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LETTERS

Revised Heat of Formation for Gaseous Boron: Basis Set Limit ab Initio Binding Energies of BF_3 and BF

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To determine the heat of formation of boron atom, a fundamental parameter in gas-phase thermochemistry, from a thermochemical cycle involving BF_3, the total atomization energy (TAE_0, $\sum D_0$) of this molecule was accurately determined ab initio in an exhaustive convergence study using coupled cluster [CCSD(T)] methods. Basis sets up to [8s7p6d5f4g3h2i] quality have been considered, and an extrapolation for further basis set incompleteness was applied. Inner-shell correlation, anharmonicity in the zero-point energy, and atomic spin−orbit splitting have all been taken into account. Our best computed TAE_0 for BF_3, 462.6 ± 0.3 kcal/mol, leads to a best heat of formation for gaseous boron at 0 K of 136.0 ± 0.4 kcal/mol, in excellent agreement with an experimental determination of 136.2 ± 0.2 kcal/mol and definitively confirming recent suggestions that the established reference value, 132.7 ± 3.0 kcal/mol, should be revised. This revision will affect most known gas-phase thermochemical data for boron compounds. As a byproduct, we obtain a dissociation energy D_0 of 180.13 ± 0.2 kcal/mol for the BF diatomic, in perfect agreement with experiment but with a much smaller uncertainty.

I. Introduction

Gas-phase heats of formation for the atoms are fundamental thermochemical properties, which not only relate gas-phase dissociation energies and other reaction enthalpies to heats of formation, but are also required in semiempirical as well as ab initio computational methods, to permit translation of the computed results into the heats of formation universally employed by thermochemists and the many chemists in industry and academia relying on thermochemical data.

Given their importance, it may strike some readers as surprising that heats of formation for several first- and second-row atoms, notably Be, B, and Si, are imprecisely known. This is perhaps the most striking for boron, where the accepted experimental $\Delta H_f^0(\mathrm{B(g)})$ value[1] of 132.7 ± 3.0 kcal/mol carries a very large error bar owing to complications involving metallic impurities. A much higher value[2] of 136.2 ± 0.2 kcal/mol was rejected by the JANAF compilers.[1]

This large uncertainty carries over into many gas-phase data for boron compounds. Moreover, any ab initio or semiempirical scheme for calculating molecular heats of formation will involve (when applied to boron compounds) the heat of formation of boron atom through the identity (at 0 K)

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$$\Delta H^\circ_{f,T}(A_kB_lC_m...) - k\Delta H^\circ_{f,T}(A) - l\Delta H^\circ_{f,T}(B) - m\Delta H^\circ_{f,T}(C) - ... = E_T(A_kB_lC_m...) + RT(1 - k - l - m - ...) - kE_T(A) - lE_T(B) - mE_T(C) - ... \quad (1)$$

(where T is the temperature), and hence uncertainties are introduced, which in some cases may dwarf the intrinsic uncertainties of the underlying methods. Given the great practical importance of boron compounds in many areas of chemistry, this is obviously an unsatisfactory state of affairs.

Storms and Mueller (SM)[2] had previously recommended a much higher and more precise value of 136.2 ± 0.2 kcal/mol. Ruscic et al.,[3] reviewing the experimental data, concluded that the JANAF value was in error and recommended the SM value. Recently, Ochterski et al.[4] combined calculated atomization energies using the CBS-APNO hybrid ab initio/empirical scheme[5] with an accurate CODATA[6] heat of formation for BF_3, 271.2 ± 0.2 kcal/mol, and the established heat of formation for F(g), 18.47 ± 0.07 kcal/mol, to obtain 135.7 kcal/mol. On the basis thereof, they too recommended the SM value. Note that this value does not include a correction for the split−orbit splitting in atomic fluorine and therefore is about 1.1 kcal/mol too high (see below). In another study, Schlegel and Harris[7] found that computed heats of formation using the Gaussian-2 (G2) method[8] for a number of boron compounds agreed much better with experiment if the reference value for gaseous boron was taken as the SM rather than the JANAF value.

Recently, the present authors developed a technique[9] that permitted the calculation of the total atomization energies of 14 small polyatomics with a mean absolute deviation from experiment of 0.12 kcal/mol. The method involves coupled cluster[10,11] [CCSD(T)] calculations with successive basis sets of spdf, spdfg, and spdfgh quality and an extrapolation[12] based on the theoretical asymptotic convergence behavior[13,14] of the correlation energy in terms of the maximum angular momentum *l* represented in the basis set. In addition, separate calculations with special core-correlation basis sets[15,16] were carried out to assess the differential effect of inner-shell correlation, and the contribution of anharmonicity to the zero-point energy was treated explicitly. All of the above were found to be necessary to achieve this accuracy, and in cases involving multiple bonds, an additional basis set step toward basis sets of spdfghi quality was in order.[12] It should be stressed that the method does not rely on *any* empirical corrections and is thus purely “ab initio”.

The formidable requirements of this method in terms of computing resources limited its applicability at the time to molecules including at most three nonhydrogen atoms. In the present work, we report its application to the total atomization energy of the BF_3 molecule and thus (indirectly) to the heat of formation of gaseous boron. As a byproduct, we obtain for the first time an accurate dissociation energy for the BF diatomic.

II. Methods

All electronic structure calculations were carried out using a prerelease version of MOLPRO 97[17] running on an SGI Origin 2000 minisupercomputer at the Weizmann Institute of Science and, for the larger calculations (which involve up to 500 basis set functions and more), on the National Partnership for Advanced Computational Infrastructure CRAY T90 at the San Diego Supercomputer Center. The CCSD(T) electron correlation method,[10,11] as implemented by Hampel et al.,[18] was used throughout. (The definition of ref 11 for the open-shell CCSD(T) energy was employed for the atoms.) From extensive studies (see ref 19 for a review), this method is known to yield correlation energies very close to the exact (full configuration interaction) basis set correlation energy for systems where nondynamical correlation is not very important. A quantitative measure for the importance of nondynamical correlation is the $\mathcal{T}_1$ diagnostic:[20] in the present case, we obtain $\mathcal{T}_1 = 0.0161$ for BF_3 and $\mathcal{T}_1 = 0.0217$ for BF at the CCSD(T)/AV5Z (see below) level, values which suggest systems largely dominated by dynamical rather than nondynamical correlation.

For the valence correlation energy, four different augmented correlation-consistent[21] polarized valence *n*-tuple ζ (aug-cc-pV*n*Z, or AV*n*Z for short) basis sets were used, with contracted sizes [5s4p3d2f] (AVTZ[22]), [6s5p4d3f2g] (AVQZ[22]), [7s6p5d4f3g2h] (AV5Z[22]), and [8s7p6d5f4g3h2i] (AV6Z[23]), corresponding to 46, 80, 127, and 189 basis functions per atom, respectively. The “augmented” refers to the presence of one low-exponent (anion region) basis function for each angular momentum: given the polar character of the B−F bond, their presence in the basis set was considered essential.

Since for basis sets as large as the one used in the present study, the Hartree−Fock part of the energy is essentially converged, it does not matter much which extrapolation formula is used, if any: in the present work, we have employed a geometric extrapolation[24] of the type $A + B{\cdot}C^{-n}$, where $n = 3$, 4, 5, 6 for AVTZ, AVQZ, AV5Z, and AV6Z basis sets, respectively. Such an extrapolation from AV*l*Z, AV*m*Z, and AV*n*Z results is denoted Feller(*lmn*).

Following ref 9, the correlation energy was extrapolated using a three-point formula of the type $A + B/(n + {}^1/_2)^\alpha$, the result of which is denoted Schwartzα(*lmn*) for extrapolation to CCSD(T)/AV*l*Z, CCSD(T),AV*m*Z, and CCSD(T)/AV*n*Z results.

Inner-shell correlation was treated using the Woon−Dunning correlation-consistent polarized core−valence *n*-tuple zeta or cc-pCV*n*Z basis sets[16] (CV*n*Z for short) and their “augmented” counterparts aug-cc-pCV*n*Z (or ACV*n*Z for short). These are obtained by adding the following sets of high-exponent (inner-shell region) basis functions to the corresponding V*n*Z or AV*n*Z basis set: [2s2p1d] for $n =$ T, [3s3p2d1f] for $n =$ Q, and [4s4p3d2f1g] for $n = 5$. The largest core correlation basis set considered here, ACV5Z, contains 181 basis functions per atom.

All calculations were carried out at CCSD(T)/cc-pVQZ reference geometries, taken from ref 25 in the case of BF_3 and calculated in this work ($r = 1.2675$ Å) in the case of BF.

The anharmonic zero-point energy for BF_3 was obtained from combining a recently computed[25] set of anharmonic constants with the experimental fundamentals (see ref 25 for detailed references).

As has been pointed out repeatedly (e.g., ref 26), since nonrelativistic calculations yield energies corresponding to an average over spin−orbit sublevels for the atoms rather than the lowest-energy spin−orbit sublevel, the computed atomization energies need to be corrected downward for spin−orbit splitting. The corrections amount to −0.029 kcal/mol per boron atom and −0.385 kcal/mol per fluorine atom, adding up to −0.41 kcal/mol for BF and −1.18 kcal/mol for BF_3.

III. Results and Discussion

All relevant energies are given in Table 1.

The SCF component of the atomization energy of BF_3 is clearly converged with the basis set, differing by −0.02 kcal/mol between AVQZ and AV5Z basis sets. (It should be noted that the geometry used is not the SCF optimum geometry with these basis sets; hence, the SCF binding energy does not necessarily increase monotonically with improvement of the

TABLE 1. Computed Thermochemical Properties for BF_3, BF, and B in the Gas Phase. All Values Are in kcal/mol

	BF_3	BF
SCF Component of TAE_e		
SCF/AVTZ	373.59	142.30
SCF/AVQZ	374.61	143.03
SCF/AV5Z	374.59	143.08
SCF/AV6Z		143.09
Feller(TQ5)	374.59	143.08_5
Feller(Q56)		143.08_7
best SCF[a]	374.59	143.09
Valence Correlation Component of TAE_e		
CCSD(T)/AVTZ	87.38	35.63
CCSD(T)/AVQZ	91.83	37.63
CCSD(T)/AV5Z	93.19	38.19
CCSD(T)/AV6Z		38.44
Schwartzα(TQ5)	94.03	38.35
Schwartzα(Q56)		38.76
best valence corr.[b]	95.13	38.76
Inner-Shell Correlation Component of TAE_e		
CCSD(T)/CVTZ	1.366	0.482
CCSD(T)/CVQZ	1.724	0.629
CCSD(T)/CV5Z		0.670
Schwartzα(TQ5)		0.696
CCSD(T)/ACVTZ	1.563	0.557
CCSD(T)/ACVQZ	1.772	0.648
CCSD(T)/ACV5Z		0.676
aug-Schwartzα(TQ5)		0.698
best core corr.[c]	1.922	0.698
best $TAE_{e,NR}$	471.65	182.54
spin−orbit correction[d]	−1.184	−0.414
best TAE_e	470.46	182.13
ZPVE	7.887[e]	1.996[f]
best TAE_0	462.63	180.13
Derivation of $\Delta H_f^\circ[B(g)]$		
$\Delta H_f^\circ[BF_3(g)]$, ref 6	-271.2 ± 0.2	
$\Delta H_f^\circ[F(g)]$, ref 1	$+18.47 \pm 0.07$	
calcd $\Delta H_f^\circ[B(g)]$	136.02 ± 0.4	
exptl JANAF,[1]	133 ± 3	
exptl SM,[2] 298 K	137.4 ± 0.2	
$\Delta H_{f,298}^\circ - \Delta H_{f,0}^\circ$, ref 1	1.219	
exptl SM,[2] 0 K	136.2 ± 0.2	

[a] Feller(TQ5)[BF_3]+3 × (Feller(Q56)[BF]−Feller(TQ5)[BF]). [b] Schwartzα(TQ5)[BF_3]+3 × (Schwartzα(Q56)[BF]−Schwartzα(TQ5)[BF]). [c] CCSD(T)/ACVQZ[BF_3]+3 × (aug-Schwartzα(TQ5)[BF]−CCSD(T)/ACVQZ[BF]). [d] Computed from atomic sublevels for electronic ground states given in ref 1. [e] From observed ν_i and computed X_{ij}, G_{ij} given in ref 25. [f] From computed CCSD(T)/VQZ $\omega_e = 1398.0$, $\omega_e x_e = 11.55$, and $\omega_e y_e = 0.054$ cm^{-1}: experimental values[29] 1402.1_3, 11.8_4, and 0.05_6 cm^{-1}, respectively. A more recent experimental study[30] found: $\omega_e = 1402.158\,65(26)$, $\omega_e x_e = 11.821\,06(15)$, $\omega_e y_e = 0.051\,595(35)$ cm^{-1}.

basis set.) The extrapolated value agrees to two decimal places with the directly calculated value with the largest basis set.

As expected, the situation for the correlation energy is rather different. Improving the basis set from AVQZ to AV5Z increases the correlation energy by some 1.39 kcal/mol, compared to 4.46 kcal/mol for AVTZ to AVQZ. The Schwartzα(TQ5) extrapolation adds on another 0.84 kcal/mol; the value of α for BF_3 is about 3.40, compared to 3.28 for F and 4.25 for B. The α found for the MP2 correlation energy of BF_3, however, amounts to 2.88, quite close to the leading $(l + 1/2)^{-3}$ behavior expected[13] for the MP2 energy. This suggests that the basis sets may actually be approaching the $(l + 1/2)^{-3}$ regime, while the difference between the MP2 and CCSD(T) values of α suggests the importance of higher-order contributions, which add[14] higher powers in $(l + 1/2)$.

The CCSD(T)/AV5Z calculation on BF_3 involved 508 basis functions and required 60 GB of disk space and 720 MB of memory on the CRAY T90. A CCSD(T)/AV6Z calculation on BF_3, at 756 basis functions, would be beyond our current capabilities. However, by considering the BF diatomic as a model system, we can gauge the effect of further basis set extension.

The SCF D_e for BF increases by only 0.05 kcal/mol from AVQZ to AV5Z: further extension of the basis set to AV6Z only adds on another 0.01 kcal/mol. Again, we may consider this component of D_e to be converged for all intents and purposes. The degree of convergence is illustrated by the fact that the Feller(Q56) total SCF energy, $-124.168\,760\ E_h$, lies only 20 μE_h above the numerical Hartree−Fock energy[27] of $-124.168\,779\,2\ E_h$.

The correlation component, however, increases by 0.55 kcal/mol from AVQZ to AV5Z, while further basis set extension to AV6Z adds on another 0.25 kcal/mol. The important thing to observe, now, is that the correlation part of D_e as directly computed with the AV6Z basis set is actually *larger* than the Schwartzα(TQ5) extrapolated value. As a result, the latter is 0.37 kcal/mol smaller than the Schwartzα(Q56) value. The value of α increases from 3.51 in the TQ5 extrapolation to 3.82 in the Q56 extrapolation: the corresponding values for the MP2 correlation energy are 2.87 and 3.29, respectively.

Since BF_3 actually contains three bonds that are quite similar to the one in BF, it seems indisputable that the difference between Schwartzα(TQ5) and Schwartzα(Q56) would be approximately three times that in BF. Hence we obtain an estimated basis set limit for the correlation part of TAE of 95.14 kcal/mol. In combination with the SCF contribution of 374.57 kcal/mol this yields a valence-only TAE, without spin−orbit correction, of 469.71 kcal/mol.

The contribution of inner-shell correlation to the TAE of BF_4 is found to be 1.37 kcal/mol at the CCSD(T)/CVTZ level and 1.72 kcal/mol at the CCSD(T)/CVQZ level. Given the polarity of the system, some mild coupling between the effects of core correlation and inclusion of diffuse functions cannot be ruled out a priori, and indeed extending the CVQZ to an ACVQZ basis set adds some 0.05 kcal/mol to the core correlation energy. Based on experience[28] we normally expect the core correlation contribution to be near convergence with such basis sets.

Again using the BF diatomic as a model system permits us to gauge the effects of further improvement of the core correlation basis set. At the CCSD(T)/ACVQZ level, the core correlation contribution to D_e(BF) is 0.65 kcal/mol, or slightly more than one-third the value in BF_3. Enlarging the basis from CVQZ to CV5Z leads to an increase of 0.04 kcal/mol: the effect from ACVQZ to ACV5Z is somewhat smaller at 0.03 kcal/mol. (The CV5Z and ACV5Z values differ by only 0.01 kcal/mol.) Carrying out a Schwartzα(TQ5) extrapolation on the ACVTZ, ACVQZ, and ACV5Z numbers leads to an estimated infinite-basis limit core correlation contribution to the BF D_e of 0.70 kcal/mol, or 0.05 kcal/mol more than the computed ACVQZ value.

If we again use three times this value as a correction for BF_3, we obtain a best estimate for the inner-shell correlation contribution to TAE(BF_3) of 1.92 kcal/mol. We hence obtain a $TAE_{e,NR}$ (i.e., without spin−orbit correction) of 471.65 kcal/mol; deducting the atomic spin−orbit corrections finally yields $TAE_e = 470.46$ kcal/mol.

From the computed CCSD(T)/VTZ harmonic frequencies and anharmonicity constants given in ref 25, we obtain ZPE = 7.89 kcal/mol. If we substitute experimental fundamentals (see ref 25 for details) and employ the computed anharmonicity constants only for the small difference between the zero-point energy and one-half the sum of the fundamentals, ZPE decreases to 7.83 kcal/mol. We hence obtain the total atomization energy for BF_3 at 0 K, $TAE_0 = 462.63$ kcal/mol.

In combination with the JANAF[1] heat of formation for F(g) of 18.47 ± 0.07 kcal/mol and the CODATA[6] heat of formation of BF_3(g), −271.2 ± 0.2 kcal/mol, we then obtain $\Delta H f^{\circ}(B(g)) = 136.0 \pm 0.3$ kcal/mol, in which the uncertainty only reflects the uncertainties in the experimental quantities. The possible further error in the calculations is somewhat more difficult to quantify: past experience suggests a mean absolute error of 0.12 kcal/mol, but in the light of the fairly substantial correction terms applied, it would probably be appropriate to increase the error margin to about 0.3 kcal/mol. This would then bring our best estimate to 136.0 ± 0.4 kcal/mol, the uncertainty of which encompasses that of the SM value of 136.2 ± 0.2 kcal/mol.

As a byproduct, we can now present our best estimate for the dissociation energy of BF. Combining the Schwartz5(56) SCF contribution of 143.09 kcal/mol with the Schwartzα(Q56) valence correlation contribution of 38.76 kcal/mol and the Schwartzα(TQ5) core correlation contribution of 0.70 kcal/mol, we obtain $D_{e,NR} = 182.54$ kcal/mol or, with spin−orbit correction, $D_e = 182.13$ kcal/mol. Our computed anharmonic ZPE at the CCSD(T)/VQZ level is 2.00 kcal/mol, a value identical to two figures with that obtained from the molecular constants in Huber and Herzberg.[29] This finally leads to $D_0 = 180.13$ kcal/mol or 7.811 eV, the latter identical to two decimal places with the experimental value of 7.8_1 eV given by Huber and Herzberg. We definitely would quantify our error as much less than 0.1 eV (2.3 kcal/mol): perhaps 0.2 kcal/mol would be a reasonable estimate.

IV. Conclusions

An exhaustive basis set convergence study on the BF_3 molecule yields best values for the total atomization energies of $TAE_e = 470.45$ and $TAE_0 = 462.61$ kcal/mol, with an uncertainty of about 0.3 kcal/mol. In combination with the accurate experimental heats of formation of BF_3(g) and F(g), we obtain a computed heat of formation at 0 K for B(g) of 136.0 ± 0.4 kcal/mol. These results definitively confirm recent suggestions[3,4,7] that the accepted heat of formation[1] for B(g), 133 ± 3 kcal/mol, is in error and that an outlying experimental determination[2] of 136.2 ± 0.2 kcal/mol should in fact be the recommended value. This revision will affect most gas-phase thermochemical data for boron compounds. As a byproduct, we obtain $D_0 = 180.13 \pm 0.2$ kcal/mol for $BF(X^1\Sigma^+)$, for which no precise dissociation energy is available.

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