J. Phys. Chem. A **1999,** *103,* 4313−4318

Accurate Heats of Formation for BF_n, BF_n^+, BCl_n, and BCl_n^+ for $n = 1-3$

Charles W. Bauschlicher, Jr.* and Alessandra Ricca*

Mail Stop-230-3, NASA Ames Research Center, Moffett Field, California 94035

Received: February 1, 1999; In Final Form: March 26, 1999

Accurate heats of formation are computed for BF_n, BF_n^+, BCl_n, and BCl_n^+, for $n = 1-3$. The geometries and vibrational frequencies are determined at the B3LYP level of theory. The energetics are determined at the CCSD(T) level of theory. Extrapolation to the basis set limit is discussed. Spin−orbit, scalar relativistic, and core−valence correlation are accounted for. The temperature dependence of the heat of formation, heat capacity, and entropy is computed for the temperature range 300−4000 K and fit to a polynomial.

I. Introduction

The chlorides and bromides of boron are used in plasma processing of semiconductor materials. For example, a weakly ionized discharge of BCl_3 is used to etch patterns in GaAs and related III−V compounds. The discharge produces atomic chlorine, which is the active species responsible for etching and for the production of a variety of radicals and ions. BF_3 is used in a similar capacity in silicon-integrated circuit manufacturing. Despite their commercial uses, our understanding of their chemistry is incomplete; for example, the ionization potential (IP) of BCl_2 has not been measured. Furthermore, the uncertainty in some of the BX_n thermochemistry is larger than desired. For example, the JANAF[1] heat of formation for BF_2 differs from that of Lau and Hildenbrand[2] by more than 20 kcal/mol. With this in mind, it is not surprising to find that some of these species have been studied using computational chemistry techniques. Rablen and Hartwig[3] have computed the atomization energies of BF_n species using the G2 and CBS4 approaches. Martin and Taylor[4] have evaluated the atomization energies of BF and BF_3 using extremely accurate methods; one conclusion of their work is that the JANAF[1] heat of formation of the boron atom is incorrect and the value of Storms and Mueller[5] should be used. Ruscic et al.[6] and Gurvich et al.,[7] on the basis of a review of the experimental literature, had previously concluded that the JANAF value was too small. Gurvich et al. recommended a value of 135 ± 1.2 kcal/mol, which is somewhat smaller than the value of Storms and Mueller, 137.4 ± 0.2 kcal/mol. Schlegel and Harris[8] have determined the atomization energies for the BCl_n systems at the G2 level of theory. Baeck and Bartlett[9] have computed the vertical and adiabatic IPs of the BCl_n systems. We are unaware of a high-level systematic study of the BF_n, IPs.

While the G2 approach[10] has been used to determine many accurate atomization energies, if it has a weakness, it is probably for halide-containing systems.[11] Therefore, given the interest in these systems, we have reinvestigated them using the same level of theory for all of the species. The methods we use are related to those of Martin and Taylor, except we have accounted for scalar relativistic effects, and therefore we can use their results to calibrate our results for the BF_n systems.

II. Methods

Geometries are optimized and the vibrational frequencies computed using density functional theory (DFT). More specifically, we use the hybrid[12] B3LYP[13] approach in conjunction with the 6-31+G* basis set.[14] The vibrational frequencies confirm that the species are minima and are used to compute the zero-point energies. The B3LYP geometries are refined using the 6-311+G(2df) basis set. For BCl_3^+ and BF_3^+, the geometries and frequencies are also determined using the MP2 level of theory[15] and using the BP86 functional.[16,17]

Using the B3LYP/6-311+G(2df) geometries, the energetics are computed using the restricted coupled cluster singles and doubles approach[18,19] including the effect of connected triples determined using perturbation theory,[20,21] RCCSD(T). In these RCCSD(T) calculations only the valence electrons (the Cl 3s and 3p and the B and F 2s and 2p) are correlated. We use the augmented correlation-consistent polarized valence (aug-cc-pV) basis sets developed by Dunning and co-workers.[22−25] Specifically, the triple-ζ (TZ), quadruple-ζ (QZ), and quintuple-ζ (5Z) sets are employed.

The scalar relativistic effect is computed using the Douglas−Kroll (DK) approach[26] with only the one-electron terms using the modified coupled pair functional[27] (MCPF) level of theory. To study the importance of core−valence (CV) correlation and scalar relativistic effects, the CV(TZ) basis set is developed from the aug-cc-pVTZ set. For B and F, the s and p spaces are uncontracted, while for Cl the inner 11 s primitives are contracted to two functions while the inner four p primitives are contracted to one function; the remaining s and the p functions and the polarization functions are uncontracted. To each basis sets two tight d and one tight f even-tempered functions are added with a β of 3.0. Note that the Cl contraction coefficients used in the molecular DK calculations are taken from DK atomic self-consistent-field (SCF) calculations.

We compute the atomization energies with only valence (val) correlation and with core and valence (CV) correlation. The core effect can be computed as MCPF(CV)-MCPF(val) or as MCPF(DK,CV)-MCPF(DK,val), and the scalar relativistic effects as the difference MCPF(DK,val)-MCPF(val) or MCPF-(DK,CV)-MCPF(CV). Tests show that the CV and scalar relativistic effects are nearly additive, so we report only the sum of these two effects, computed as MCPF(DK,CV)-MCPF(val).

Several different structures are possible for BCl_3^+. In this case, we compare the results obtained with the CCSD(T) approach with those obtained using the Bruekner doubles, BD, approach.[28] In the BD calculations, the effect of triples (T) or triples and quadruples (TQ) are included using perturbation theory.[29]

10.1021/jp9903662 CCC: $18.00

TABLE 1: Comparison of the Optimized BF_n B3LYP/6-311+G(2df) Geometries[a] with Previous Work

	BF	BF^+	BF_2	BF_2^+	BF_3	BF_3^+
Present Work						
state	$^1\Sigma^+$	$^2\Sigma^+$	$^2A_1$	$^1\Sigma_g^+$	$^1A'_1$	$^2B_2$[b]
r(B−F)	1.262	1.212	1.308	1.227	1.313	1.261, 1.764
∠(FBF)			121.5	180.0	120.0	151.4
Pak and Woods[37] CCSD(T)/cc-pVTZ						
r(B−F)					1.313	
Pak and Woods[37] CCSD(T)/cc-pVQZ						
r(B−F)					1.310	
Summary in JANAF[1]						
r(B−F)	1.265		[1.30][c]	[1.31]	1.307	
∠(FBF)			[112]	180.0	120.0	
Dyke et al.[36]						
r(B−F)		1.208 ± 0.005				

[a] The bond lengths are in angstroms, and the bond angles, in degrees. [b] The MP2/6-31+G* geometry is reported. The molecule has C_{2v} symmetry with one long B−F bond and two short B−F bonds. The unique FBF angle is given. The B3LYP approach yields a D_{3h} structure with r(B−F) = 1.311 Å. [c] The values in square brackets are estimates.

To improve the accuracy of the results, we extrapolate the CCSD(T) results to the complete basis set (CBS) limit using the three-point ($n^{-4} + n^{-6}$) extrapolation scheme described by Martin.[30] In a few cases, we only have the results for the TZ and QZ basis sets, and in these cases, we use the two-point n^{-4} extrapolation.[30] The RCCSD(T) calculations are performed using Molpro[31] and the MCPF calculations are performed using Molecule-Sweden,[32] while all other calculations are performed using Gaussian94.[33] The calculations are run on SGI Origin 2000 and IBM RS6000/595 computers. To give some measure of the time required for these calculations, we note that the BCl_3^+ CCSD(T) calculations using the aug-cc-pV5Z basis set required 159 h of Origin 2000 time.

The zero-point energies are computed as one-half the sum of the harmonic frequencies. The heat capacity, entropy, and temperature dependence of the heat of formation are computed for the temperature range 300−4000 K using a rigid rotor/harmonic oscillator approximation. We include the effect of electronic excitation for the atoms using the data from Moore.[34] The B3LYP/6-31+G* frequencies are used in these calculations, excluding BF_3^+ where the MP2 frequencies are used. These results are fit in two temperature ranges, 300−1000 and 1000−4000 K, using the Chemkin[35] fitting program and following their constrained three-step procedure. We ignore any molecular spin−orbit effects, since we do not treat any linear molecules with degenerate states, and only account for the effect of atomic spin−orbit coupling on the dissociation energy, which we compute as the difference between the lowest J level and the m_j weighted average for all J levels.[34]

III. Results and Discussion

The computed geometries are summarized in Tables 1 and 2 and the harmonic frequencies are summarized in Tables 3 and 4. Also included in the tables are selected experimental and previous theoretical results. BF_3^+ and BCl_3^+ are interesting cases and are discussed in detail below. Excluding these two special cases, our optimized geometries are in good agreement with the experimental values summarized in JANAF but differ from many of the estimated values given in JANAF, shown with square brackets in Tables 1 and 2. Our value for BF^+ is in good agreement with the experimental value deduced by Dyke et al.[36] The agreement between our geometries and previous theory is very good. For BF_3 our DFT value of 1.313 Å is in good agreement with the CCSD(T) results of Pak and Woods,[37] 1.313 and 1.310 Å for the cc-pVTZ and cc-pVQZ basis sets, respectively. Our DFT BCl_n geometries are in good agreement with the CCSD(T) results of Baeck and Bartlett,[9] especially for their larger cc-pVTZ basis set. Our computed results also agree with the MP2/6-31G(d) results of Harris and Schlegel.[8] Our computed harmonic frequencies, excluding BF_3^+ and BCl_3^+, are in good agreement with experiment[36,38−41] and with previous theory (not given in the tables).

TABLE 2: Comparison of the Optimized BCl_n B3LYP/6-311+G(2df) Geometries[a] with Previous Work

	BCl	BCl^+	BCl_2	BCl_2^+	BCl_3	BCl_3^+
Present Work						
state	$^1\Sigma^+$	$^2\Sigma^+$	$^2A_1$	$^1\Sigma_g^+$	$^1A'_1$	$^2A'_2$[b]
r(B−Cl)	1.722	1.600	1.728	1.613	1.747	1.729
∠(ClBCl)			125.9	180.0	120.0	120.0
Baeck and Bartlett[9] (CCSD(T) with their "Basis I")						
r(B−Cl)	1.755	1.626	1.746	1.633	1.755	1.741
∠(ClBCl)			124.6	180.0	120.0	120.0
Baeck and Bartlett[9] (CCSD(T) with cc-pVTZ basis)						
r(B−Cl)	1.720	1.602	1.720	1.610		
∠(ClBCl)			125.1	180.0		
Schlegel and Harris[8]						
r(B−Cl)	1.714		1.720		1.735	
∠(ClBCl)			125.3		120.0	
Summary in JANAF[1]						
r(B−Cl)	1.716	[1.73][c]	[1.73]	[1.74]	1.75	
∠(ClBCl)			[112]	[180.0]	120.0	

[a] The bond lengths are in angstroms, and the bond angles, in degrees. [b] The B3LYP/6-311+G(2df) D_{3h} results are given. At the MP2 and CCSD(T) levels of theory we find the most stable structure to have C_{2v} symmetry with two long and one short B−Cl bond. Baeck and Bartlett also found the C_{2v} structure to be the most stable. [c] The values in square brackets are estimates.

Haller et al.[42] suggested that BF_3^+ does not have D_{3h} symmetry but instead has one long and two short B−F bonds, denoted 1L2S; the species is planar with C_{2v} symmetry. For BCl_3^+, Baeck and Bartlett found three species, the D_{3h}, 1L2S, and a second C_{2v}, species with two long and one short B−F bonds, denoted 2L1S. We therefore started the B3LYP optimizations for BF_3^+ and BCl_3^+ from all three structures, and in all cases, the B3LYP approach converged to the D_{3h} structure. For BF_3^+, the BP86 functional also yields the D_{3h} structure, but the vibrational frequencies are very different from those obtained using the B3LYP functional. For BCl_3^+ the B3LYP and BP86 harmonic frequencies are similar. For both BF_3^+ and BCl_3^+, the DFT vibrational frequencies are not in good agreement with experiment. Thus the DFT approach may not be appropriate for the study of these systems, especially for BF_3^+ where the BP86 and B3LYP harmonic frequencies differ. Given the potential problem with the DFT description, the geometries were optimized and the harmonic frequencies determined at the MP2/6-31+G* level of theory. Unlike the B3LYP, the MP2 approach yields three minima for both BF_3^+ and BCl_3^+. For BF_3^+ the 1L2S structure was the most stable at the MP2 level, while for BCl_3^+ the 2L1S structure was the most stable.

The 1L2S structure of BF_3^+ is best viewed as BF_2^+ with a weakly bound F atom. Since the polarizability of F is underestimated using the 6-31+G* basis, the MP2 calculations were repeated using the aug-cc-pVTZ basis set. The B−F distances contracted slightly from 1.261 to 1.254 Å and from 1.764 to 1.713 Å. Optimization of the 1L2S structure at the CCSD(T) level using the aug-cc-pVTZ basis yields essentially the same

TABLE 3: BF_n Frequencies (Intensities) in cm^{-1} (km/mol)

neutral		cation				
B3LYP	expt[a]	B3LYP	MP2[b] (D_{3h})	MP2 (2L1S)	MP2 (1L2S)	expt
			BF			
1362 (174)	1410.3	1670 (186)				1765 ± 20[c]
			BF_2			
508 (23.7)	523.7	452 (146)				
		452 (146)				
1132 (109)	1151.4	1013 (0.0)				
1388 (398)	1394.0	2056 (458)				
			BF_3			
468 (13.8)	480.7	94 (20.1)	415 (77.3)	398 (41.7)	251 (4.6)	
468 (13.8)	480.7	94 (20.1)	415 (77.3)	455 (13.7)	287 (73.6)	
618 (109)	696.7	553 (114)	555 (110)	523 (123)	432 (210.8)	
875 (0.0)	888	851 (0.0)	836 (77.3)	872 (2.4)	532 (129)	
1438 (470)	1463.3	997 (113)	2218 (7615)	1734 (467)	1047 (105)	
1438 (470)	1463.3	997 (113)	2218 (7615)	3583 (>10^5)	1880 (472)	1661.6[d]

[a] BF and BF_3 are taken from the tabulation in JANAF,[1] while BF_2 is taken from Jacox and Thompson.[40] [b] The MP2 results are computed using the 6-31+G* basis set. [c] Reference 36. [d] Reference 40.

TABLE 4: BCl_n Frequencies (Intensities) in cm^{-1} (km/mol)

neutral		cation				
B3LYP	expt[a]	B3LYP	MP2[b] (D_{3h})	MP2 (2L1S)	MP2 (1L2S)	expt
			BCl			
819 (253)	828.9	1137 (165)				
			BCl_2			
287 (1.3)		291 (18.1)				
		291 (18.1)				
689 (29.1)	731	564 (0.0)				
969 (430)	967	1454 (564)				1436.3[c]
			BCl_3			
260 (0.7)	243.0	163 (9.4)	298 (81)	236 (2.9)	60 (0.1)	
260 (0.7)	243.0	163 (9.4)	298 (81)	255 (13.0)	243 (4.9)	
453 (6.9)	407.6	415 (5.7)	430 (3.9)	398 (6.9)	409 (9.6)	
472 (0.0)	471.0	474 (0.0)	497 (0.0)	488 (0.6)	425 (5.5)	
946 (389)	986.3	823 (11.5)	1587 (12316)	1172 (457)	752 (122)	
946 (389)	986.3	823 (11.5)	1587 (12316)	8323 (>10^5)	1153 (329)	1090[d]

[a] BCl is taken from Huber and Herzberg,[41] BCl_2 from Miller and Andrews,[38] and BCl_3 from the tabulation in JANAF.[1] [b] The MP2 results are computed using the 6-31+G* basis set. [c] Reference 39. [d] Reference 38.

structure as the MP2. The MP2/aug-cc-pVTZ vibrational frequencies are not significantly different from the MP2/6-31+G* results given in Table 3. Overall, the 1L2S result agrees the best with experiment, but the agreement is qualitative. At the CCSD(T)/aug-cc-pVTZ level of theory, the 1L2S structure is 0.55 eV below the D_{3h} structure. The 2L1S structure is only 0.09 eV above 1L2S. Thus, while the ground state of BF_3^+ probably has a 1L2S structure, we cannot completely rule out the 2L1S structure. It is clear, however, that the structure is not D_{3h}, and as discussed below, a distortion away from D_{3h} symmetry is consistent with the ionization spectra of BF_3.

For BCl_3^+, we found 2L1S to be the most stable structure at the MP2 level, as found by Baeck and Bartlett. However, at this level, the agreement between theory and experiment is poor; in fact, the frequency of the highest band and its intensity show the symptoms of symmetry breaking (see Table 4). This is also true of the highest MP2 frequency of the D_{3h} structure. Therefore, the relative separations between the different structures were considered at several levels of theory, which are summarized in Table 5. At the spin-restricted HF level, the 1L2S structure is the most stable, but once correlation is included, 2L1S is the most stable. Improving the basis set to aug-cc-pVQZ increases the CCSD(T) separation between the 2L1S and 1L2S structures, suggesting that the true structure is either 2L1S or D_{3h}. Reducing the size of the basis set from aug-cc-pVTZ to 6-31+G* still places the 2L1S structure below the D_{3h} structure, and this is the basis set that we used to study the correlation treatment in more detail. First we note that changing from spin-restricted to spin-unrestricted does not make a significant difference. The BD(TQ) approach gives results very similar to

TABLE 5: Separations between the BCl_3^+ Structures, in kcal/mol

method	2L1S	D_{3h}	1L2S
At the Baeck and Bartlett Geometries[a]			
RHF/aug-cc-pVTZ	0.0	14.81	−7.30
RCCSD/aug-cc-pVTZ	0.0	7.41	3.67
RCCSD(T)/aug-cc-pVTZ	0.0	4.75	5.44
RHF/aug-cc-pVQZ	0.0	14.80	−6.81
RCCSD(T)/aug-cc-pVQZ	0.0	4.92	27.74
RHF/6-31+G*	0.0	12.18	
RCCSD/6-31+G*	0.0	3.97	
RCCSD(T)/6-31+G*	0.0	1.67	
UHF/6-31+G*	0.0	12.55	
UMP2/6-31+G*	0.0	0.96	
UCCSD/6-31+G*	0.0	3.88	
UCCSD(T)/6-31+G*	0.0	1.70	
UBD-REF/6-31+G*	0.0	12.90	
UBD/6-31+G*	0.0	4.04	
UBD(T)/6-31+G*	0.0	1.72	
UBD(TQ)/6-31+G*	0.0	1.71	
At the UMP2/6-31+G* Geometry			
UMP2/6-31+G*	0.0	1.06	5.47

[a] The geometries are their MBPT(2)/basis I results.

TABLE 6: Summary of the CCSD(T) Ionization Potentials, in eV

	TZ	QZ	5Z	CBS	+other[a]	+SO	expt
			Adiabatic IPs				
B	8.211	8.230	8.240	8.251	8.249	8.250	8.298
BF	11.069	11.077	11.082	11.088	11.070		11.12 ± 0.01[36]
BF_2	8.579	8.576	8.581	8.588	8.604		8.84 ± 0.10[2]
BF_3 (D_{3h})	16.045	16.131	16.161	16.187	16.042		
BF_3 (1L2S)	15.566	15.654		15.70	15.61[b]		15.55 ± 0.04[43]
			Vertical IPs				
BF	11.130	11.156	11.165				11.12 ± 0.01[36]
BF_2	10.285	10.314	10.324				
BF_3	16.044	16.131		16.18			15.99[c]
			Adiabatic IPs				
BCl	9.950	9.975	9.975	9.970	9.942		10.03 ± 0.10[44]
BCl_2	7.285	7.332	7.332	7.321	7.310		
BCl_3 (D_{3h})	11.709	11.813	11.839	11.856	11.770		
BCl_3 (2L1S)	11.511	11.613		11.67	11.62[d]		11.60 ± 0.02[45]
			Vertical IPs				
BCl	10.161						
BCl_2	8.721						
BCl_3	11.725			(11.87)[e]			11.81[f]

[a] Includes zero-point energy, core correlation, and scalar relativistic effects. [b] Computed using the B3LYP frequencies for BF_3 and the MP2 frequencies for BF_3^+. [c] Estimated from the figure of experimental data;[43] the uncertainty is unknown. [d] Includes only core correlation and scalar relativistic effects. [e] Estimated using the difference between the CBS and TZ D_{3h} adiabatic results. [f] Estimated from the figure of experimental data;[45] the uncertainty is unknown.

the CCSD(T) approach. Using the MP2/6-31+G* geometry (or MP2/aug-cc-pVTZ geometry) instead of that from Baeck and Bartlett does not significantly affect the results. The inclusion of core−valence and scalar relativistic effects favor the D_{3h} structure by 0.15 kcal/mol.

For BCl_3^+ it is clearly difficult to definitively determine the structure. The computed separations support a 2L1S structure, while the frequencies appear to support a 1L2S structure. The infrared experiments[38,39] have been interpreted in terms of a D_{3h} symmetric cation. Because of the small energy differences involved, we are unable to contradict this conclusion of a D_{3h} structure.

The ionization potentials have been measured[2,36,43−45] for several of these species, and we compare the computed results with experiment in Table 6. The computed values for B and BF, where there is no question about geometry, are in excellent agreement with experiment. Also note that both theory and experiment agree that the vertical and adiabatic IP of BF are very similar. The value for BF_2 is in reasonable agreement with experiment;[2] clearly the true value must lie at the lower end of the experimental range or even slightly smaller. For BF_3, Dibeler and Liston[43] determined a value of 15.55 eV. Using the B3LYP D_{3h} geometry for the cation yields an adiabatic IP of 16.04 eV, which is clearly too large. However, using the MP2/6-31+G* lL2S geometry yields a value that is in much better agreement with experiment, with the difference between theory and experiment being only 0.06 eV. An inspection of the experimental spectra shows a peak at about 15.99 eV, which is in reasonable agreement with our vertical IP. Thus a comparison of the computed and experimental IPs for BF_3 supports a distorted structure for BF_3^+.

The BCl IP is in good agreement with experiment.[44] We are unaware of an experimental value for BCl_2. For BCl_3, the Dibeler and Walker[45] spectrum shows an onset at 11.60 eV and a maximum at 11.81 eV. Our computed aug-cc-pVTZ results show a vertical value of 11.725 eV. Considering the very small change in geometry between BCl_3 and BCl_3^+ (D_{3h}), we correct the vertical IP by the difference between the TZ and CBS values (0.147 eV) to yield our best estimate of 11.87 eV for the vertical IP, which is in very good agreement with experiment. The inclusion of scalar relativistic and core−valence effects will slightly improve this agreement. The adiabatic value of 11.77 eV for the D_{3h} structure has an error of 0.17 eV with experiment, while the adiabatic value for the 2L1S has an error of only 0.02 eV. Thus the ionization spectra of BCl_3 would appear to support some distortion for BCl_3^+. Perhaps the molecule pseudorotates, so that it appears to have D_{3h} symmetry in the IR experiments. However, the small energy difference and known problems with treating symmetry breaking prevent us from ruling out the D_{3h} structure deduced from IR experiments.[38,39]

The computed atomization energies are summarized in Table 7. The first three columns are the CCSD(T) results, without zero-point energy. The results in the fourth column are obtained using the three-point $n^{-4} + n^{-6}$ extrapolation procedure, excluding BF_3^+(1L2S) and BCl_3^+(2L1S), where the n^{-4} approach is used. The results in the fifth column are corrected for zero-point effects using the B3LYP/6-31+G* frequencies, excluding BF_3^+(1L2S) where the MP2 frequencies are used. The sixth column uses experiment to account for spin−orbit effects. The last column accounts for core−valence correlation and scalar relativistic effects. It is a bit difficult to estimate the errors in these values; however, on the basis of previous work, we suspect that they are accurate to ±1−2 kcal/mol. We also note that our best atomization energy for BF_3, without scalar relativistic effects, is 461.72 kcal/mol, which is in excellent agreement with the best value (462.63 kcal/mol) of Martin and Taylor.

Our best results from Table 7 are compared with previous work in Table 8. We should note that in the column labeled JANAF,[1] we have used the B heat of formation from Gurvich et al.[7] and not the value recommended by JANAF. The heats of formation of BF^+, BF_3^+, and BCl_3^+ are computed using the JANAF heats of formation for the corresponding neutrals and the experimental IPs. The first observation is the excellent mutual agreement between the theoretical results. The comparison with JANAF shows that for about half the systems theory and JANAF agree, but for half they differ significantly. Given the level of theory used in this work, and the agreement between the different theoretical approaches, it is clear that theory is more consistent and reliable than the values given in JANAF. It is also very interesting to note that the G2 approach

TABLE 7: Summary of the Atomization Energies, in kcal/mol

	TZ	QZ	5Z	CBS	+ZPE	+SO	+CV +DK[a]
BF	178.010	180.788	181.402	181.728	179.780	179.365	179.847
BF_2	288.830	293.493	294.499	295.009	290.679	289.878	290.711
BF_3	460.293	466.805	468.139	468.749	461.075	459.889	460.907
BF^+	112.109	115.123	115.859	116.315	113.928	113.543	114.871
BF_2^+	280.344	285.504	286.643	287.246	281.565	280.795	282.600
BF_3^+ (D_{3h})	279.638	284.604	285.486	285.754	280.628	279.473	281.281
BF_3^+ (1L2S)	290.687	295.597		298.431[b]	292.087[c]	290.932	292.558
BCl	118.859	121.305	122.328	123.315	122.143	121.273	121.493
BCl_2	195.439	200.170	202.221	204.235	201.455	199.745	200.408
BCl_3	312.806	319.681	322.600	325.436	320.663	318.114	318.896
BCl^+	78.742	81.053	82.316	83.679	82.053	81.213	82.521
BCl_2^+	216.792	220.861	223.162	225.673	221.955	220.276	222.146
BCl_3^+ (D_{3h})	232.136	237.055	239.606	242.307	238.216	235.697	237.772
BCl_3^+ (2L1S)	236.695	241.662		244.528[d]	240.437[e]	237.919	239.849

[a] Includes the effect of core−valence correlation and scalar relativistic effects computed at the MCPF level, see the text. [b] A comparison of two-point and three-point extrapolation for the D_{3h} structure suggests that the two-point extrapolation could be about 2 kcal/mol too large. [c] The MP2/6-31+G* frequencies are used for the zero-point energy. [d] A comparison of two-point and three-point extrapolation for the D_{3h} structure suggests that the two-point extrapolation could be about 2 kcal/mol too small. [e] The zero-point energy is taken from the D_{3h} structure since we do not have reliable frequencies for the 2L1S structure.

TABLE 8: Comparison of the Present Work with Previous Results for the Atomization Energies, in kcal/mol

	PW	JANAF[a]	MT[4]	RH (G2)[3]	RH (CBS4)[3]	LH[2]
BF	179.85	180.71	180.13	180.8	178.8	
BF_2	290.71	311.87		290.5	289.0	290.9
BF_3	460.91	459.90	462.63	462.5	460.0	
BF^+	114.87	116.64				
BF_2^+	282.60	286.62				
BF_3^+ (1L2S)	291−293	294.49				

	PW	JANAF[a]	SH[8]	H[44]
BCl	121.49	129.31	122.95	121.3 ± 1
BCl_2	200.41	210.32	200.31	
BCl_3	318.90	315.65	320.15	
BCl^+	82.52	60.96		81.4 ± 2.6
BCl_2^+	222.15	223.30		
BCl_3^+ (D_{3h})	237.77	239.50		
BCl_3^+ (2L1S)	240−242			

[a] The JANAF heats of formation of B and B^+ are not used. The Gurvich et al.[7] heat of formation is used for B. The value for B^+ is determined using this value for B and the experimental[34] IP. JANAF does not have heats of formation for BF^+, BF_3^+ and BCl_3^+; these values are determined using the JANAF value for the neutral and the experimental[36,43,45] IPs.

TABLE 9: Summary of the BX_n Heats of Formation[a] at 298 K, in kcal/mol

	X = F		X = Cl	
n	neutral	cation[b]	neutral	cation
3	[−271.42]		[−96.32]	
2	−118.91	76.56	−5.92	187.24
1	−25.91	169.57	44.88	238.04
0	135.95	331.43	138.27	331.43

[a] The values in square brackets are taken from JANAF, as are the heats of formation of F and Cl. [b] The B^+ heat of formation is derived from the average of the B values deduced from the BF_n and BCl_n series.

works very well for the BF_n, and BCl_n, systems; therefore the problem found in other systems is not simply due to the halogen atom. Finally, we note the very good agreement between the present work and the experimental results of Hildenbrand and co-workers.[2,44]

An inspection of the results in Table 8 shows that sequential bond energies vary greatly; B−F = 179.9, FB−F = 110.9, F_2B−F = 170.2, B^+−F = 114.9, FB^+−B = 167.7, and F_2B^+−F is about 10 kcal/mol. This can be explained in terms of the boron hybridization; boron does not have to hybridize to form the first bond but must sp^2 hybridize to form the second bond, which results in a large decrease for the strength of the second bond. The third B−F bond forms with the BF_2 radical orbital, without changing the boron hybridization, and as a result the third bond is about as strong as the first. B^+ must hybridize to form the first bond, and not surprisingly, the B^+−F bond is about the same strength as the FB−F bond where hybridization occurs. For the FB^+−F bond there is no change in the boron hybridization, and this bond is similar in strength to the first and third bonds in the neutral. Since B^+ has only two valence electrons, it is not surprising that the third bond is so small for the cation. Similar arguments apply to the analogous Cl systems.

The heats of formation at 298 K are computed using the sequence BX_3, BX_2, BX, B, B^+, BX^+, and BX_2^+. The BX_3^+ values are not computed, because they are weakly bound and therefore of limited importance in plasma processes, and we do not have accurate vibrational frequencies for these species. The experimental[34] IP of B is also used. This approach is used, since the BF_3, BCl_3, F, and Cl heats of formation are accurately known,[1] while as discussed in the Introduction, there is some uncertainty in the boron heat of formation. The bond energies are taken from Table 7 and corrected to 298 K. Our heats of formation are given in Table 9. We first note that the values computed for B from the BF_n and BCl_n series differ by 2.3 kcal/mol, which is consistent with our estimated error of 1−2 kcal/mol. Since the BF_n calculations are probably more accurate than the BCl_n calculations, we suspect that the true boron heat of formation is closer to 136 kcal/mol than 138 kcal/mol, but this is difficult to quantify, so we average our two values for our best estimate (137.1 kcal/mol) for the boron heat of formation. This is close to the value of 137.4 ± 0.2 kcal/mol deduced by Storms and Mueller.[5] We expect the values for the cations to be about as accurate as the neutrals. Therefore, we believe that our heats of formation are the most consistent set of data for these species. The temperature dependence of the heat of formation, heat capacity, and entropy is computed for the temperature range 300−4000 K and fit to a polynomial. These data are available on the web.[46]

IV. Conclusions

The atomization energies of BF_n, BF_n^+, BCl_n, and BCl_n^+, for $n = 1-3$, are computed using the CCSD(T) results, which have been extrapolated to the complete basis set limit. The ionization potentials are also reported. The structures of BF_3^+ and BCl_3^+ are studied. BF_3^+ is clearly not D_{3h}, while for BCl_3^+ our calculations and a comparison of our calculations and the experimental IPs suggest that BCl_3^+ also distorts away from D_{3h}. However, the energy difference between the C_{2v} and D_{3h} structures is very small. Thus theory cannot definitely rule out a D_{3h} structure that has been suggested by the infrared experiments. The temperature dependence of the heat of formation, the heat capacity, and entropy is computed and fit to the standard 14 coefficients,[35] which are available on the web.[46]

Acknowledgment. A.R. was supported by NASA Contract No. NAS2-14031 to ELORET. These authors would like to acknowledge helpful discussions with Don Hildenbrand.

References and Notes

(1) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

(2) Lau, K. H.; Hildenbrand, D. L. *J. Chem. Phys.* **1980**, *72*, 4928.

(3) Rablen P. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4648.

(4) Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem. A* **1998**, *102*, 2995.

(5) Storms, E.; Mueller B. *J. Phys. Chem.* **1977**, *81*, 318.

(6) Ruscic, B.; Mayhew, C. A.; Berkowitz, J. *J. Chem. Phys.* **1988**, *88*, 5580.

(7) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*; CRC Press: Boca Raton, FL, 1994; Vol. 3.

(8) Schlegel, H. B.; Harris, S. J. *J. Phys. Chem.* **1994**, *98*, 11178.

(9) Baeck, K. K.; Bartlett, R. J. *J. Chem. Phys.* **1997**, *106*, 4604.

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

(11) Ricca, A.; Bauschlicher, C. W. *J. Phys. Chem.* **1998**, *102*, 876.

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

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

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

(15) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(16) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(17) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822; **1986**, *34*, 7406 (erratum).

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

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

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

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

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

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

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

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

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

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

(28) Handy, N. C.; Pople, J. A.; Head-Gordon, M.; Raghavachari, K.; Trucks, G. W. *Chem. Phys. Lett.* **1989**, *164*, 185.

(29) Raghavachari, K.; Pople, J. A.; Replogle, E. S.; Head-Gordon, M. *J. Phys. Chem.* **1990**, *94*, 5579.

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

(31) 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.

(32) 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.

(33) 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.

(34) Moore, C. E. Atomic energy levels. *Natl. Bur. Stand. Circ. (U.S.)* **1949**, No. 467.

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

(36) Dyke, J. M.; Kirby, C.; Morris, A. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 483.

(37) Pak, Y.; Woods, R. C. *J. Chem. Phys.* **1997**, *106*, 6424.

(38) Miller, J. H.; Andrews, L. *J. Am. Chem. Soc.* **1980**, *102*, 4900.

(39) Jacox, M. E.; Irikura, K. K.; Thompson, W. E. *J. Chem. Phys.* **1996**, *104*, 8871.

(40) Jacox, M. E.; Thompson, W. E. *J. Chem. Phys.* **1995**, *102*, 4747.

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

(42) Haller, E.; Koppel, H.; Cederbaum, L. S.; von Niessen, W.; Bieri, G. *J. Chem. Phys.* **1983**, *78*, 1359.

(43) Dibeler, V. H.; Liston S. K. *Inorg. Chem.* **1968**, *7*, 1742.

(44) Hildenbrand, D. L. *J. Chem. Phys.* **1996**, *105*, 10507.

(45) Dibeler, V. H.; Walker J. A. *Inorg. Chem.* **1969**, *8*, 50.

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