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Boron Heat of Formation Revisited: Relativistic Effects on the BF_3 Atomization Energy

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The one-electron Douglas−Kroll approach, and perturbation theory including only the mass−velocity and Darwin terms, are used to compute the scalar relativistic contribution to the atomization energies of BF_3. Both approaches predict an approximately 0.7 kcal/mol reduction in the atomization energy. In combination with improved one-particle extrapolation techniques, this leads to a revised estimate for the heat of formation of gaseous boron, $\Delta H^\circ_{f,0}[B(g)] = 135.1$ kcal/mol and $\Delta H^\circ_{f,298}[B(g)] = 136.3$ kcal/mol, with error bars ±0.75 kcal/mol or less.

1. Introduction

Essentially there are two recommended values for the heat of formation of boron gas at 298 K ($\Delta H^\circ_{f,298}[B(g)]$) in the reference literature: the older value of 133.8 ± 3 kcal/mol adopted by JANAF[1] and in the 1978 CODATA[2] report, and the more recent value of 135.0 ± 1.2 kcal/mol from Gurvich[3] and the 1988 CODATA report.[4] The Gurvich[3] recommendation is based on a review of the five most recent measurements, namely 134.6 ± 0.7 kcal/mol (Robson and Gilles),[5] 135.3 ± 0.7 kcal/mol (Hildenbrand and Hall[6]), 134.1 ± 0.6 kcal/mol (Mar and Bedford[7]), 137.4 ± 0.2 kcal/mol (Storms and Mueller[8]), and 135.2 ± 0.9 kcal/mol (Nordine et al.[9]). Since the ($\Delta H^\circ_{f,298}[B(g)]$) is used whenever one attempts to directly compute the heat of formation of any boron compound from the computed (ab initio, density functional, or semiempirical) total atomization energy (TAE) of the molecule, there is considerable interest in determining this quantity as accurately as possible.

Martin and Taylor[10] recently computed the atomization energy of BF_3 using a high-level computational approach, namely the coupled cluster singles and doubles approach, including a perturbational estimate of the connected triples[11] (CCSD(T)). They accounted for both valence and core correlation effects as well as for spin−orbit effects. They estimated that their value of 462.6 kcal/mol had an error bar of only ±0.3 kcal/mol. Using this atomization energy and the well-established[4] heats of formation of BF_3 and F, they determined[10,12] ($\Delta H^\circ_{f,298}[B(g)]$) = 136.4 ± 0.4 kcal/mol, which they noted was in very good agreement with the Storms and Mueller[8] value of 136.2 ± 0.2 kcal/mol.

Hildenbrand[13] was surprised by this result, because he felt that the experiment of Storms and Mueller, which used a second-law approach, was probably less accurate than the other four recent experiments, which used a third-law approach. In fact, he suggested that the Storms and Mueller value was probably about 1 kcal/mol too large. With this in mind, we have reconsidered the BF_3 atomization energy. While it would be hard to perform better calculations for the treatment of electron correlation than those of MT, there are some aspects of the calculations that can be improved; first, the recent work of Martin and de Oliveira[14] offers new insight into the best approach for extrapolating the computed results to the complete basis set (CBS) limit and second, MT neglected scalar relativistic effects.

We should note that MT did not estimate the importance of imperfections in the CCSD(T) electron correlation method, but these are hard to quantify since more elaborate calculations (e.g., CCSDT or full configuration interaction) are at present not feasible for a 24-valence electron system in an adequately sized basis set. However, in light of the fact that electron correlation in BF_3 is dominated by dynamical correlation effects, we may expect CCSD(T) to be close to an exact solution to the electron correlation problem.[15] Thus we also assume that the use of the CCSD(T) approach does not introduce any significant errors, and in this paper we focus on the scalar relativistic effect and on improved estimates of the CBS limit.

A few years ago it would have been assumed that the scalar relativistic effects on the binding energy of BF_3 would be very small. However, there is increasing evidence[14,16−18] that scalar relativistic effects must be included to obtain highly accurate results even for the first-row systems. One open question is what is the best approach to compute these effects, e.g. what basis set, what level of correlation treatment, and what level to include the relativistic effect. Currently the most popular alternatives are the one-electron Douglas−Kroll (DK) approach,[19] and accounting for the mass−velocity and Darwin (MVD) terms using perturbation theory.[20,21] Davidson et al.[22] suggested that

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for first-row systems perturbation theory should work well. However, this was based on numerical wave functions and does not comment on the basis set requirements for this property. In this regard, we note that Blomberg and Wahlgren[23] found that no-pair approaches, like DK, tend to have much less basis set dependence than MVD. Thus, it might be more effective to compute the scalar relativistic effect using the DK than the MVD approaches. In this work we consider both approaches using several basis sets.

Martin and de Oliveira[14] extensively studied the behavior of various infinite-basis extrapolation techniques to the CBS limit. Of the different extrapolations considered, they found that, while the Martin three-parameter extrapolation[24] used by MT for the valence correlation energy yields excellent results with very large basis sets, the simple two-parameter formula $A + B/l^3$ of Halkier et al.[25] yields results of the same quality, but is much less sensitive to reducing the sizes of the underlying basis sets. On the basis of their findings, Martin and de Oliveira proposed two standard computational protocols for ab initio thermochemistry denoted W1 and W2 theory, which yield mean absolute errors as low as 0.30 and 0.17 kcal/mol, respectively, for molecules in which dynamical correlation effects dominate. Since MT found that BF_3 is a somewhat pathological molecule for basis set extrapolations, we shall also consider the W1 and W2 approaches for BF_3.

2. Methods

The scalar relativistic effect is computed at the modified coupled-pair functional[26] (MCPF) and averaged coupled-pair functional[27] (ACPF) levels of theory in two ways: (1) the Douglas−Kroll[19] (DK) approach is used, including only the one-electron contributions and (2) accounting for the mass-velocity and Darwin (MVD) terms using perturbation theory.[20,21] In order to verify the adequateness of the MCPF and ACPF methods for this purpose, we also carried out CCSD and CCSD(T) Douglas−Kroll calculations with one of the basis sets.

A variety of the latter are used, including standard (cc-pV*n*Z or V*n*Z for short, $n = \mathrm{T,Q}$)[28] and augmented (aug-cc-pV*n*Z or AV*n*Z for short)[29] correlation-consistent polarized valence *n*-triple zeta basis sets, uncontracted versions of the above (denoted by the suffix “uc”), and versions augmented with 2d1f core correlation functions (denoted "+tight") with exponents in geometric series with factor 2.5. One of these basis sets, cc-pVTZuc+tight is essentially equivalent to the “MTsmall” core correlation basis set used in W1 and W2 theory for the inner-shell correlation and scalar relativistic contributions. The combination of a cc-pV*n*Z basis set on B with the corresponding aug-cc-pV*n*Z basis set on F is indicated by the notation (A)-V*n*Z. In the DK calculations, the same exponents are used and the basis sets are contracted to the same size, but the contraction coefficients are taken from DK atomic calculations.

The BF_3 geometry is taken from experiment.[30] Only the valence electrons are correlated unless otherwise noted. The MCPF and some of the ACPF calculations are performed using Molecule-Sweden.[31] The DK integrals are computed using a modified version of the program written by Hess.[32] Most of the ACPF/MVD calculations are carried out using MOLPRO.[33] The protocols for the W1 and W2 methods are described in detail in ref 14. The valence correlation CCSD(T) energies computed in ref 10 could be reutilized for this purpose; the remaining calculations were carried out using MOLPRO.

3. Results and Discussion

A. Scalar Relativistic Contribution. The results are summarized in Table 1. We first consider basis set convergence for the MVD results. From Table 1, we see that results with the cc-pVTZ basis set are anything but converged. Adding diffuse functions affects the computed contributions by about 0.1 kcal/mol at both the SCF and MCPF levels; the effect of omitting diffuse functions on B is insignificant. The largest effect is a drop by about 0.20 kcal/mol at the SCF level, and 0.26 kcal/mol at the MCPF level, upon uncontracting the basis set. Any further additions to the cc-pVTZ(uc) basis set affect the computed result most insignificantly, including the addition of diffuse functions. We therefore may assume that the 0.1 kcal/mol effect they have on the *contracted* basis set results is simply an artifact of overcontracting the primitive basis set for this property.

TABLE 1: Convergence of the Computed Scalar Relativistic Contribution (kcal/mol) to the Total Atomization Energy of BF_3

		Electrons correlated		
		none[a]	valence	all
MCPF/VTZ	MVD	−1.065	−0.927	
	DK	−1.129	−0.710	
MCPF/VTZuc	MVD	−0.870	−0.665	
	DK	−0.870	−0.710	
MCPF/(A)VTZ	MVD	−0.968	−0.824	
	DK	−0.875	−0.714	
CCSD/(A)VTZ	DK	−0.875	−0.718	
CCSD(T)/(A)VTZ	DK	−0.875	−0.694	
MCPF/(A)VTZuc	MVD	−0.875	−0.666	
	DK	−0.874	−0.714	
MCPF/(A)VTZuc+tight	MVD	−0.875	−0.669	−0.689
	DK	−0.875	−0.716	−0.721
ACPF/(A)VTZuc+tight	MVD	−0.875	−0.669	−0.688
	DK	−0.875	−0.715	−0.718
MCPF/(A)VQZ	MVD	−0.874	−0.666	
	DK	−0.874	−0.713	
MCPF/(A)VQZuc+tight	MVD	−0.869	−0.669	
	DK	−0.874	−0.678	
ACPF/(A)VQZuc+tight	MVD	−0.875	−0.667	−0.685

[a] The SCF treatment.

In order to verify the suitability of the MCPF and ACPF methods for the correlation effects in the scalar relativistic corrections, we have also carried out a Douglas−Kroll CCSD(T)/(A)VTZ calculation. The resulting scalar relativistic contribution is marginally smaller in absolute value (0.020 kcal/mol) than the corresponding MCPF result. Most of the difference is due to the inclusion of connected triple excitations, since the DK CCSD/(A)VTZ result is only 0.004 kcal/mol higher than its MCPF counterpart.

Using the largest basis set considered here—which consists of uncontracted cc-pVQZ and aug-cc-pVQZ basis sets on B and F, respectively, augmented with (2d1f) inner-shell correlation functions—we obtain scalar relativistic contributions of −0.87 kcal/mol at the SCF level, −0.67 kcal/mol using valence correlation, and −0.69 kcal/mol with all electrons correlated. The reduction with electron correlation is what is found in most cases. We also note that the ACPF(all)/MTsmall treatment used in W1 and W2 theory yields the same result as the most extensive calculation to two decimal places.

The basis set convergence behavior for the Douglas−Kroll results is quite different from the MVD results. First of all, we note that the MCPF and ACPF treatments yield essentially the same result to two decimal places. Uncontracting the basis set has essentially no effect on the results (in stark contrast to MVD), and increasing the basis set from cc-pVTZ to cc-pVQZ makes only a very small reduction in the value. Thus, it appears

TABLE 2: Summary of the Extrapolation of BF Atomization Energy (kcal/mol)

	SCF	CCSD	(T)
AVDZ	132.43	29.33	2.61
AVTZ	142.30	31.99	3.64
AVQZ	143.03	33.79	3.85
AV5Z	143.08	34.27	3.92
AV6Z	143.09	34.49	3.95
$A + B/(l + 1/2)^C$ Three-Point Extrapolation[24]			
DTQ		54.27	3.94
TQ5		34.56	3.99
Q56		34.81	3.97
$A + B/l^3$ Two-Point Extrapolation[25]			
TQ		35.10	3.99
Q5		34.77	4.00
56		34.79	3.98
Components of W1 and W2 theory			
W1	143.08	34.97	4.03
W2	143.08	34.77	3.99

TABLE 3: Summary of the BF_3 Atomization Energy and Heat of Formation (kcal/mol)

	SCF	CCSD	(T)
AVDZ	354.32	70.51	4.87
AVTZ	373.59	78.90	7.43
AVQZ	374.61	83.90	7.93
AV5Z	374.59	85.09	8.10
$A + B/(l + 1/2)^C$ Three-Point Extrapolation[24]			
DTQ		107.53	8.18
TQ5		85.73	8.25
$A + B/l^3$ Two-Point Extrapolation[25]			
TQ		87.54	8.30
Q5		86.34	8.28
Components of W1 and W2 Theory			
W1	374.66	87.17	8.38
W2	374.59	86.34	8.30
	TAE_e	TAE_0	*a*
W1 theory[b]	470.17	462.28	461.62
W2 theory[b]	469.17	461.29	461.33
best estimate	469.3 ± 0.7	461.4 ± 0.7	
	$\Delta H^\circ_{f,0}$[B(g)]	$\Delta H^\circ_{f,298}$[B(g)]	
W1 theory	136.03	137.25	
a	135.37	136.59	
W2 theory	135.04	136.26	
a	135.08	136.30	
best estimate	135.1 ± 0.75	136.3 ± 0.75	

[a] Corrected using 3 × (D_e[BF,56]-D_e[BF,level]) (see text). [b] Core correlation +1.812 kcal/mol at CCSD(T)/MTsmall level; effect of atomic spin−orbit splitting −1.184 kcal/mol as in ref 10; scalar relativistic contribution at ACPF(all)/MTsmall level taken from Table 1. [c] Auxiliary thermodynamic data were taken from ref 4: $\Delta H^\circ_{f,298}$ [BF_3(g)] = −271.5 ± 0.2 kcal/mol, $H_{298} - H_0$[BF_3(g)] = 2.784 ± 0.005 kcal/mol; $H_{298} - H_0$[B(g)] = 1.5096 ± 0.0005 kcal/mol; $H_{298} - H_0$ [B(cr,rhombic)] = 0.292± 0.002 kcal/mol; $\Delta H^\circ_{f,298}$[F(g)] = 18.97 ± 0.07 kcal/mol; $H_{298} - H_0$[F(g)] = 1.5578 ± 0.0003 kcal/mol; $H_{298} - H_0$[F_2(g)] = 2.1092 ± 0.0003 kcal/mol.

that the basis set requirements for the DK approach follow those for an accurate nonrelativistic treatment of the electron correlation.

Despite any variation of results with basis set, it is encouraging that the two approaches agree quite well for the largest basis set considered, converging to a value of about −0.67 kcal/mol. We should note that our best value at the SCF level (−0.86 kcal/mol) is very similar to the value of −0.812 kcal/mol found by Pople and co-workers.[17] The inclusion of electron correlation is expected to bring the value of Pople and co-workers into better agreement with our best value.

B. Infinite-Basis Extrapolation. The largest basis sets that MT were able to use for BF_3 were of aug-cc-pV5Z quality. They were able to calculate D_e[BF] at the CCSD(T)/aug-cc-pV6Z level, and considered 3 times the difference between aug-cc-pV{T,Q,5}Z and aug-cc-pV{Q,5,6}Z $A + B/(l + 1/2)^C$ extrapolations as a further correction to their computed TAE[BF_3]. In light of recent benchmark calculations, we have reconsidered the extrapolation, using both the $A + B/(l + 1/2)^C$ and $A + B/l^3$ approaches; these results are summarized in Tables 2 and 3.

For the (T) contribution in BF, both extrapolations yield essentially the same result, even when the largest basis set involved is only AVQZ. For the CCSD valence correlation, the two extrapolations yield fundamentally the same result, if basis sets up to AV6Z quality are used. However, while $A + B/l^3$ yields the same limit to within 0.03 kcal/mol from AV{Q,5}Z basis sets and to within 0.3 kcal/mol using AV{T,Q}Z basis sets, a difference of −0.24 kcal/mol is seen for $A + B/(l + 1/2)^C$ from AV{T,Q,5}Z, while the AV{D,T,Q}Z result is essentially nonsensical. It is therefore clear that the $A + B/l^3$ scheme is the more well behaved of the two extrapolation methods.

Likewise, we see for BF_3 that the two formulas are in agreement for the (T) contribution, while they differ quite substantially for the CCSD contribution. The $A + B/l^3$ AV{Q,5}Z extrapolated limit is about 0.6 kcal/mol higher than its $A + B/(l + 1/2)^C$ counterpart. For BF, the difference between the CCSD correlation contribution to the atomization energy using the $A + B/l^3$ AV{Q,5}Z and AV{5,6}Z extrapolations is 0.02 kcal/mol, while the $A + B/(l + 1/2)^C$ result increases by 0.25 kcal/mol between AV{T,Q,5}Z and AV{Q,5,6}Z. If we apply the "3 times BF" correction to the CCSD contribution, we obtain 86.40 kcal/mol for the corrected $A + B/l^3$ value and 86.48 kcal/mol for the corrected $A + B/(l + 1/2)^C$ result. While these two values are similar, the greater consistency for the $A + B/l^3$ extrapolation leads us to pick this as the more reliable one.

Our best atomization energy of 461.39 kcal/mol is determined by adding the following contributions: the AV5Z SCF (374.59), the $A + B/l^3$ AV{Q,5}Z CCSD (86.34) and (T) (8.28), the Pak and Woods[34] zero-point energy (−7.887) used by MT, MT's inner-shell correlation effect (1.922), the scalar relativistic effect discussed above (−0.67), and the spin−orbit contribution (−1.184 kcal/mol).

In order to help establish an uncertainty for this quantity, we also apply the W2 procedure, which is closely related to the methods discussed above. This approach has recently been applied[14] to 28 systems where the atomization energy is accurately known. Applied to BF_3 it yields 461.29 kcal/mol, in excellent agreement with our best estimate. The mean absolute error of W2 theory over its reference molecules is 0.23 kcal/mol. Since systems with very polar strong bonds are underrepresented in the W2 reference set, we multiply the mean absolute error by 3, to account for the three strong bonds in BF_3. This yields a quite conservative error estimate of 0.69 kcal/mol for TAE[BF_3]; considering the experimental uncertainties on ΔH°_f[F(g)] and ΔH°_f[BF_3(g)], this finally leads to an estimated uncertainty of ±0.75 kcal/mol on our predicted ΔH°_f[B(g)].

Feller and Peterson[18] recently reported an atomization energy, not including zero-point energy, of 467.1 kcal/mol for BF_3, which is 2.2 kcal/mol smaller than our best value. We suspect that their method of extrapolation and calculation of the scalar relativistic effects are less accurate than ours, leading to a value that is too small. Finally, we note that the computationally less demanding W1 approach yields an atomization energy of 462.28 kcal/mol, which is in good agreement with our best estimate.

C. Heat of Formation. Our best atomization energy is consistent with a $\Delta H^\circ_{f,0}$[B(g)] = 135.1 ± 0.75 kcal/mol. This should be compared with the MT value of 136.32 ± 0.3 kcal/mol (after correcting[12] for a misprint in $H_{298} - H_0$ in ref 35), or 135.7 ± 0.5 kcal/mol in ref 16. Upon applying the precise $H_{298}-H_0$ functions of B(g) and B(cr) from the CODATA tables,[4] we obtain finally $\Delta H^\circ_{f,298}$[B(g)] = 136.3 ± 0.75 kcal/mol. This value is near the upper limit of the JANAF[1] (133.8 ± 3 kcal/mol) and Gurvich[3] (135.0 ± 1.2 kcal/mol) recommendations. In addition, our value suggests that the Storms and Mueller[8] value of 137.4 ± 0.2 kcal/mol is indeed about 1 kcal/mol too large as suggested by Hildenbrand.[13] We note in passing that our calculation fortuitously agrees perfectly with an older measurement by Paule and Margrave,[36] 136.4 ± 0.2 kcal/mol.

4. Conclusions

Scalar relativistic effects reduce the atomization energy of BF_3 by about 0.7 kcal/mol. In combination with improved infinite-basis extrapolations, we determine a best atomization energy of BF_3 of 461.39 kcal/mol. Our estimated error is ±0.75 kcal/mol or less. Using this atomization energy and the well-established heats of formation of boron trifluoride and fluorine atom, we obtain a revised heat of sublimation of boron, $\Delta H^\circ_{f,0}$[B(g)] = 135.1 kcal/mol or $\Delta H^\circ_{f,298}$[BF_3(g)] = 136.3 kcal/mol, which is near the upper limit of the recommendations by JANAF and by Gurvich.

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