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Theoretical Study of Novel Bonding in Molecules: Metastable Molecular Fuels

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Interim Report

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The goal of this program is to theoretically evaluate compounds comprised of first row-atoms that might serve as the basis of new propulsion schemes. This theoretical work is based on the premise that species which show promise as high energy density materials may exhibit novel bonding mechanisms which distinguish them from conventional stable molecules. Two, possibly overlapping, categories of species have been considered: (1) electron deficient compounds, which are certain compounds of B and Be not having sufficient valence electrons to distribute two per chemical bond, and (2) mixed metal clusters of the form $Li_nB_mH_k$. A comprehensive study of the electron deficient compound BH_4 as well as results for the mixed metal clusters Li_3Be and Li_3B is presented. In addition, results for the excited states and correlation diagram of BH_2 obtained in support of the experimental program at Phillips Laboratory are detailed. Preliminary I_{sp} estimates, used in program planning as well as calculations exploring the "superalkali-superhalogen" concept that was judged not to be promising are summarized.

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APPENDIX:

THEORETICAL INVESTIGATION OF THE STRUCTURE AND ENERGY OF THE BH_4 RADICAL

INTRODUCTION

Further improvement in chemical rocket technology is restricted by the fundamental limitation that single-stage devices, independent of engine efficiency, will always have negative payloads. Therefore, novel concepts that might serve as the basis of new propulsion schemes are of great interest. One concept that had been under consideration since the inception of the HEDM program is that of metastable molecular fuels: long-lived, high-energy content molecular species that do not decay by radiation, tunneling, or other means when isolated in vacuum. Consideration of specific impulse virtually requires that candidate species be composed of first-row atoms.

The goal of this theoretical research program is to evaluate compounds that might serve as the basis of new propulsion schemes. The program was originally based on the premise that species that show promise as high energy density materials may exhibit novel bonding mechanisms which distinguish them from conventional stable molecules.

Two possibly overlapping categories of molecules were defined and investigated: (1) electron deficient compounds, which are certain compounds of B and Be not having sufficient valence electrons to distribute two per chemical bond and (2) mixed metal clusters of the form $Li_nB_mH_k$. As the HEDM program, in general, and this research program, in particular, evolved, emphasis has shifted from seeking new metastable compounds to serve as high energy fuels by themselves to improving on conventional liquid hydrogen/liquid oxygen systems by devising a way to incorporate appropriate additives into solid hydrogen.

The boron atom has been identified as a promising additive to sH_2. In studying the effects of additives, one needs knowledge of all possible compounds of boron and hydrogen. Thus, calculations of other compounds of boron and hydrogen have also been performed.

The classes of molecules originally proposed included compounds based on "superalkalis" and "superhalogens", extraordinarily stable cations and anions that should combine to give species unusually resistant to charge transfer. After a short investigation, it was determined that this category was unlikely to lead to compounds of sufficient heat of formation to be viable HEDM candidates.

This report describes the completed study of the electron deficient compound, BH_4, as well as characterization of the clusters Li_3B and Li_3Be. The calculations of the previously unknown excited states of BH_2 undertaken in support of the experimental program at the Phillips Laboratory are presented and a brief report of the exploration of the superalkali concept is provided.

Theoretical I_{sp} calculations tabulating the predicted effects of including these compounds as additives to the liquid hydrogen/liquid oxygen system are also included.

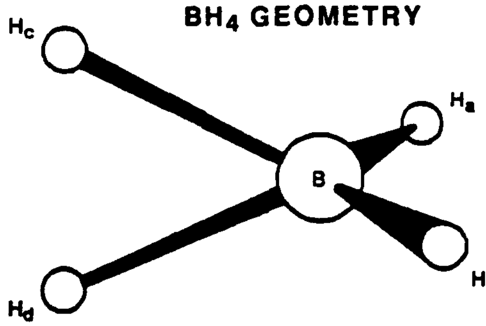
STRUCTURE AND ENERGY OF THE BH_4 RADICAL

Full details of our calculations[1] of BH_4 are given in a paper that will appear in the Journal of Physical Chemistry late in 1993 and is attached as the Appendix. A brief summary of principal results is provided here.

In this work, geometries of BH_4, the dissociation products $BH_2 + H_2$ and $BH_3 + H$, and the possible transition state for the addition reaction of BH_2 and H_2 were optimized at the MCSCF level with a B(4s3p2d)H(4s2p) basis set. As illustrated in Table 1, the minimum geometry for BH_4 is predicted to have C_{2v} symmetry with one pair of short B-H bonds and one pair of longer B-H bonds. The structure may be described qualitatively as a BH_2 molecule to which a stretched H_2 has been added in the perpendicular plane. Analysis of the wavefunction indicates that of the seven valence electrons, four are contained in the B-H_a and B-H_b bonds while there are only three electrons contained in the longer B-H_c, B-H_d bonds. Comparison with calculations[2] of the C_{2v} symmetry bidentate form of the ionic compound $LiBH_4$ is also given in Table 1. In this form, the metal ion lies in the H_c-B-H_d plane. The principal observation is that the longer bonds in $LiBH_4$ are shorter than in BH_4 due to the additional electron in the H_cBH_d moiety as compared with the radical.

Table 1.

BH_4 GEOMETRY



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	BH_4[a]	$LiBH_4$[b]
B-H_a	1.201Å	1.200Å
B-H_c	1.315Å	1.253Å
$<H_a$-B-H_b	131.7°	115.2°
$<H_c$-B-H_d	44.4°	109.1°
H_c-H_d	0.994Å	2.041Å

[a] MCSCF/TZP (this work) [b] Ramondo, et al., Ref. 2.

Harmonic frequencies for BH_4 and $LiBH_4$ are listed in Table 2, which includes a qualitative description of the modes. Normal modes of BH_4 corresponding to the BH_2 symmetric and asymmetric stretches (a_1 and b_2 symmetries respectively) can be easily identified. Considering the other hydrogens, H_c and H_d, together with the central atom as a BH_2 unit, the corresponding modes may also be noted with reduced frequencies, as expected from the longer bond lengths.

Table 2.

CALCULATED HARMONIC FREQUENCIES (cm^{-1})

	BD_4[a]	BH_4[a]		$LiBH_4$[b]
a_1	1832	2534	BH_2 sym stretch	2570
	1520	2086	BH_2 (long) sym stretch	2133
	1003	1413	scissors (in phase)	1500
	751	996	scissors (out of phase)	1261
b_1	1396	1962	BH_2 (long) asym stretch	2059
	497	634	rock	1170
b_2	1999	2656	BH_2 asym stretch	2612
	783	1053	twist	1342
a_2	628	888	twist	1244

BH_2: 2456 sym stretch
2636 asym stretch
1022 bend

[a] MCSCF/TZP (this work).
[b] Ramondo, et al., Ref. 2.

Relative energies for the BH_4 system determined from multireference single- and double-excitation CI calculations using MCSCF molecular orbitals are reported in Table 3. The electronic energy of the BH_4 minimum is predicted to lie 19.23 kcal/mol below BH_3 + H and 20.10 kcal/mol below $BH_2 + H_2$. Including our calculated zero point energies, the BH_4 species is bound by 14.83 and 14.55 kcal/mol, respectively, with respect to BH_3 + H and $BH_2 + H_2$. Values for the heat of formation of BH_4 and dissociation limits at 0 K and 298 K are also listed in Table 3. We have chosen to base these numbers at 0 K on a value of 22 kcal/mol for $\Delta H_f^o(BH_3)$, taken from experimental[3] and theoretical[4] work, and the standard value of 51.6 kcal/mol for H. Corrections to 298 K were made following the procedure given by Curtiss and Pople.[4] Note that while the value in the JANAF compilation[5] for $\Delta H_f^o(BH_3)$ of 26.4 kcal/mol is reasonably similar to the 22 kcal/mol value adopted here, the JANAF tables give an incorrect value for $\Delta H_f^o(BH_2)$ of 48.3 kcal/mol as compared with 73.3 kcal/mol calculated in this work.

Table 3.

BH_4 SYSTEM HEATS OF FORMATION (kcal/mol)

	Relative Energy/ZP	ΔH_f^o	ΔH_f^{298}
BH_4	-14.83	58.5	56.6
$BH_3 + H$	0.0	73.6	73.2
$BH_3 + H_2$	-0.28	73.3	73.4
BH_2			
JANAF entry[a]		48.3	

[a] JANAF thermochemical Tables, Third Edition, J. Phys. Chem. Ref. Data **14**, 51 (1985).

EXCITED STATES OF BH_2

As stated in the introduction, the boron atom has been identified as a promising additive to sH_2. The combustion energy of B is second only to that of Be, among the first row atoms[6] and model calculations by Carrick[7] have predicted addition of 5 mole percent of boron atoms to sH_2 would result in an increase in theoretical I_{sp} of 80 seconds or 21% over LH_2/LO_2.

Accurate predictions of the I_{sp} resulting from boron atoms or small molecules containing boron as additives to solid hydrogen requires accurate heats of formation. As part of the gas phase spectroscopic experimental program at the Phillips Laboratory, Carrick and Brazier have been investigating the spectrum of the B_2 molecule produced by corona discharge of diborane in helium.[6,8] It was originally hypothesized that unidentified lines in that investigation around 7000 Å could be due to BH_2, although it was later shown[8] that they can be attributed to B_2. While the two lowest states of BH_2, the X $^2A_1$ and A $^2B_1$, have been characterized experimentally[9] and theoretically[10] we were unable to find any previous knowledge of the higher-lying excited states of BH_2. Therefore, we have theoretically predicted the excited state spectrum of the BH_2 molecule.

The results of our investigation are presented graphically in the correlation diagram in Figure 1. Relative energies with respect to the BH_2 $^2A_1$ ground state equilibrium geometry are given in Table 4. In constructing this diagram, the heat of formation determined in our study of BH_4 was used along with tabulated atomic levels and BH molecular excitation energies calculated in this work. The adiabatic correlations have been drawn in planar, Cs symmetry. The energetics give the BH_2 ground state bound by 83.6 kcal/mol (3.62 eV) with respect to BH + H including zero point energy and by 57.7 kcal/mol (2.57 eV) with respect to BH + H.

Table 4.

RELATIVE ENERGIES[a] (eV) OF BH_2 EXCITED STATES

State	Bent (R =1.206 Å, θ =127°)	State	Linear (R =1.206 Å)
$^2A_1$	0.0	$^2A_1$	0.386
$^2B_1$	1.262	$^2B_1$	0.387
$^2A_1$, 3s	5.724	$^2A_1$, 3s	4.671
$^2B_2$	6.263	$^2A_1$	4.996
$^2B_2$, 3p	6.612	$^2B_2$, 3p	5.604
$^2A_1$, 3p	6.734	$^2A_1$, 3p	5.902
$^2B_1$, 3p	6.836	$^2B_1$, 3p	5.908
$^2B_2$	7.359	$^2B_2$	6.645
$^2A_1$	7.559	$^2B_2$	7.878

a) With respect to X^2A_1, equilibrium geometry; Energies calculated at second order CI level.

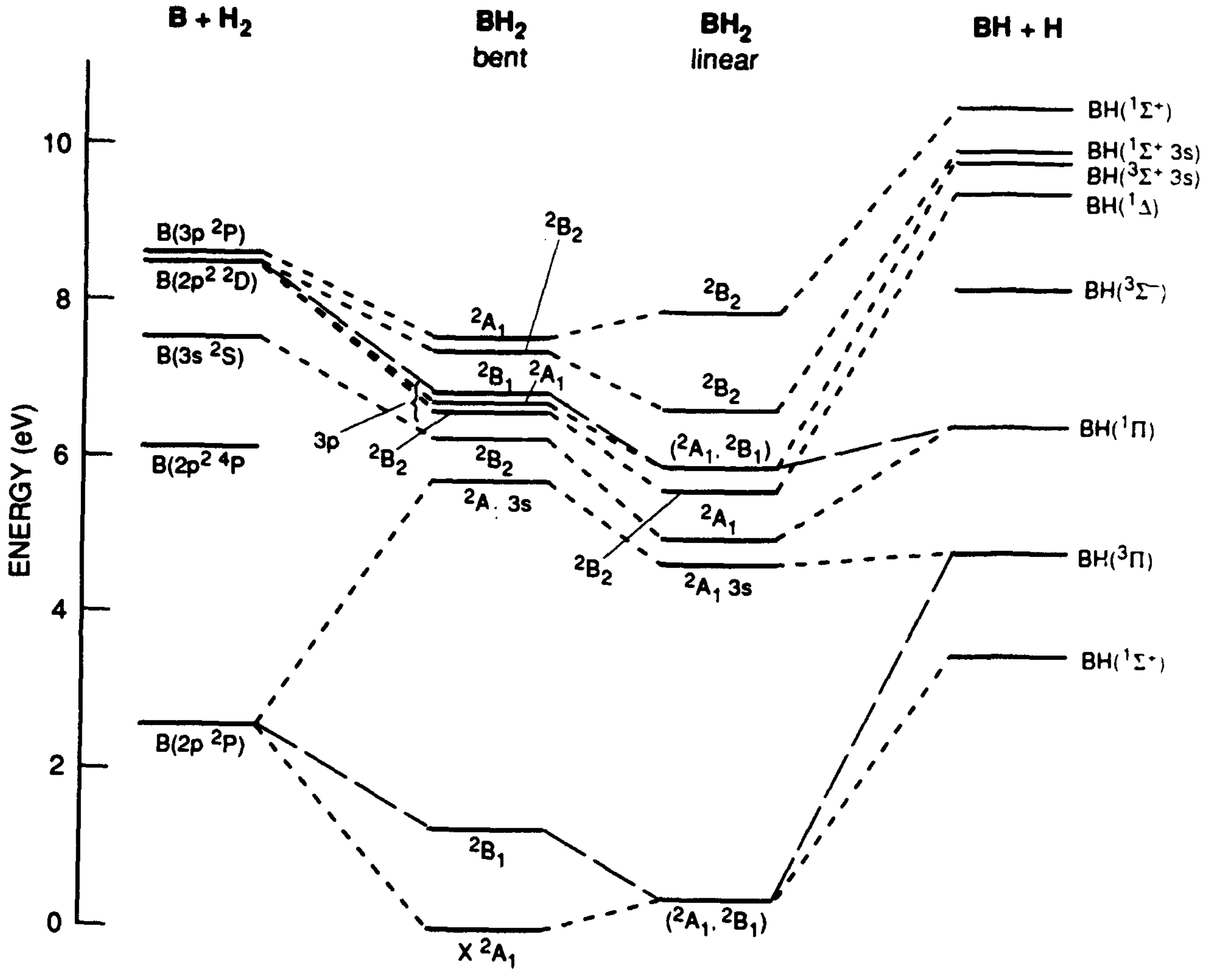

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Figure 1. Correlation diagram for BH$_2$. States are connected adiabatically in C$_s$ symmetry. Bent geometry: Calculated equilibrium geometry of the X^{2}A$_1$ state (R=1.206Å, θ = 127°); Linear geometry: R=1.206Å; BH asymptote: R=1.206Å. Energies from second order CI calculations.

The energies displayed here were determined by Second Order CI (SOCI) calculations using state-averaged MCSCF orbitals with the basis set from our study of BH_4 extended by two 3s and two 3p diffuse functions on boron and one diffuse s and p on hydrogen. In each molecular symmetry, the active space in the MCSCF calculation was extended by the appropriate number to accommodate the B 3s and 3p Rydberg orbitals of that symmetry. The energies labeled BH_2 bent in Figure 1 have been plotted at the BH_2 ground state geometry (BH bond length = 1.206 Å and bond angle = 127°). At this geometry, the 3s Rydberg state lies 5.72 eV above the ground state and the three components of the 3p state lie between 6.61 and 6.84 eV. However, the underlying BH_2^+ ion has a linear geometry. One would therefore expect the Rydberg states to have a strong dependence on bond angle. This effect is illustrated in Figure 2 where the excited states are shown adiabatically in C_{2v} symmetry as a function of bond angle. The excitation energies at the linear geometry ($R(BH) = 1.206$ Å, $\theta = 180°$) are also shown in Figure 1. All of the Rydberg states are predicted to have a linear equilibrium geometry as are the valence excited states with the exception of the third $^2B_2$, the highest state plotted.

We have also studied the dissociation path (lengthening one BH bond) from the linear geometry to BH + H. The computational procedure included state-averaged CASSCF calculations in C_s symmetry (7 states for a' symmetry and 2 states for a" symmetry) followed by first order CI calculations. The adiabatic potential curves along this path are given qualitatively in Figure 3. There is an avoided crossing between the first two $^2A'$ states. Thus, it is quite possible that the 3s Rydberg state could be predissociated to BH + H. The accuracy with which the BH excited state energies have been calculated at the second order CI level is demonstrated in Table 5.

Table 5.

BH ASYMPTOTES

BH State	Calculated Excitation Energy (eV) (R=1.206Å)	T_e (eV) Experiment/ Literature	
$X^1\Sigma^+$	0		
$a\,^3\Pi$	1.30	[1.21]	Theory, CISD[a]
$A\,^1\Pi$	2.95	2.868	Luh and Stwalley[b]
$b^3\Sigma^-$	4.70	[4.66]	Huber and Herzberg b → a
$C'\ 1\Delta$	5.90	5.70	Huber and Herzberg
$C\,^3\Sigma^+$ 3s	6.31	[6.41]	Huber and Herzberg quote Pearson, Bender, Schaefer
$B\,^1\Sigma^+$ 3s	6.42	6.489	Luh and Stwalley[b]
$c\,^1\Sigma^+$	7.00	6.86	Huber and Herzberg

[a] Scuseria, Geertsen, and Oddershede, J. Chem. Phys. **90**, 2338 (1989).

[b] Luh and Stwalley, J. Mol. Spectrosc. **102**, 212 (1983).

[c] Pearson, Bender, Schaefer, J. Chem. Phys. **55**, 5235 (1971).

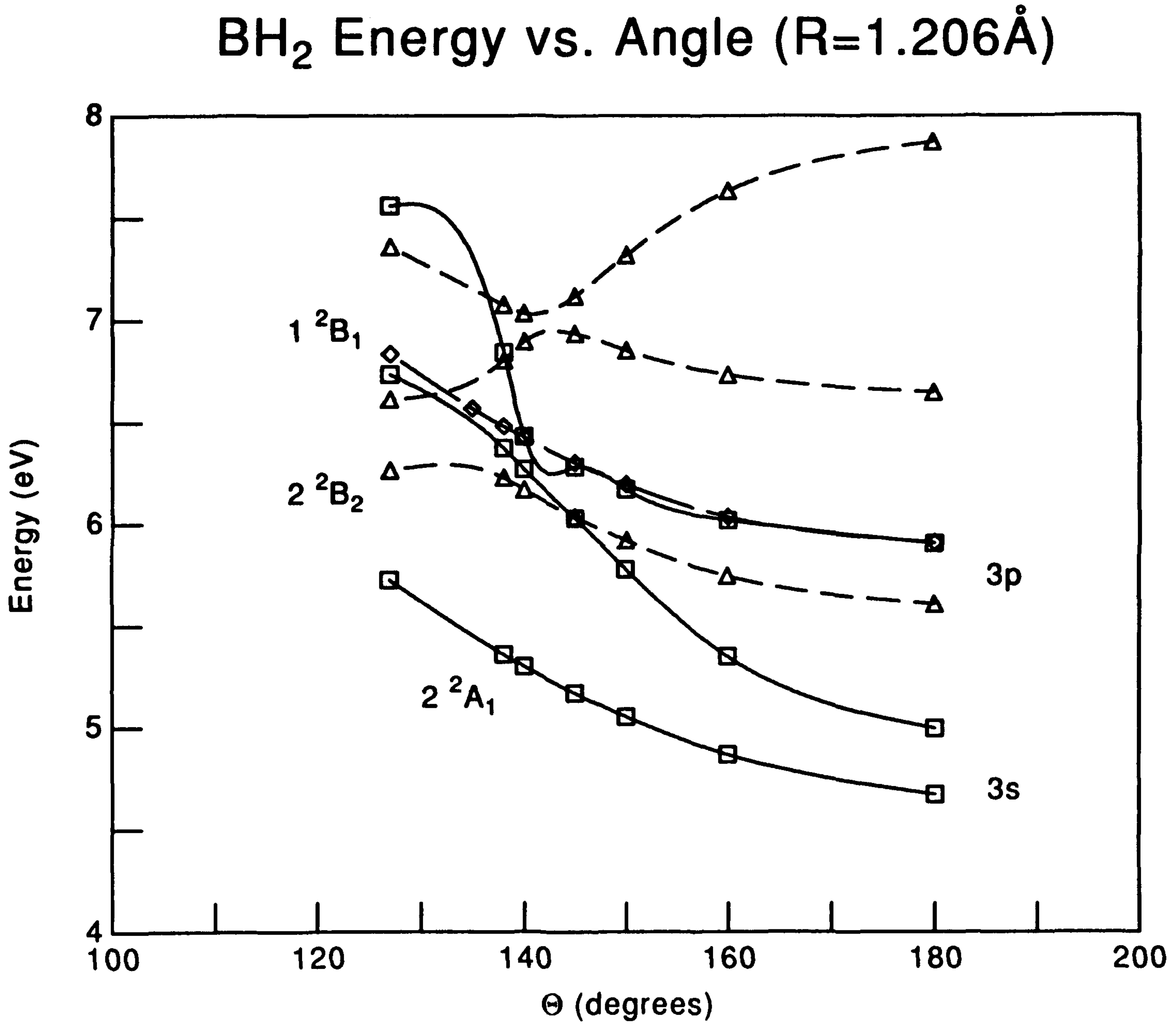

Figure 2. BH$_2$ excited states as function of bond angle for R(BH)=1.206Å. States are connected adiabatically in C_{2v} symmetry. Energies from second order CI calculations.

BH_2 DISSOCIATION

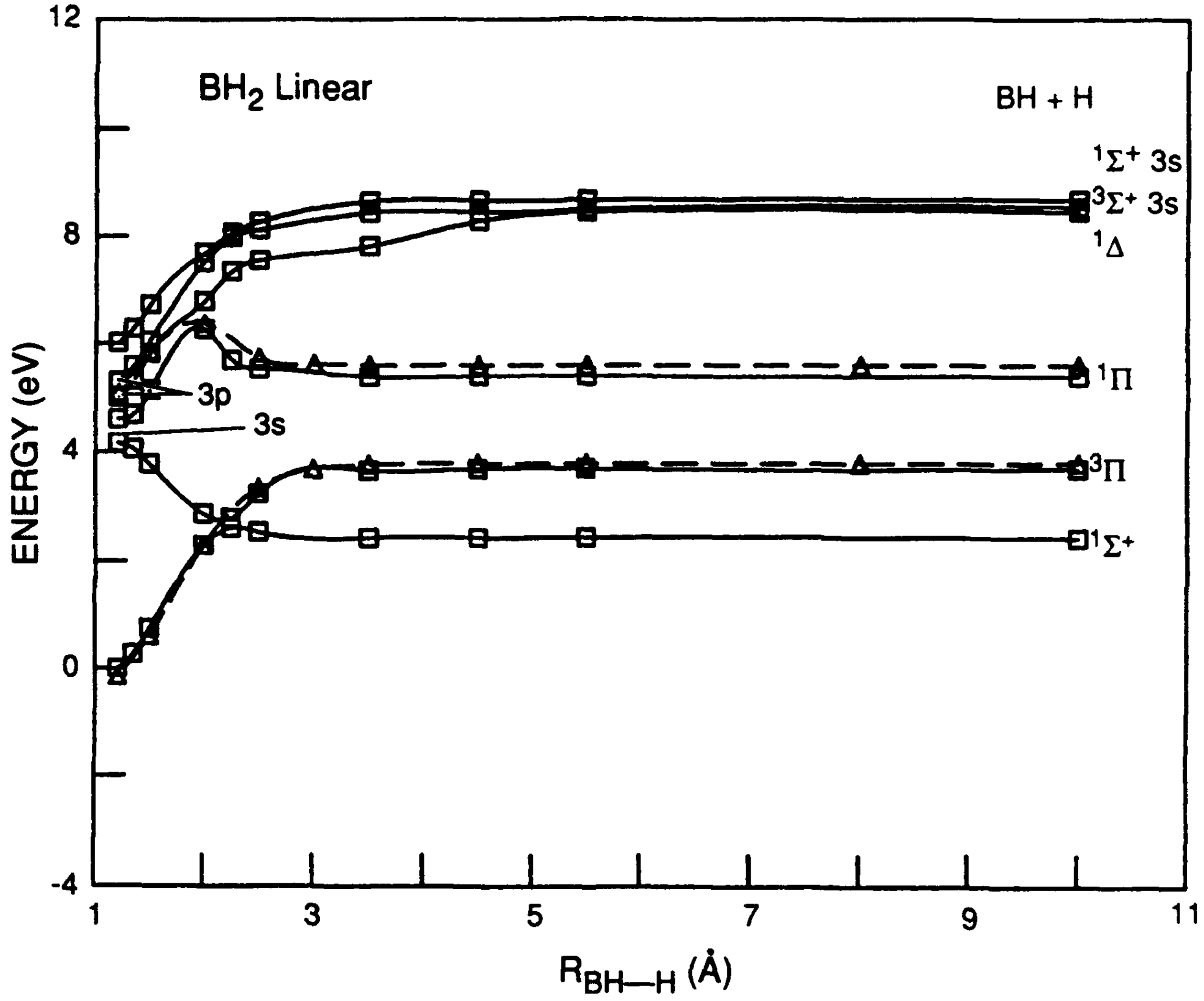

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Figure 3. Dissociation of linear BH_2 to BH + H. Potential curves are drawn adiabatically in C_s symmetry as a function of the BH - H internuclear distance. Energies from first order CI calculations. $^2A_1$ states are shown by solid lines and $^2A''$ states are given by dashed lines.

The possible transitions of the BH_2system that could be observed experimentally in emission have been estimated from calculations of the transition moment at the linear geometry. The crude estimate of the band oscillator strength, $f=2/3\Delta E<r>^2$ was used along with the standard relationship between oscillator strength and Einstein A coefficient. For the calculations of the transition moment, the wavefunctions were recomputed in a common orbital set. The allowed vertical transitions with significant strength are displayed in Figure 4 where the wavelength in nm and Einstein A value in sec^{-1} are shown. Although the 3s Rydberg state is likely to be predissociated, the rich excited state structure of BH_2 should lead to emissions that may be observed experimentally.

The calculations of BH_2 were performed in collaboration with Dr. Dahbia Talbi who spent four months as an international fellow at SRI International during the contract period.

BH_2 VERTICAL TRANSITIONS

(R = 1.206 Å, θ = 180°)

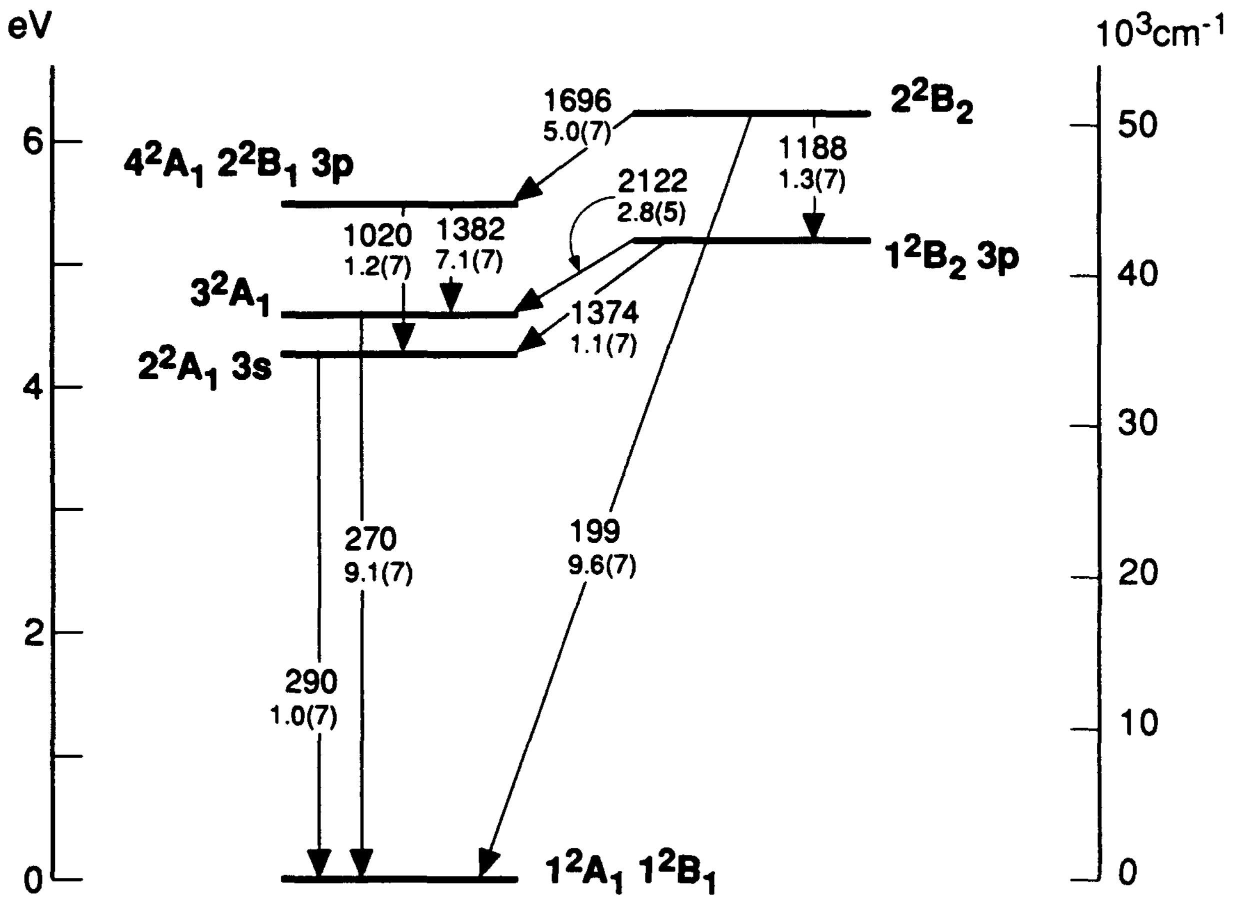

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Figure 4. Vertical transitions in emission for linear BH_2(R=1.206Å, θ=180°). Transitions labeled by wavelength in nm (top line) and A value in sec^{-1} (lower line), estimated as described in the text.

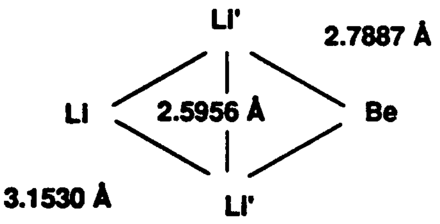
MIXED METAL CLUSTERS: Li_3BE AND Li_3B

As tabulated in the following section, clusters of Li with beryllium and boron are theoretically predicted to improve performance when used as additives to liquid hydrogen. Calculations were performed to determine the structure and energy of the Li_3Be system. The computational design was analogous to that described above for calculations of BH_4 and BH_2. The complete active space for geometry optimization included 5 electrons distributed in 4 orbitals. For the CI calculation of energies, the active space was enlarged to include the most important part of the 2p space, as determine by testing of the full 2p space.

Optimized geometries are reported in Table 6. The equilibrium geometry of Li_3Be is a planar symmetric species in agreement with the previous report of Pewestorf et al.[11]

Table 6.
Li_3Be GEOMETRIES[a]

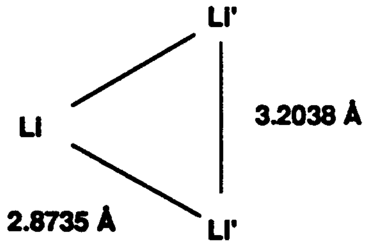
Li_3Be Minimum



Li_3Be

	Present Work MC/DZ	Pewestorf et al.[11] HF/3-21G
Li Be	2.7787	2.61
Li Li'	3.1530	3.13
Li' Li'	2.5956	3.02

Li_3 + Be



Li_3 ($^2B_2$)

	Present Work MC/DZ	Talbi and Saxon[13] MC/(5s2p1d)
Li Li'	2.8735	2.820
Li' Li'	3.2038	3.271

Li_2 + Be

$Li_2\left({}^1\Sigma_g^+\right)$ $R_e = 2.9820$

$LiBe\left({}^2\Sigma^+\right)$ $R_e = 2.5640$

Experiment (Verma, Koch, Stwalley)[14]

[a] Distances in Å

Energies for the Li_3Be system are listed in Table 7. The heat of formation, ΔH_f^o = 138 kcal/mol reported here is referenced to the heat of formation of gaseous atomic Be from the JANAF tables[5] and the experimentally derived Li_3 heat of formation given by Wu.[12]

Table 7.

RELATIVE ENERGIES WITH RESPECT TO Li_3 + Be AND HEATS OF FORMATION (kcal/mol)[a]

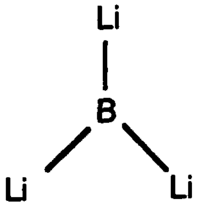
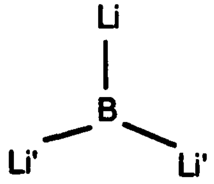
	Li_3Be	Li_3 + Be	Li_2 + LiBe
Relative electronic energy	-12.4	0.0	8.5
Zero point energy	1.9	1.0	0.9
ΔH_f^0	137.9	149.5[b]	157.9

a) Assuming ΔH_f^0(Be) = 76.5 kcal/mol from JANAF tables, Ref.5.
ΔH_f^0(Li) = 73.0 kcal/mol from Wu, Ref.12.

Geometry optimization of Li_3B at the MCSCF level with a double zeta basis set gives a diamond-shaped C_{2v} symmetry isomer analogous to the global minimum in the Li_3H system and a planar D_{3h} symmetry isomer, analogous to the BH_3 geometry. However, the lowest energy isomer is a T-shaped, planar, C_{2v} symmetry species that lies 1.4 kcal/mol below the symmetric D_{3h} structure at the MCSCF level. These isomers have also been investigated with the MP2 method. Geometrical parameters are listed in Table 8.

Table 8.

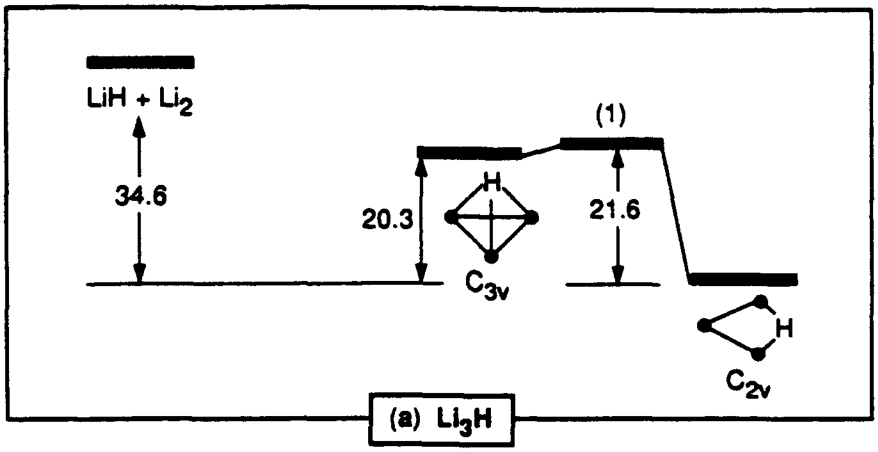
Li_3B BOND LENGTHS (Å)

		MC/DZ	SCF/DZ	MP2/DZ
D_{3h} Symmetry 	B-Li	2.204	2.195	2.233
	# imaginary frequencies	(0)	(0)	(2)
		MC/DZ		MP2/DZ
C_{2v} Symmetry 	B-Li	2.419		2.321
	B-Li'	2.282		2.224
	∠Li'-B-li	97.9		92.4
	# imaginary frequencies	(0)		(0)

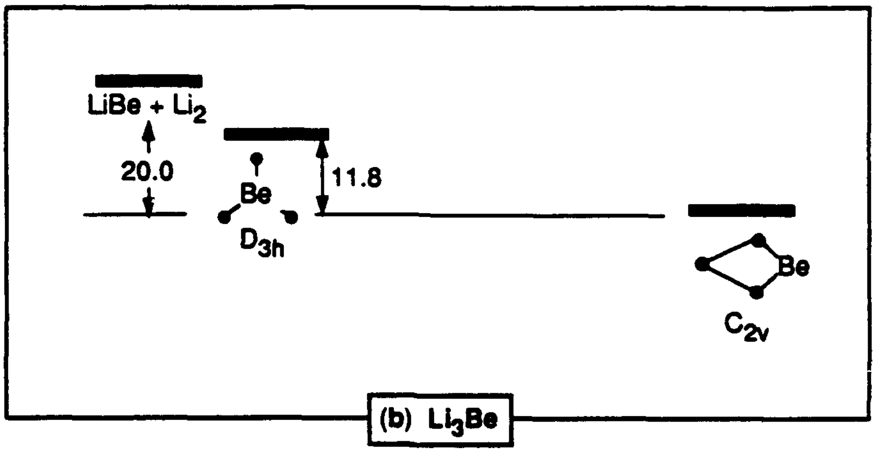
The MP2 method does not predict stability for the high energy diamond-shaped isomer. Examination of the MCSCF wavefunction indicates sufficient differences from the single configuration description of the MP2 approach to lead to different conclusions. In addition, we determined three extrema with one imaginary frequency that lie between the planar diamond and the other isomers in energy at the MCSCF level.

Combining these results with our previous work on Li_3H[13] provides an interesting comparison. Relative energies of the corresponding structures in Li_3H, Li_3Be, and Li_3B are displayed graphically in Figure 5. CI energies are given for Li_3H[9] and Li_3Be[8] while MCSCF results are used for Li_3B. Significant contrasts can be observed. In Li_3B, the planar diamond is not the global minimum and it is the only system for which a T-shaped isomer has been found.

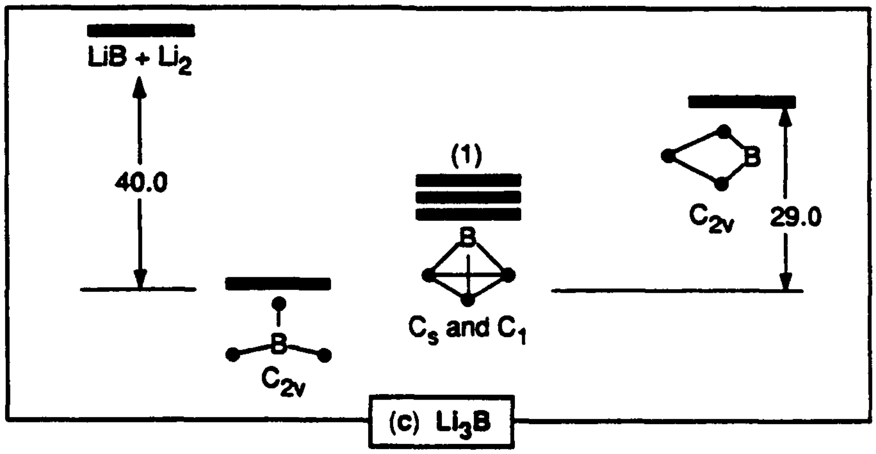
Earlier in the HEDM program, interest was focused on high energy, metastable isomers, but when use of atoms as additives is being considered, it is necessary to predict the lowest energy compounds that could be formed if these atoms recombined. It is clear from these results that various stable clusters of Li are to be expected and must be characterized in detail.



(a) Li$_3$H



(b) Li$_3$Be



(c) Li$_3$B

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Figure 5. Relative energies in kcal/mol for Li$_3$H, Li$_3$Be, and Li$_3$B systems. Energies were determined at the CI level for Li$_3$H and Li$_3$Be and at the MCSCF level for Li$_3$B, as described in the text.

ESTIMATED THEORETICAL I_{SP} CALCULATIONS

As an integral part of program planning, theoretical I_{sp} values were calculated using the AFAL Theoretical I_{sp} Program (micro version) for various compounds of boron, lithium, hydrogen, and beryllium, considered as additives to liquid oxygen and liquid hydrogen. Results of those calculations, carried out early in the contract period and modified using information obtained later, are summarized in Table 9. To the best of our knowledge, none of the compounds listed in Table 9 have been characterized experimentally. Heats of formation were taken from calculations or approximated by analogy to other compounds. The value for B_2H provided by the calculations of Adams and Page[15] should be quite reliable. Those for BH_4 and Li_3Be are taken from present work. The heats of formation of Li_3B and LiB_6 should be viewed as guesses. The Li_2B_2 system has been studied by Lammertsma.[16] All of the compounds listed in Table 9 were theoretically predicted to potentially offer an advantage over the LH_2/LO_2 system.

Table 9.

ESTIMATED THEORETICAL I_{sp}[a]

Additive	ΔH_f (kcal/mol)	Mole Fraction: Additive	O_2 (liq)	H_2 (liq)	I_{sp} (sec)
none			1	4	421
B_2H	175	1	1	10	522
		4	1	15	531
		3	1	16	534
		2	1	16	534
BH_4	53	2	1	9	488
		2	1	8	490
		2	1	7	490
Li_3B	145	1	1	16	496
LiB_6	500	1	1	16	517
		1	1	18	520
	400	1	1	16	487
		1	1	17	490
		1	1	18	492
Li_2B_2	162	1	1	18	489
		1	1	16	489
Li_3Be	138	1	1	13	513
		1	1	14	512

[a] Calculated with AFAL Theoretical I_{sp} Program (Micro Version). Density of additives taken as 1.5 grams/cc. Chamber pressure 1000 psia. Exhaust pressure 14.696 psia.

"SUPERALKALI - SUPERHALOGEN" COMPOUNDS

On the basis of simple molecular symmetry and molecular orbital arguments, Gutsev and Boldyrev[17] have suggested combinations of alkalis and halogens or chalcogens, e.g. Li_2F, Li_3O which they termed "superalkalis" because they are expected to have anomalously low ionization potentials (IP's), lower than that of the isolated alkali. Similarly, they have identified[18] "superhalogens", e.g. BeF_3, BF_4, with anomalously large electron affinities (EA's), larger than that of the isolated halogen. Combinations of these exceptionally stable cations and anions might be expected to lead to stable ionic species. Charge-separated species have been of interest as HEDM candidates but the stability of the ion-pair species investigated previously was found to be limited by back-charge transfer. Thus it was thought these unusually stable ions could lead to interesting possibilities depending on the heat of formation of the resulting compounds.

The first step was to ascertain whether the qualitative arguments[17,18] based on approximate calculations are found to hold with more rigorous theoretical methods. Calculations on the molecules BO_2 and BF_2 at the SCF level substantiated the arguments based on orbital energies.

A more quantitative study was undertaken on the BF_4 system, which was selected as the first superhalogen candidate. MCSCF calculations indicated BF_4^- lies more than 100 kcal/mol below BF_3 + F. The gas phase BF_3 species has a known[5] heat of formation of -270.6 kcal/mol, and that of the F atom[5] is given as 18.4 kcal/mol. These values indicate that, consistent with the "superhalogen" argument, BF_4^- is an extraordinarily stable anion. However, it is unlikely any cation could be found with a heat of formation high enough to make the combined charge-separated system sufficiently energetic. In addition, the recent model study of Fajardo[19] points out possible limitations on the densities that could theoretically be achieved for charge separated species. It was, therefore, determined to redirect the program toward the studies of BH_4, BH_2, and the mixed metal clusters described above.

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Appendix

THEORETICAL INVESTIGATION OF THE STRUCTURE AND ENERGY OF THE BH_4 RADICAL

THEORETICAL INVESTIGATION OF THE STRUCTURE AND ENERGY OF THE BH_4 RADICAL

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ABSTRACT

Calculations of the BH_4 radical, the dissociation products BH_3 + H and $BH_2 + H_2$, and the addition reaction of BH_2 and H_2 to form BH_4 are reported. Structures have been optimized at the MCSCF level with a polarized basis set. The C_{2v} symmetry equilibrium geometry may be approximately described as a BH_2 radical with a stretched H_2 in the bisecting, perpendicular plane. Energies have been obtained by large-scale multireference single- and double-excitation CI calculations. Including zero-point energy, BH_4 is predicted to be bound by 14.55 kcal/mol with respect to $BH_2 + H_2$. Heats of formation at 0 K and 298 K are also reported. Calculations at the CI level suggest the addition reaction proceeds without an energetic barrier.

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INTRODUCTION

Electron-deficient compounds can exhibit a variety of forms due to the rich possibilities provided by large numbers of empty molecular orbitals and thus have been of fundamental interest in investigations of chemical bonding mechanisms. All the hydrides of boron, for example, from BH to BH_5 have been identified directly or indirectly.[1-9] Boron compounds are of interest, as well, because their high energy content makes them attractive as components of energetic materials,[10] yet the actual value of the heat of formation of some simple boron hydrides is still a matter of lively debate.[1-2,5,7] It is widely recognized that the standard reference[11] for heats of formation contains significant inaccuracies for some of these species.

In an attempt to understand the energetics, a number of calculations of the smaller hydrides, BH, BH_2, and BH_3 have been reported.[1-5] At the other end, the possible existence of the fully saturated compound, BH_5, proposed as an intermediate in the hydrolysis of BH_4^- has attracted attention for a number of years.[8-9] Theoretical studies culminating in the careful work of Stanton, Lipscomb, and Bartlett[9] have established that BH_5 is an intermolecular complex between BH_3 and molecular hydrogen and that the very modest binding is due entirely to electron correlation effects.

The open-shell species BH_4 has not been examined with the same intensity although an ESR spectrum[12-13] and theoretical geometry predictions[13-14] have been reported. Electron correlation effects noted in previous studies on boron hydrides[2,9] may be expected to be, perhaps, even more important for this radical species. In this paper, we use multiconfiguration methods to determine the structure and stability of the BH_4 radical. Geometries have been optimized at the MCSCF level and the energy with respect to dissociation to the possible dissociation products, $BH_2 + H_2$ and $BH_3 + H$, has been determined by MCSCF/CI calculations. The reaction path for addition of H_2 to BH_2 to form BH_4 has been investigated as well.

CALCULATIONS

Geometries of BH_4, the dissociation products $BH_2 + H_2$ and $BH_3 + H$, and the possible transition state for the addition reaction of BH_2 and H_2 were optimized at the MCSCF level using analytic second derivatives at each step to facilitate the optimization. Calculations for the asymptotes were carried out on the supermolecule. In the MCSCF calculations, seven electrons were distributed without restriction in the complete active space of eight orbitals arising from B 2s and 2p and four H 1s orbitals. Geometry optimizations were performed first with a double zeta Gaussian basis set[15] B(3s2p)H(2s) and refined with the B(4s3p2d)H(4s2p) basis[16] used for the final calculations of energies. In the latter basis, the scaled triple zeta s basis of Dunning[17] for hydrogen was augmented with a diffuse s function with exponent 0.09. With the H(4s2p) basis, the SCF energy for the hydrogen atom is 0.499880 h as compared with 0.492654 h for the same basis without the diffuse function.

Energies were determined by multireference single- and double-excitation CI calculations using MCSCF molecular orbitals. The same eight orbital active space as for the MCSCF calculations was used; the lowest occupied orbital corresponding to B 1s was frozen; and the remaining orbitals comprised the external space. The configuration list included all single and double excitations from the active space with at most one electron in the external space and all double excitations from the active space to the external space which differed by no more than two electrons from a set of reference configurations. From 4 to 7 reference configurations were used in these calculations resulting in 160,000 to 200,000 configurations in C_{2v} symmetry. The weight of the reference configurations in the CI wavefunctions was approximately 0.94 for all calculations. The ALCHEMY II program system[18] was used throughout the study.

RESULTS AND DISCUSSION

GEOMETRIES AND FREQUENCIES

Geometrical parameters for BH_4 and the dissociation products BH_3, BH_2, and H_2 optimized at the MCSCF level are given in Table 1. The identification of the atoms is illustrated in Figure 1. The global minimum on the potential surface for BH_4 is predicted to have C_{2v} symmetry with one pair of short B-H bonds and one pair of longer B-H bonds. The structure may be described qualitatively as a BH_2 molecule to which a stretched H_2 has been added in the perpendicular plane. The bond length of the short B-H bond, 1.201 Å is very close to that of the isolated BH_2, 1.206 Å, and the H_a-B-H_b bond angle is also similar, 131.7° as compared with 127.0° for BH_2. The H_c-H_d separation of 0.994 Å may be compared with the 0.755 Å bond distance in H_2 at the same level of calculation.

Harmonic frequencies for BH_4 and dissociation fragments are listed in Table 2, which includes a qualitative description of the modes. Normal modes of BH_4 corresponding to the BH_2 symmetric and asymmetric stretches (a_1 and b_2 symmetries respectively) can be easily identified. Considering the other hydrogens, H_c and H_d, together with the central atom as a BH_2 unit, the corresponding modes may also be noted with reduced frequencies, as expected from the longer bond lengths. (The asymmetric stretch in this case has b_1 symmetry because the group lies in a perpendicular plane.) All other modes link the two parts of the molecule. Harmonic vibrational frequencies for BD_4 are also reported in Table 2. The ratio of BD_4 to BH_4 frequencies varies from 0.71 to 0.78, which is not unexpected. The square root of the ratio of the BD to BH reduced mass is 0.74.

Geometries and frequencies from the preliminary determinations with the double zeta basis set and results of previous calculations are also reported in Tables 1 and 2. In these MCSCF calculations, use of the larger, polarized basis set had only a modest effect on the predicted structures and frequencies. The greatest differences were noted for the B-H_c-H_d subunit. The B-H_c bond length was reduced by 0.013 Å and the H_c-B-H_d bond angle was reduced by 7.1° with the final basis set leading to a reduction in the H_c-H_d separation of 0.159 Å. Reasonable agreement with the geometries reported previously[13-14] for BH_4 and for the smaller hydrides is also noted in Table 1. Previous workers did not list harmonic frequencies for BH_4. The MCSCF frequencies for BH_3 and BH_2 tend to be as much as 10% smaller than the scaled HF frequencies[1,5] which is consistent with the slightly longer MCSCF bond lengths resulting from the modest level of electron correlation included in the MCSCF computational model.

The MCSCF wavefunction for BH_4 is strongly dominated by the single SCF configuration (CI coefficient 0.98). Analysis of the molecular orbitals indicates that of the seven valence electrons, four are contained in the B-H_a and B-H_b bonds while there are only three electrons contained in the longer B-H_c, B-H_d bonds. The singly occupied orbital is in the plane perpendicular to the BH_2 fragment resulting in the $^2B_1$ symmetry of the molecule. Thus, the long B-H bonds in BH_4 are real, but electron-deficient, covalent bonds.

Results for BH_4 determined in this work may be compared with values predicted for the bidentate form of the ionic compounds $LiBH_4$ and $NaBH_4$. The equilibrium geometry of the BH_4^- negative ion is tetrahedral and according to calculations[19,20] and experimental observations[21] the stable configuration of $LiBH_4$ is the tridentate form in which the BH_4^- ion is only modestly distorted from a tetrahedron. A better comparison is provided, however, by the C_{2v} symmetry bidentate form that is predicted[19] to be a transition state with one imaginary frequency.

Using the notation of Figure 1, the metal ion lies in the H_c-B-H_d plane and is bonded to both H_c and H_d. Corresponding bond distances and bond angles are tabulated in Table 3. The principal observation is that in $LiBH_4$ and $NaBH_4$, the longer bonds (labeled B-H_c) are shorter than in BH_4. Assuming these compounds are really ionic in nature, i.e., $Li^+BH_4^-$, there is an additional electron in the H_cBH_d moiety as compared with BH_4 resulting in a shorter bond length. This also results in a larger H_c-B-H_d bond angle and correspondingly longer H_c-H_d bond length in these compounds. Analogous vibrational frequencies are listed in Table 2. They may be observed to be somewhat larger, particularly for the lowest frequencies, than the corresponding frequencies in BH_4, although some of the difference may be accounted for by use of different theoretical methods.

The bonding in BH_4 provides an interesting contrast to the tightly bound small boron hydrides at one extreme and to the situation in BH_5 at the other, where there is no bonding between the BH_3 and H_2 fragments at the SCF level. The bond length of 1.315 Å in BH_4 is intermediate between the ~1.2 Å B-H bond of the smaller hydrides and the 1.47-1.53 Å B-H bond length,[9] depending on basis set and type of calculation, between the BH_3 and H_2 segments of BH_5. Note also that the increased H_c-H_d separation of 0.994 Å in BH_4 also supports the interpretation that these atoms are significantly bound to the central atom in contrast to BH_5 where the corresponding H-H separation is 0.75-0.79 Å, depending on the calculation.[9]

The BH_4 isomer of D_{2d} symmetry, in which the B-H_a and B-H_c bond lengths and corresponding bond angles are equal, was also investigated with the double zeta basis set. In agreement with the previous report,[14] it was found to have a doubly degenerate imaginary frequency and to lie higher in energy than the global minimum C_{2v} structure. It is therefore not expected to be chemically significant and was not considered further.

ENERGIES

Total energies for BH_4 and the dissociation limits as well as relative energies with respect to BH_3 + H are listed in Table 4. Comparing results at the MCSCF level for the preliminary geometry optimized with the double zeta basis and the final geometry obtained with the large basis shows a very modest effect on the energy of the two geometries, corresponding to ~1 kcal/mol for BH_4. Final results are given by the calculation labeled CID which includes the multireference Davidson correction for the effects of quadruple excitations.

The electronic energy of the BH_4 minimum is predicted to lie 19.23 kcal/mol below BH_3 + H and 20.10 kcal/mol below BH_2 + H_2. Including our calculated zero point energies, the

BH_4 species is bound by 14.83 and 14.55 kcal/mol, respectively, with respect to BH_3 + H and BH_2 + H_2. These results may be compared with the values 12.91 and 14.79 kcal/mol reported previously[14] from MP4 calculations. The calculated binding energy in BH_4, although modest by the standards of most small hydrides, may be compared with the largest hydride, BH_5, which is predicted[9] to lie 5.4 kcal/mol below BH_3 + H_2 in electronic energy, which reduces to 0.9 kcal/mol when zero point energy is taken into account. This is consistent with the shorter B-H bond lengths in BH_4 than in BH_5 as noted previously.

Values for the heat of formation of BH_4 and dissociation limits at 0 K and 298 K resulting from the energy differences in Table 4 are given in Table 5. We have chosen to base these numbers at 0 K on a value of 22 kcal/mol for $\Delta H_f^0(BH_3)$ and the standard value of 51.6 kcal/mol for H. While there remains some uncertainty as to the heat of formation number for both BH_3 and BH_2, the former is undoubtedly more reliably known. The photoionization studies combined with careful analysis of several different reactions of Ruscic et al.[7] provides a range of 22.2 ± 3.4 to 25.8 ± 1.7 kcal/mol for $\Delta H_f^0(BH_3)$ while theoretical values of 20.6 kcal/mol[1] and 22.3 ± 3.3 kcal/mol[3] have been reported. Corrections to 298 K were made following the procedure given by Pople et al.[1] based on calculated enthalpy differences for BH_n and experimental differences for the atoms B and H in the standard state. This results in $\Delta H_f^{298}(BH_2)$ of 73.4 kcal/mol which may be compared with a previous theoretical value[1] of 74.8 kcal/mol. As pointed out in that work[1], the JANAF[11] value of 48 kcal/mol is based on old appearance potential data subject to large uncertainties. Extrapolations[11] are based on an assumed linear geometry, while this work and other studies[1-2] agree on a bent structure.

The heat of formation of BH_4 at 0 K and 298 K is predicted to be 58.5 and 56.5 kcal/mol respectively. The only previous value of $\Delta H_f^0(BH_4)$ in the literature, to our knowledge, is 53.2 kcal/mol calculated within the MNDO approximation.[12]

ADDITION REACTION

Because the equilibrium structure of the BH_4 molecule has a C_{2v} geometry that resembles a BH_2 radical with a slightly stretched H_2 species in the bisecting plane, the addition reaction of H_2 to BH_2 to form this structure is of interest. Geometry optimization of a transition state for the addition reaction analogous to those for BH_4 and the dissociation limits was performed resulting in the structure listed in Table 1. At this geometry, the approaching H_2, which is barely stretched from its equilibrium distance, lies in the plane bisecting the BH_2 radical. The distance between the closest approaching H and the B atom is 1.844 Å. At the MCSCF level, the transition state lies 0.46 kcal/mol above the $BH_2 + H_2$ asymptote. The transition state is characterized by an imaginary frequency of 448i cm^{-1}, which is surprisingly large given the very small energy difference between the transition state and the asymptote.

When the energy of this structure was determined at the multireference Cl level, however, the electronic energy was 3.18 kcal/mol below that of the asymptote. The "transition state" structure, located at the MCSCF level, cannot represent the location of a barrier on the true potential energy surface. Even when the zero-point energy of this point, 18.35 kcal/mol, is taken into account, the "transition state" lies 0.4 kcal/mol below $BH_2 + H_2$.

In order to see whether calculation at the CI level merely alters the location of the true transition state, we also performed CI calculations for several interpolated points in between the "transition state" and the asymptote that constitute a pseudo reaction path. For these points, the distance between the approaching H and the B was fixed and the other coordinates were interpolated between their values at the transition state and the asymptote, defined as a separation of 5Å between the approaching H in H_2 and the B in BH_2. The energy difference between an asymptotic separation of 5Å and one of 40Å is 0.025 kcal/mol at the MCSCF level. Relative energies at the MCSCF and CI levels are listed in Table 6. It appears that when correlation energy is taken into account, the energy of the system goes down smoothly as the hydrogen molecule approaches BH_2. These calculations suggest that there is no energetic barrier to the addition of H_2 to BH_2.

The observation of a small barrier in a radical addition reaction "disappearing" when reevaluated with a larger basis set and/or degree of electronic correlation has been noted previously. For the BH_4 system, Paddon-Row and Wong[14] determined a similar geometry for a transition structure, also noted in Table 1, which was found to be slightly lower in energy than the asymptote when recomputed with a greater degree of electronic correlation. Studies of insertion of methylene into methane and silane[22] and of halocarbene cycloaddition[23] also reported barriers at the SCF but not at correlated levels of calculation.

SUMMARY AND CONCLUSIONS

The structure and energy of the BH_4 radical has been studied by multiconfiguration theoretical techniques. The equilibrium geometry of BH_4 is found to have C_{2v} symmetry and can be approximately described as a BH_2 radical to which a stretched H_2 has been added in the perpendicular plane. From an analysis of the geometry, frequencies, and MCSCF wavefunction, all of the bonds in BH_4 may be considered real, covalent bonds, of which one pair is electron-deficient having only three electrons. This is in contrast to the well studied[8-9] BH_5 system which is more properly described as a complex of BH_3 and H_2. The BH_4 binding energy is predicted to be 14.55 kcal/mol with respect to $BH_2 + H_2$ including calculated zero-point energy which may be contrasted to the calculated[9] binding of 0.9 kcal/mol of BH_5 with respect to $BH_3 + H_2$.

The addition reaction of BH_2 to H_2 to form the C_{2v} equilibrium geometry of BH_4 was investigated. Although a transition state characterized by a single imaginary frequency and a very small barrier on the potential energy surface was determined at the MCSCF level, subsequent investigation at the CI level indicated that the addition reaction takes place without an energetic barrier. The reduction in predicted energy barriers when treated with larger basis sets and greater inclusion of electronic correlation was reported in other studies, as well. The theoretical determination of energetic barriers in radical addition reactions appears to require sophisticated calculations for reliable results.

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Table 1.

OPTIMIZED GEOMETRICAL PARAMETERS
(In angstroms and degrees)

BH_4 (C_{2v}) $^2B_1$	MCSCF[a] (this work)	MP2/6-31G(d,p)[b]	UHF/6-311G**[c]
B-H_a	1.201 (1.207)	1.117	1.182
B-H_c	1.315 (1.328)	1.272	1.288
∠H_a-B-H_b	131.7 (128.7)	129.2	128.4
∠H_c-B-H_d	44.4 (51.5)	47.7	48.4
H_c-H_d	0.994 (1.153)	1.029	1.056

BH_2 (C_{2v}) $^2A_1$	MCSCF[a] (this work)	MP2/6-31G*[d]	HF/6-31G(d)[e]	Expt[f]
B-H	1.206 (1.216)	1.188	1.185	1.181
∠H-B-H	127.0 (128.4)	127.6	126.5	131

H_2 ($D_{\infty h}$) $^1\Sigma_g^+$	MCSCF[a] (this work)	HF/6-31G(d)[e]	Expt[g]
H-H	0.755 (0.755)	0.730	0.742

BH_3 (D_{3h}) $^1A_1'$	MCSCF[a] (this work)	MP2/6-31G*[d]	HF/6-31G(d)[e]
B-H	1.210 (1.217)	1.191	1.188

"Transition State"[h] C_s ($^1A'$)	MCSCF[a] (this work)	MP2/6-31G(d,p)[b]
B-H_a	1.205 (1.211)	1.180
∠H_a-B-H_b	128.5 (131.8)	128.4
B-H_d	1.844 (1.689)	2.069
H_c-H_d	0.766 (0.781)	0.742
∠H_c-B-H_d	100.7 (103.4)	97.1

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[a] Results from optimization with double zeta basis in parenthesis.

[b] Paddon-Row and Wong, Reference 14.

[c] Claxton et al., Reference 13.

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[h] Structure predicted as transition state at MCSCF level (see text). Atoms H_c and H_d which comprise the approaching H_2 are in symmetry plane bisecting H_a-B-H_b. H_d makes the closest approach to B.

Table 2.

CALCULATED HARMONIC FREQUENCIES
(cm^{-1})

BH_4	BH_4 MCSCF (this work)			BD_4 MCSCF (this work)	$LiBH_4$[b] HF/6-31G**	$NaBH_4$[b] HF/6-31G**
a_1	2534	(2535)	BH_2 sym. stretch	1832	2570	2533
	2086	(1941)	BH_2 (long) sym. stretch	1520	2133	2153
	*1413	(1185)	scissors (in phase)	1003	1500	1441
	*996	(611)	scissors (out of phase)	751	1261	1278
b_1	1962	(1770)	BH_2 (long) asym stretch	1396	2059	2083
	*634	(742)	rock	497	1170	1164
b_2	2656	(2670)	BH_2 asym stretch	1999	2612	2566
	*1053	(1043)	twist	783	1342	1286
a_2	*888	(781)	twist	628	1244	1240

BH_2	MCSCF[a] (this work)			HF/6-31G(d)[c]
a_1	2456	(2460)	sym. stretch	2728
	1022	(971)	bend	1128
b_1	2636	(2631)	asym stretch	2867

H_2	MCSCF[a] (this work)	Expt[d]
	4226 (4259)	4401

BH_3	MCSCF[a] (this work)		HF/6-31G(d)[c]	MBPT[e]	Expt[f]
a_1'	2455 (2436)	sym stretch	2693	2609	
a_2''	1124 (1120)	out-of-plane bend	1225	1185	1140.88
e'	2579 (2587)	stretch	2813	2756	2808 (Ar)
	1201 (1147)		1305	1226	

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*Modes which couple the two parts of the molecule.

[a] Results from optimization with double zeta basis in parenthesis.

[b] C_{2v} symmetry, bidentate form, Ramondo et al., Reference 19.

[c] Pople et al., Reference 1.

[d] Huber and Herzberg, Table 1.

[e] MBPT with B(3s2p1d) H (2s1p) basis. Stanton et al., Reference 9.

[f] M. Jacox, J. Phys. Chem. Ref. Data 19, 1387 (1990).

Table 3.

COMPARISON OF GEOMETRIES FOR BH_4, $LIBH_4$, and $NaBH_4$

(in Angstroms and Degrees)

	BH_4[a]	$LiBH_4$[b]	$NaBH_4$[b]
$B\text{-}H_a$	1.201	1.200	1.204
$B\text{-}H_c$	1.315	1.253	1.249
$<H_a\text{-}B\text{-}H_b$	131.7	115.2	114.1
$<H_c\text{-}B\text{-}H_d$	44.4	109.1	111.1
$H_c\text{-}H_d$	0.994	2.041	2.060

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[a] MCSCF (this work).

[b] Ramondo, et al., Reference 19, MP2, 6-31G**.

Table 4.

CALCULATED TOTAL ENERGIES (hartrees) ZERO-POINT ENERGIES (kcal/mol) and RELATIVE ENERGIES (kcal/mol) WITH RESPECT TO BH_3 + H

Total Energies[a]

	MCSCF[b]	CI	CID[c]	Zero Pt Energy
BH_4	-0.960307 (-0.958922)	-1.054502	-1.061982	20.33
$BH_3 + H$	-0.949652 (-0.949585)	-1.026921	-1.031334	15.93
$BH_2 + H_2$	-0.945395 (-0.945284)	-1.024962	-1.029944	14.78

Relative Energies[d]

	MCSCF[b]	CI	CID[c]
BH_4	-6.69 (-5.86)	-17.31	-19.23
$BH_2 + H_2$	2.67 (2.70)	1.23	0.87

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[a] With respect to -26.0 hartrees.

[b] Final geometry (DZ optimized geometry).

[c] CI with Davidson correction for quadruple excitations.

[d] Difference in electronic energy (without zero-point vibration).

Table 5.

RELATIVE ENERGIES WITH ZERO POINT WITH RESPECT TO $BH_3 + H$ AND HEATS OF FORMATION (kcal/mol)

	Relative energy/ZP	ΔH_f^o	ΔH_f^{298}
BH_4			
This work	-14.83	58.5	56.6
MP2/6-31G(d,p)[a]	-12.91		
$BH_3 + H$	—	73.6	73.2
$BH_2 + H_2$			
This work	-0.28	73.3	73.4
MP2/6-31G(d,p)[a]	1.89		

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[a] Paddon-Row and Wong, Reference 14.

Table 6.

RELATIVE ENERGIES (kcal/mol) WITH RESPECT TO $BH_2 + H_2$ FOR ADDITION REACTION

	MCSCF	CI	CID[c]
"Transition State"[a] $B\text{-}H_d = 1.84$ Å	0.46	-2.12	-3.18
$B\text{-}H_d = 2.9$ Å[b]	0.27	-0.24	-0.50
$B\text{-}H_d = 3.9$ Å[b]	-0.02	-0.10	-0.12

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[a] See discussion in text.

[b] Interpolation procedure for geometries described in text.

[c] CI with Davidson correction for quadruple excitations.

FIGURE CAPTION

Figure 1. BH_4 equilibrium geometry. (C_{2v} symmetry: H_a and H_b are equivalent and H_c and H_d are equivalent).

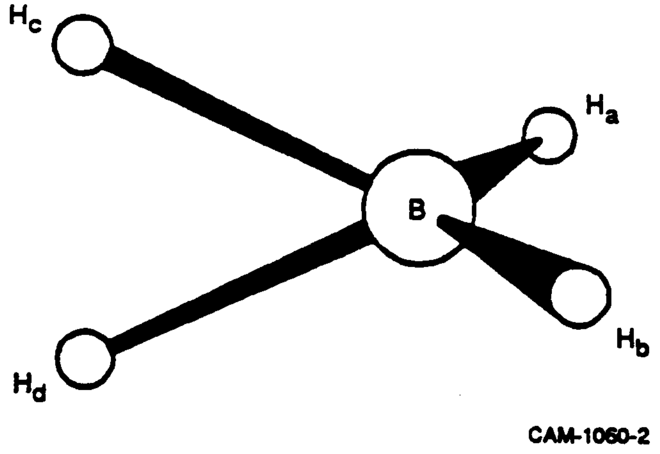

Figure 1