correlation treatment, the energy is invariant to the mixing of the Ga $3d$ and Cl valence orbitals. Thus the MCPF(3d) approach should be the most reliable. The scalar relativistic effect is small for GaCl because the bonding involves the Ga $4p$ orbital. For GaCl$_2$ and GaCl$_3$, the Ga sp hybridizes and, since relativity mostly affects the s electrons, there is a much larger effect than found for GaCl.

The results for GaF$_n$ are summarized in Table 2. In light of the results for GaCl$_n$ and because the F $2s$ orbital energy is below that of the Ga $3d$ orbital, Ga $3d$ correlation is included in all of the MCPF calculations. The relativistic effects are larger for the GaF$_n$ species than for the analogous GaCl$_n$ species. In addition, the agreement between the $+R$ and DK approaches is not as good for GaF$_n$ as for GaCl$_n$.

Table 1. Summary of the scalar relativistic effect on the GaCl$_n$ atomization energies, in kcal/mol. The cc-pVTZ(3d)′ basis sets are used

	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

Because of the differences in the relativistic effects between GaF_n and $GaCl_n$, several additional tests were run for GaF_2. Correlating the Ga 3s and 3p electrons was found to have little effect on either the atomization energy or on the relativistic effects. That is, the Ga 3s and 3p electrons are core and can be removed from the correlation treatment. Uncontracting the Ga p and d space further (not shown in the table) has almost no effect on the results. Thus we conclude that the difference between GaF_n and $GaCl_n$ is real and is not due to a computational artifact.

The bonding in the GaF_n and $GaCl_n$ systems is similar, but the populations show a larger transfer of charge from Ga to F than from Ga to Cl (Table 3). As the number of halogen atoms increases, the difference in net Ga charge between the GaF_n and $GaCl_n$ species increases; thus, while the difference in the Ga populations between GaCl and GaF is small, the difference is quite large for GaX_3. We believe that this trend is true, despite any population artifacts.

The lower Ga 4s population for the GaF_n compounds and the larger relativistic effects for s electrons suggests

Table 2. Summary of the scalar relativistic effect on the GaF_n atomisation energies, in kcal/mol. The cc-pVTZ(3d)′ basis sets are used, except in the calculations with separate general contractions

	SCF	MCPF(3d)	MCPF(3s3p3d)
GaF			
Nonrelativistic	102.618	137.261	
+ R	101.263	136.329	
DK	101.275	136.261	
+ R−nonrelativistic	−1.356	−0.932	
DK−nonrelativistic	−1.343	−1.001	
GaF₂			
Nonrelativistic	154.685	205.710	205.195
+ R	148.703	200.826	200.289
DK	148.571	200.566	200.023
+ R−nonrelativistic	−5.982	−4.884	−4.906
DK−nonrelativistic	−6.114	−5.144	−5.172
GaF₃			
Nonrelativistic	245.028	327.392	
+ R	236.567	320.021	
DK	236.373	319.514	
+ R−nonrelativistic	−8.461	−7.371	
DK−nonrelativistic	−8.656	−7.878	
GaF₂ separate general contractions			
Nonrelativistic	154.421	206.723	
+ R	148.192	201.606	
DK	148.309	201.589	
+ R−nonrelativistic	−6.229	−5.116	
DK−nonrelativistic	−6.112	−5.134	

Table 3. Ga nonrelativistic SCF populations

	4s	4p	Ga net
GaF	1.85	0.31	0.79
GaF₂	0.86	0.46	1.57
GaF₃	0.30	0.25	2.30
GaCl	1.88	0.48	0.56
GaCl₂	1.04	0.76	1.03
GaCl₃	0.55	0.73	1.53

that the difference between the + R and DK approaches for the GaF_n systems arises from the greater Ga to F donation. To investigate this effect, the first and second ionization potentials (IP) of Ga were computed at the MCPF(3d) level. For the first IP, which removes the 4p electron, the scalar relativistic effect is computed to be −0.78 and −0.70 kcal/mol at the DK and + R levels of theory, respectively. For the second IP the relativistic effect grows to 7.40 and 7.01 kcal/mol for the DK and + R levels, respectively. In addition to the increase in magnitude of the scalar relativistic effect when ionization changes the 4s population, the difference between DK and + R grows. Using the TZ, QZ, and 5Z basis sets, the nonrelativistic CCSD(T) CBS first and second IPs are determined to be 137.64 and 465.33 kcal/mol, respectively. Adding on the MCPF DK scalar relativistic effect and the experimental spin-orbit effect, yields 138.44 and 472.72 kcal/mol, which are in excellent agreement with experiment (138.33 and 473.07 kcal/mol) [3]. Using the MCPF + R correction yields 138.51 and 472.34 kcal/mol for the first two IPs. The DK correlated values are in slightly better agreement with experiment. In addition, the difference in the DK and + R contributions to the second IP is similar to the difference in DK and + R contributions to the GaF_3 atomization energy. Thus, the Ga ionization potential calculations support the view that the larger disagreement between the + R and DK approaches for GaF_n than for $GaCl_n$ is due to smaller Ga s populations in the GaF_n compounds arising from the larger Ga charge donation. Since for the Ga IPs, the DK approach agrees better with experiment, we conclude that the DK approach is superior to the + R approach.

In Table 2 we include GaF_2 calculations where two separate general contractions are performed: one for the nonrelativistic and + R calculations and the second for the DK calculations. The nonrelativistic and + R calculations use the cc-pV(3d) set without the Ga g function; this basis has the same primitive set as the cc-pVTZ(3d)′ basis set, but the cc-pV(3d) is contracted to a much smaller size. The DK basis set contracts the same primitive set to the same size as the cc-pV(3d) basis, but the contraction coefficients are taken from DK atomic calculations. Since the same primitive set is used, we first compare these contracted sets with the lightly contracted cc-pVTZ(3d)′ basis set. When the more contracted basis set is used, the nonrelativistic atomization energies increase by about 1 kcal/mol relative to the cc-pVTZ(3d)′ calculations; this is due to the basis set superposition error (BSSE), which increases from 2.64 to 4.30 kcal/mol when the basis set is contracted more heavily. The relativistic effect computed at the DK level is virtually identical to that computed using the less contracted basis set. Unlike the DK approach, the + R values change when the basis set contraction is changed; surprisingly, the + R MCPF value is in better agreement with the DK value for the smaller basis set than for the larger basis set. The + R SCF effect changes from being smaller than the DK value to being larger when the contraction is changed. The change in + R with basis set can be much larger, for example, Blomberg and Walhgren [22] found an almost 8 kcal/mol variation with basis set for the Pd atom.

The weaker basis set dependence of the DK results is typical of what we have found in other cases. We also note that Blomberg and Wahlgren [22] found a weak basis set dependence for a different no-pair approach. Thus, in addition to the better agreement with experiment, the ability to more heavily contract the basis set is another advantage of the DK approach.

In Table 4 we summarize our previous work on $GaCl_n$, along with experimental results [4, 27, 28]. The best D_e is obtained by extrapolating the CCSD(T) results to the complete basis set limit. The zero-point energy is computed at the B3LYP level. The spin-orbit effect is taken from experiment [3] and the scalar relativistic effect is the MCPF(3d) DK value; note in the previous work [6] we averaged the DK and $+R$ values, but on the basis of the present work we take the DK values since we believe they are superior. The temperature correction is computed using the rigid rotor/harmonic oscillator approximation in conjunction with the B3LYP geometries and frequencies. The atomization energies for GaCl and $GaCl_3$ are in good agreement with experiment, while the experimental value for $GaCl_2$ is clearly too large.

The extrapolated CCSD(T) GaF_n atomization energies (without zero-point energies) are summarized in

Table 4. Summary of $GaCl_n$ atomization energies, in kcal/mol

	GaCl	GaCl$_2$	GaCl$_3$
Best D_e	113.64	164.31	266.54
Zero-point energy (ZPE) (B3LYP)	−0.50	−1.24	−2.42
Spin orbit(Expt)	−2.42	−3.26	−4.10
Scalar rel	−0.46	−3.65	−5.82
Spin orbit + scalar rel	−2.88	−6.91	−9.92
Best atomization energy 0 K	110.26	156.16	254.20
Correction to 298 K	0.77	1.33	1.88
Best atomization energy 298 K	111.03	157.49	256.09
Experiment 298 K	110.94[a]	180.82[a]	255.40[a]
	114.38[b]		260.45[b]
Experiment 0 K	113.46[c]		

[a] Ref. [28]
[b] Ref. [27]
[c] Ref. [4]

Table 5. Summary of GaF_n extrapolated CCSD(T) atomization energies at 0 K, in kcal/mol

Method	GaF	GaF$_2$	GaF$_3$
n^{-3}(TZ,QZ)	143.76	217.31	344.93
n^{-3}(QZ,5Z)	143.40		
n^{-4}(TZ,QZ)	143.50	216.87	344.26
n^{-4}(QZ,5Z)	143.30		
$n^{-4}+n^{-6}$(TZ,QZ,5Z)	143.22		
$n^{-\alpha}$(TZ,QZ,5Z)	143.19 (4.999)[a]		
Corrected for Basis set superposition error			
n^{-3}(TZ,QZ)	143.89	217.63	345.50
n^{-3}(QZ,5Z)	143.47		
n^{-4}(TZ,QZ)	143.47	216.91	344.42
n^{-4}(QZ,5Z)	143.29		
$n^{-4}+n^{-6}$(TZ,QZ,5Z)	143.23		
$n^{-\alpha}$(TZ,QZ,5Z)	143.19 (4.513)		

[a] The optimal α value is given in parentheses

Table 5. For GaF it is possible to perform the extrapolation of all three basis sets. The three-point $n^{-4}+n^{-6}$ and variable α approaches are in good agreement. Even the two-point extrapolation methods agree relatively well with the three-point approaches. This is despite an α of nearly 5, which we previously suggested [29] might indicate a problem. Correcting the CCSD(T) values for BSSE does not affect the GaF results significantly. For GaF_2 and GaF_3, the 5Z calculations are very large, but as for GaF the two different two-point approaches are in reasonable agreement, as are the extrapolations with and without the BSSE correction. On the basis of the GaF calculations, it appears that the BSSE-corrected n^{-4} exptrapolation is the most reliable and we therefore take this as our best estimate for GaF_2 and GaF_3.

In Table 6 we correct our best estimate for the atomization energy for zero-point energy, spin-orbit and scalar relativistic effects as was done for $GaCl_n$. The experimental values [27, 30] are given at the bottom of the table. The GaF value is in good agreement with the value given by Gurvich et al. [30], while the agreements for GaF_2 and GaF_3 are not as good, even after considering the experimental error bars. We suspect that the extrapolated CCSD(T) results have an error of less than 2 kcal/mol. The error in the zero-point energy is expected to be small and experimental values are used for the spin-orbit correction. It is harder to estimate the error in the scalar relativistic correction, but the DK values for the first and second IP of Ga are accurate and the agreement between theory and experiment is very good for GaCl and $GaCl_3$. Thus it appears that the GaF_2 and GaF_3 experimental values are too large; however, more rigorous calibration calculations of the scalar relativistic effect in GaF_2 and GaF_3 would be ideal.

4 Conclusions

The computed atomization energies of GaCl, $GaCl_3$, and GaF suggest that correcting the CCSD(T) CBS values for zero-point energy, spin-orbit and scalar relativistic effects yields reliable results. The calculation of the first and second IP for Ga also supports this approach, as well as showing that the DK approach is more accurate than the $+R$ approach. The good agreement of the $+R$ and DK approaches for $GaCl_n$, but not for GaF_n, shows that the $+R$ approach can have problems for systems as light as Ga. In addition, it shows that very careful calibration calculations are required for

Table 6. Summary of GaF_n atomization energies, in kcal/mol

	GaF	GaF$_2$	GaF$_3$
Best D_e	143.22	216.9	344.3
ZPE(B3LYP)	−0.915	−2.168	−3.885
Spin orbit (expt)	−1.960	−2.345	−2.730
Scalar rel	−1.001	−5.144	−7.878
Best atomization energy 0 K	139.3	207.2	329.8
Expt			
Wagman et al. [27]	144.3		
Gurvich et al. [30]	138.6 ± 2.7	224.6 ± 12.0	339.6 ± 6.5

the $+R$ approach. The computed values for GaF_2 and GaF_3 suggest that the somewhat uncertain experimental values are too large; however, additional calibration calculations of the scalar relativistic effect would be very desirable.

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