7424 *J. Phys. Chem. A* **2004,** *108,* 7424−7428

Ground State and Heat of Formation of MgB_2

Edmond P. F. Lee[†,‡] **and Timothy G. Wright***[,§,||]

School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, U.K., Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong, and Department of Chemistry, University of Sussex, Falmer, Brighton BN1 9QJ, U.K.

Received: June 11, 2004; In Final Form: July 2, 2004

A survey of the low-lying states of the MgB_2 and MgBB molecules is made, and it is found that different levels of theory lead to different calculated ground states. By employing high-level, up to RCCSD(T)/aug-cc-pCVQZ, ab initio calculations, we conclude that the lowest energy structure is a T-shaped $\tilde{X}^1A_1$ state, but that there is a $\tilde{a}^3B_1$ state lying within 1 kcal mol^{-1} higher in energy, with $^3\Sigma^-$ and $^5\Sigma^-$ MgBB states lying ~12 kcal mol^{-1} above that. The ground state is confirmed at the CASSCF+MRCI+Q level. We also calculate $\Delta H_f[MgB_2(\tilde{X}^1A_1)]$, obtaining a value of 194 ± 5 kcal mol^{-1}.

I. Introduction

MgB_2 was recently discovered to exhibit superconductivity at 39 K,[1] and much theoretical work has been undertaken to characterize the electronic structure of the solid.[2] In addition, there is a push toward the efficient in situ growth of thin films of MgB_2 for high-technology applications, as discussed in ref 3. To understand better the deposition process in growing thin films,[4] it is useful to have probes of the species concentrations as functions of the various variables (temperature, pressure, etc.), and one of the most useful techniques to obtain this information is optical emission spectroscopy, in its various forms.[5] This technique allows the remote sensing of the species in the reaction region, and careful measurements and calibrations can lead to absolute concentration profiles. Of course, to be able to employ the technique, one must have a knowledge of the emission spectrum of the various species to be monitored, and Amoruso et al. have used atomic emission lines of Mg, Mg^+, and B in order to investigate the plasma produced by the laser ablation of MgB_2 under various conditions.[3,6] As yet, no monitoring of MgB nor MgB_2 species appear to have been made, presumably since no electronic spectroscopy of these species is known, to our knowledge. Another means of understanding thin-film growth is thermodynamics—both the thermodynamics of the gas-phase species as well as the thermodynamics of the growth process itself.[7] We aim, in this work, to address the first question for the spectroscopy of MgB_2: namely, what is the electronic ground state. Second, we wish to establish the heat of formation of the MgB_2 molecule.

To answer these questions, the possibility of MgBB as well as BMgB structures must be addressed and, owing to the possibility of ionicity, the states arising from Mg/B_2, Mg^+/B_2^-, and Mg^{2+}/B_2^{2-} need to be considered. Since B_2 has a $^3\Sigma_g^-$ ground state, and Mg has a ^1S ground state, then this leads to the possibility of triplet states; B_2^- is expected to have a $^2\Pi$ ground state, and when coupled with the ^2S state of Mg^+, then triplet or singlet states are possible; and finally singlet states are expected from the Mg^{2+}/B_2^{2-} combination. In addition, it is possible that the 2pσ orbital may become involved in the diboride moieties, leading to the possibility of quintet states.

We note that recently, Erkoç[8] has studied the magnesium diboride molecule using the PM3, RHF, MP2, and B3LYP methods; the basis set employed was 6-31G*. It appears only closed-shell singlets were considered and that both linear and bent symmetric structures were obtained, with the bent structure being the lowest in energy. Both of these states exhibited real harmonic frequencies, suggesting each was a minimum.

It is the purpose of the present work to perform a more complete survey of the various electronic states that may arise, to determine their energetic ordering and also to consider both MgBB and BMgB orderings of the atoms.

II. Calculational Details

B3LYP/6-311+G(3df) optimizations and harmonic vibrational frequency calculations were initially performed; a larger range of states was studied at the MP2/6-311+G(3df) level. The three lowest states at the MP2 level were then studied at the QCISD/6-311+G(3df) and CCSD(T)/6-311+G(3df) levels of theory. All of the above calculations were performed with Gaussian,[9] and the frozen core approximation was employed for the correlation treatments. Unrestricted electronic wave functions were employed in open-shell cases, and $\langle S^2\rangle$ values are reported in cases where the spin contamination was high.

We then moved onto a larger basis set. For boron, we employed the standard aug-cc-pVQZ basis set. For magnesium, the cc-pVQZ basis set was employed and was augmented with a set of diffuse spdfg functions, with exponents as follows: $\zeta_s = 0.01$, $\zeta_p = 0.008$, $\zeta_d = 0.03$, $\zeta_f = 0.05$, and $\zeta_g = 0.08$—these were simply obtained in an even-tempered way from the corresponding most diffuse function in the cc-pVQZ basis set, with a factor of 3. The total number of basis functions was 244, and for simplicity, we refer to the molecular basis set as simply aVQZ in the below. This basis set was used to obtain optimized geometries and relative energies using the RCCSD(T) procedure,[10] as implemented in MOLPRO.[11]

We then performed RCCSD(T) calculations employing a basis set that could describe the correlation of all of the electrons of

---

* Corresponding author fax: +44 1273 677196; e-mail: Timothy.Wright@nottingham.ac.uk.

[†] University of Southampton.

[‡] Hong Kong Polytechnic University.

[§] University of Sussex.

[||] Present address: School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

10.1021/jp0474677 CCC: $27.50

TABLE 1: Geometries, Harmonic Vibrational Frequencies, Atomic Charges, and Spin and Relative Energies for Magnesium Diboride: B3LYP/6-311+G(3df)[a] Calculations[b]

		geometry					
state	configuration	R_{MgB}	R_{BB}	$\theta/°$	vibrational frequency (cm^{-1})	charge; spin	E_{rel}[c]
$BMgB(^5\Sigma_g^+)$	$\cdots(1\pi_g)^2(2\pi_u)^2$	2.184		180.0	$(61{,}101)\pi_u$; $418\sigma_g$; $593\sigma_u$	Mg(0.73;0.66); B(−0.37;0.68)	96.7
$BMgB(^1\Sigma_g^+)$		2.536		180.0	$65\pi_u$; $303\sigma_g$; $415\sigma_u$	Mg(0.62); B(−0.31)	84.4
$BMgB(^3\Sigma_g^-)$	$\cdots(1\pi_g)^2$	2.402		180.0	$(43{,}63)\pi_u$; $278\sigma_g$; $390\sigma_u$	Mg(0.64;0.08); B(−0.32;0.96)	84.1
$BMgB(^3B_2)$	$\cdots(2b_1)^1(1a_2)^1$	2.402		179.9	43π; 278σ; 390σ	Mg(0.64;0.08); B(−0.32;0.96)	84.1
$MgBB(^1\Sigma^+)$		2.226	1.623	180.0	$(136i{,}84)\pi$; 367σ; 1040σ	Mg(0.29); B(−0.01); B(−0.29)	34.8
$^5A_2$	$\cdots(3b_2)^1(2b_1)^1$ $(7a_1)^1(8a_1)^1$	2.546	1.488	34.0	$420ib_2$; $291a_1$; $1337a_1$	Mg(0.28;0.70); B(−0.14;1.65)	28.4
$MgBB(^5\Sigma^-)$	$\cdots(8\sigma)^1(2\pi)^2(9\sigma)^1$	2.265	1.546	180.0	149π; 386σ; 1217σ	Mg(0.19;0.88); B(−0.16;1.40); B(−0.03;1.73)	8.6
$^1A_1$		2.199	1.547	41.2	$447a_1$; $1130a_1$; $487b_2$	Mg(0.35); B(−0.17)	8.5
$MgBB(^3\Sigma^-)$	$\cdots(2\pi)^2$	2.254	1.563	180.0	130π; 384σ; 1159σ	Mg(0.22;−0.73); B(−0.12;1.23); B(−0.11;1.50)	7.3
$^3B_1$	$(2b_1)^1(7a_1)^1$	2.254	1.604	41.7	$328b_2$; $443a_1$; $1003a_1$	Mg(0.41;0.00); B(−0.25;1.00)	0.0

[a] r in Å;θ in°. [b] Symmetries of the vibrational modes are given after the numerical value. [c] In kcal mol^{-1}

boron and all but the 1s electrons of Mg. For boron, the basis set was the standard aug-cc-pCVQZ basis set, for magnesium the basis set employed was the "aVQZ" one noted in the preceding paragraph, augmented with tight functions as follows: four s ($\zeta = 20.25$, 6.75, 2.25 and 0.75); four p ($\zeta = 13.5$, 4.5, 1.5 and 0.5); two d ($\zeta = 4.0$ and 1.0); one f ($\zeta = 1.5$); and one g ($\zeta = 1.5$). These basis functions are even-tempered and were obtained by inspection of other cc-pCVQZ basis sets and noting the range of the exponents. This resulted in 344 basis functions, and for simplicity, we refer to the molecular basis set as aCVQZ in the below.

Finally, we performed CASSCF[12,13] and CASSCF+MRCI[14,15] calculations with the aVQZ basis set, using the method as implemented in MOLPRO.[11]

III. Results and Discussion

B3LYP. The results of the B3LYP optimizations and harmonic vibrational frequency calculations are given in Table 1. Interestingly, these led to the conclusion that the T-shaped $^3B_1$ state was the ground state, arising from a $\cdots(2b_1)^1(7a_1)^1$ configuration. The spin density suggests that this state has the character of $Mg(^1S)$ interacting with $B_2(^3\Sigma_g^-)$, but the Mulliken charges indicate that there is significant covalency. The next highest state is the linear MgBB $^3\Sigma^-$ state arising from the $\cdots(2\pi)^2$ configuration. The spin density in this case suggests that this state has a significant contribution from $Mg^+(^2S)$ interacting with $B_2^-(^2\Pi_u)$, with again the Mulliken charges indicating significant covalency. The closed-shell, symmetric $BMgB(^1A_1)$ state is calculated to lie 8.5 kcal mol^{-1} above the $^3B_1$ state and is covalent in nature. A $^5\Sigma^-$ state lies close in energy to the latter state, and then a large gap occurs before the next states. We note that the symmetric linear $BMgB(^1\Sigma_g^+)$ state lies over 80 kcal mol^{-1} higher in energy than the $^3B_1$ state at this level of theory, with the asymmetric MgBB linear $^1\Sigma^+$ state lying at ~35 kcal mol^{-1}. Note that Erkoç[8] only appears to have considered symmetric, closed-shell structures.

MP2. We now move onto the MP2/6-311+G(3df) calculations, shown in Table 2. It may be immediately seen, by comparing the lower parts of Tables 1 and 2, that the energy ordering of the lowest states has changed, with the closed-shell T-shaped $^1A_1$ structure becoming the lowest in energy, followed by the open-shell $^3B_1$ state T-shaped structure. The $^5\Sigma^-$ state now lies lower in energy than the $^3\Sigma^-$ state, and again there is a large energy gap before the other states. Again the linear, closed-shell MgBB and BMgB states lie high in energy. We refrain from further analysis of all of the states considered, but simply report the results in Table 2.

It is important to note that we have not undertaken to calculate the position of every low-lying state of magnesium diboride but to establish the ground state. Thus, for example, there will be an open-shell $^1B_1$ state with electronic configuration $\cdots(2b_1)^1(7a_1)^1$, which will lie above the $^3B_1$ state (by Hund's rules), but it is unclear whether it lies above or below the $^5\Sigma^-$ state. In addition, there will be low-spin $^3\Sigma^-$ and $^1\Sigma^-$ states arising from the $\cdots(8\sigma)^1(2\pi)^2(9\sigma)^1$ configuration. In addition, other Δ and Σ states also arise from this configuration, and there will be interactions between states of the same symmetry. Our aim here is not to characterize every low-lying state but to establish the lowest lying state, and hence we concentrate on the lowest-lying states that arise from the lowest-lying configurations.

Comparing our results with those of Erkoç,[8] we find that the present MP2 results are in agreement with the conclusion that the lowest energy state is a T-shaped, closed-shell structure, $\tilde{X}^1A_1$. The highest two of our vibrational frequencies of 441, 479, and 1105 cm^{-1} are in fair agreement with the values obtained in ref 8, 329, 432, and 1007 cm^{-1}, but the lowest one is not in good agreement. Regarding the MgB bond length, our value here of 2.245 Å is in reasonable agreement with Erkoç's value[8] of 2.263 Å, and our bond angle of 41° is the same as that obtained in ref 8.

QCISD and (R)CCSD(T) Calculations. The three lowest-lying states, $^1A_1$, $^3B_1$, and $^5\Sigma^-$, were also studied at the QCISD/6-311+G(3df) level of theory, and the results form part of Table 3. As may be seen, the $^3B_1$ state is now calculated to lie lowest in energy, with the $^1A_1$ state lying 4.4 kcal mol^{-1} higher in energy; the $^5\Sigma^-$ state is close to the $^1A_1$ state.

Performing CCSD(T)/6-311+G(3df) calculations, we find that the $^1A_1$ state becomes the lowest in energy again, with the $^5\Sigma^-$

TABLE 2: Geometries, Harmonic Vibrational Frequencies, Atomic Charges, and Spin and Relative Energies for Magnesium Diboride: MP2/6-311+G(3df) Calculations[d]

structure; states	configuration	geometry			vibrational frequency (cm^{-1})	q		σ		E_{rel}[a]
		R_{MgB}	R_{BB}	θ/°		Mg	B	Mg	B	
BMgB($^5\Sigma_g^+$)	$\cdots(1\pi_g)^2(2\pi_u)^2$	2.089		180.0	$158\pi_u;501\sigma_g;659\sigma_u$	1.37	−0.68	−0.24	2.12	126.4
BMgB($^3\Sigma_u^-$)	$\cdots(1\pi_g)^3(2\pi_u)^1$	2.386		180.0	$62,65\pi_u;264\sigma_g;394\sigma_u$	0.65	−0.32	−0.05	1.02	97.1
BMgB($^1\Sigma_g^+$)	$\cdots(5\sigma_g)^2(4\sigma_u)^2$	2.514		180.0	$79\pi_u$; $326\sigma_g$; $447\sigma_u$	0.81	−0.41			95.3
BMgB($^3\Pi_g$)	$\cdots(4\sigma_u)^1(2\pi_u)^1$	2.380		180.0	$(125;454)\pi_u$; $355\sigma_g;510\sigma_u$	0.55	−0.27	−0.06	1.03	93.9
$^3B_2$	$\cdots(2b_1)^1(1a_2)^1$	2.461	1.757	41.8	$381ib_2$; $496a_1;2086a_1$	0.56	−0.28	−0.72	1.36	86.2
BMgB($^1\Sigma_g^+$)	$\cdots(1\pi_g)^4$	2.347		180.0	$152\pi_u$; $367\sigma_g$; $708\sigma_u$	1.24	−0.62	0.00	0.00	76.1
BMgB($^3\Sigma_g^-$)	$\cdots(5\sigma_g)^2(2\pi_u)^2$	2.253		180.0	$149\pi_u$; $399\sigma_g$; $619\sigma_u$	0.58	−0.24	0.72	0.64	72.0
BMgB($^3\Sigma_g^-$)	$\cdots(5\sigma_g)^2(1\pi_g)^2$	2.292		180.0	$225\pi_u$; $384\sigma_g$; $604\sigma_u$	0.73	−0.36	−0.01	1.00	70.4
$^5B_1$	$\cdots(3b_2)^1(2b_1)^1(7a_1)^1(4b_2)^1$	2.343	1.660	41.5	$377b_2$; $407a_1$; $974a_1$	0.53	−0.27	−0.62	2.31	69.5
BMgB($^1\Delta_g$)	$\cdots(5\sigma_g)^2(1\pi_g)^2$	2.318		180.0	$(168;204)\pi_u$; $357\sigma_g;591\sigma_u$	0.69	−0.34	0.00	0.00	68.9
MgBB($^1\Sigma^+$)		2.016	1.475	180.0	99π; 526σ; 1265σ	0.45	−0.20, −0.25	0.00	0.00, 0.00	59.6
$^5B_2$	$\cdots(3b_2)^1(6a_1)^1(7a_1)^1(8a_1)^1$	2.365	1.495	36.8	$287b_2$; $383a_1$; $1301a_1$	0.51	−0.25	1.13	1.44	52.2
BMgB($^1A_1$)	(became linear)	2.222		180.0	$(296;309)\pi_u;527\sigma_g$; $708\sigma_u$	0.83	−0.42	0.00	0.00	43.2
$^3A_1$	$\cdots(6a_1)^1(7a_1)^1$	2.022	1.586	44.8	$650a_1$; $716b_2$; $1064a_1$	0.58	0.29	0.51	0.75	36.0
$^5B_1$	$\cdots(2b_1)^1(6a_1)^1(7a_1)^1(8a_1)^1$	2.412	1.632	39.5	$368a_1$; $533b_2$; $1008a_1$	0.55	−0.28	1.12	1.44	32.0
MgBB($^3\Pi$)	$\cdots(8\sigma)^1(2\pi)^3$	2.386	1.494	180.0	$381ib_2$; $496a_1;2086a_1$	0.38	−0.37, −0.01	−0.08	0.26, 1.81	30.1
$^5A_2$	$\cdots(3b_2)^1(2b_1)^1(7a_1)^1(8a_1)^1$	2.490	1.497	35.0	$355a_1$; $1318a_1;3464a_1$	0.33	−0.17	0.60	1.70	25.1
MgBB($^3\Sigma^-$)[b]	$\cdots(2\pi)^2$	2.267	1.556	180.0	169π; 404σ; 1213σ	0.31	−0.43, 0.11	−0.92	1.17, 1.75	7.7
MgBB($^5\Sigma^-$)	$\cdots(8\sigma)^1(2\pi)^2(9\sigma)^1$	2.270	1.550	180.0	167π; 401σ; 1228σ	0.28	−0.42, 0.14	0.86	1.36, 1.78	6.3
$^3B_1$[c]	$\cdots(2b_1)^1(7a_1)^1$	2.270	1.626	42.0	$412a_1$; $963b_2$; $1037a_1$	0.50	−0.25	−0.78	1.39	2.0
$^1A_1$		2.245	1.574	41.0	$453b_2$; $493a_1$; $1073a_1$	0.53	−0.26	0.00	0.00	0.0

[a] kcal mol^{-1}. [b] $\langle S^2\rangle = 3.00$. [c] $\langle S^2\rangle = 2.71$. [d] Symmetries of the vibrational modes are given after the numerical value.

TABLE 3: Geometries, Harmonic Vibrational Frequencies, Atomic Charges, and Spin and Relative Energies for Magnesium Diboride Employing QCISD and CCSD(T) Calculations[c]

structure; states	configuration	geometry			vibrational frequency (cm^{-1})	q		σ		E_{rel}[a]
		R_{MgB}	R_{BB}	θ/°		Mg	B	Mg	B	
					QCISD/6-311+G(3df)					
$^5\Sigma^-$	$\cdots(8\sigma)^1(2\pi)^2(9\sigma)^1$	2.270	1.553	180.0	160π; 395σ; 1217σ	0.28	−0.42, 0.14	0.86	1.36, 1.78	5.0
$^1A_1$		2.213	1.562	41.4	$442b_2$; $475a_1$; $1115a_1$	0.53	−0.26	0.00	0.00	4.4
$^3B_1$	$\cdots(2b_1)^1(7a_1)^1$	2.268	1.624	42.0	$364b_2$; $441a_1$; $986a_1$	0.50	−0.25	−0.78	1.39	0.0
					CCSD(T)/6-311+G(3df)					
$^5\Sigma^-$	$\cdots(8\sigma)^1(2\pi)^2(9\sigma)^1$	2.270	1.560	180.0	155π; 394σ; 1191σ					10.7
$^3B_1$[b]	$\cdot\cdot(2b_1)^1(7a_1)^1$	2.269	1.625	42.0	$287b_2$; $443a_1$; $979a_1$					1.4
$^1A_1$	$\cdot$	2.225	1.574	41.2	$441b_2$; $479a_1$; $1105a_1$					0.0
					RCCSD(T)/ aVQZ					
$^3\Sigma^-$	$\cdots\pi^2$	2.263	1.556	180.0						11.9
$^5\Sigma^-$	$\cdots(8\sigma)^1(2\pi)^2(9\sigma)^1$	2.270	1.556	180.0						11.8
$^3B_1$	$\cdots(2b_1)^1(7a_1)^1$	2.274	1.616	41.6						1.2
$^1A_1$		2.224	1.560	41.1						0.0

[a] kcal mol^{-1}. [b] $\langle S^2\rangle = 2.71$. [c] Symmetries of the vibrational modes are given after the numerical value.

state rising in energy compared to both the $^1A_1$ and the $^3B_1$ state—see Table 3.

We did not study the $^3\Sigma^-$ state using UCCSD(T) or UQCISD, owing to the high spin contamination detected at the UMP2 level; however, RCCSD(T) calculations were performed—see below.

RCCSD(T)/aVQZ optimizations were then performed on these states, and as may be seen from Table 3, the ordering remains the same as at the CCSD(T)/6-311+G(3df) level, and the energy separations remain very similar. We report the relative energies additionally in Table 4, together with the RCCSD relative energies.

TABLE 4: Relative Energies (kcal mol^{-1}) from Single-Point RCCSD and RCCSD(T) Calculations[a]

state	RCCSD/ aVQZ	RCCSD/ aCVQZ	RCCSD(T)/ aVQZ	RCCSD(T)/ aCVQZ	RCCSD(T)/ aCVQZ energy/E_h
$^3\Sigma^-$	12.9	13.6	11.9	12.8	−249.363625
$^5\Sigma^-$	−0.4	−0.4	11.8	12.6	−249.364048
$^3B_1$	3.7	−4.1	1.2	1.4	−249.381839
$^1A_1$	0.0	0.0	0.0	0.0	−249.384060

[a] All performed at the RCCSD(T)/aVQZ optimized geometry.

Finally, we not only performed single-point RCCSD(T)/aCVQZ calculations on the same three states but also included the $\cdots(2\pi)^2$ $^3\Sigma^-$ state, employing the RCCSD(T)/aVQZ geometry, with the RCCSD and RCCSD(T) relative energies shown in Table 4. As may be seen, for the lowest three states, the relative energies agree closely at the CCSD(T) level with the aVQZ and aCVQZ basis sets, but the RCCSD(T) relative energies are very different from the RCCSD ones, and the RCCSD energy ordering is different with the aVCQZ and aCVQZ basis sets. Thus, high order electron correlation is critical in the determination of the energy ordering.

From the close agreement of the RCCSD(T) relative energies employing the 6-311+G(3df), aVQZ, and aCVQZ basis sets, we feel confident in concluding that the final energy ordering is correct and that therefore the ground state of magnesium diboride is $\tilde{X}^1A_1$—i.e. a T-shaped molecule of C_{2v} symmetry. The $^3B_1$ state lies only 1.4 kcal mol^{-1} (T_e = 490 cm^{-1}) above.

Multireference Character. From the RCCSD(T) calculations, an estimate of the multireference character of the lowest

TABLE 5: Relative Energies (kcal mol^{-1}) from Single-Point Multireference Calculations[a]

state	CASSCF	CASSCF+MRCI	CASSCF+MRCI+Q[b]
$^5\Sigma^-$	7.9	12.5	12.4
$^3\Sigma^-$	5.9	11.2	11.4
$^3B_1$	2.4	0.9	0.4
$^1A_1$	0	0	0

[a] All performed at the RCCSD(T)/aVQZ optimized geometry. [b] Q denotes the multireference variant of the Davidson correction for quadruple excitations.

states could be deduced from the T1 diagnostic.[16] The values obtained were as follows: 0.0396 for the $\tilde{X}^1A_1$ state, 0.0256 for the $^3B_1$ state, 0.019 for the $^5\Sigma^-$ MgBB state, and 0.0645 for the $^3\Sigma^-$ MgBB state. Thus, there is some indication of a reasonable amount of multireference behavior present in the closed-shell ground state and particularly the open-shell $^3\Sigma^-$ state. Consequently, we performed single-point CASSCF/avQZ and CASSCF+MRCI/avQZ calculations at the RCCSD(T)/aVQZ optimized geometries for the four lowest states. In addition, we also made use of the multireference version of the Davidson correction,[17,18] to estimate the effect of quadruple excitations. The results are presented in Table 5, and it may be seen that the same energy ordering for the $^1A_1$ and $^3B_1$ states is obtained as at the RCCSD(T)/avQZ and RCCSD(T)/aCVQZ levels of theory but that the energy difference is much smaller, coming down to only 0.4 kcal mol^{-1} at the CASSCF+MRCI+Q level of theory. We also note that the $^3\Sigma^-$ and $^5\Sigma^-$ states change their ordering.

We note that the small energy difference between the $^1A_1$ state, and the $^3B_1$, plus consideration of zero-point vibrational energy effects, means that both states will be present in most situations.

Heat of Formation. We calculate the heat of formation from the atomization process:

$$MgB_2 \rightarrow Mg + 2B$$

We employ the energy of $MgB_2(\tilde{X}^1A_1)$ from the RCCSD(T)/aCVQZ//RCCSD(T)/aVQZ calculations, together with RCCSD(T)/aCVQZ energies of Mg(^{2}S) and B(^{2}P). We convert the energy difference to $\Delta H^{298.15}$ using standard statistical mechanical procedures and employ the CCSD(T)/6-311+G(3df) vibrational frequencies. We then use the established $\Delta H^{298.15}$ values for Mg (35.1 ± 0.2 kcal mol^{-1}) and B(133.8 ± 2.9 kcal mol^{-1}) from JANAF[19] to obtain $\Delta H_f{}^{298.15}[MgB_2(\tilde{X}^1A_1)] = 194.3 \pm 2.9$ kcal mol^{-1} and cite a value of 194 ± 5 kcal mol^{-1} to include residual errors in the calculations. This value is in good agreement with the PM3 value of 191 kcal mol^{-1} reported by Erkoç,[8] although no details of the method employed were given in that work.

IV. Concluding Remarks

Detailed ab initio calculations have shown that the MgB_2 molecule has a T-shaped, C_{2v}, closed-shell ground state, $\tilde{X}^1A_1$. We note that lower levels of calculations lead to different lowest states being obtained and that therefore caution is required. We highlight that the B3LYP method is shown to be inadequate for this species. By obtaining consistent energy ordering and relative energies at the CCSD(T)/6-311+G(3df), RCCSD(T)/aVQZ, and RCCSD(T)/aCVQZ levels of theory, and the same ordering at the CASSCF+MRCI+Q level for the lowest two states, we are confident that we have established the ground state of MgB_2 reliably. Our best geometry is that obtained at the RCCSD(T)/aVQZ level and has $R_{MgB} = 2.25$ Å and $\theta = 41°$. The lowest energy asymmetric, MgBB, structure appears to be a linear $^5\Sigma^-$ state at the RCCSD(T) level, lying just over 12 kcal mol^{-1} (4400 cm^{-1}) higher in energy; however, at the CASSCF+MRCI+Q level, the $^3\Sigma^-$ state is the lowest energy MgBB state. Somewhat fortuitously, we feel, Erkoç[8] reported the same lowest energy $^1A_1$ state for MgB_2 at a much lower level of theory. The zero-point energy correction implies that the zero-point levels of the $^1A_1$ and the $^3B_1$ states are very close in energy.

On analyzing the electronic wave function, we find that the bonding in the $\tilde{X}^1A_1$ state has a fair amount of covalent character, as deduced from the charge and spin densities (vide supra). Particularly, we note that the HOMO, the 6a$_1$ orbital, has contributions from the Mg 3s orbital and the B 2s and 2p$_z$ orbitals, with the dominant contribution being from the Mg 3s orbital. The occupied orbitals below this are the 2b$_1$ and 2b$_2$ orbitals, which are admixtures of the Mg 3p$_x$ and B 2p$_x$ orbitals, and the Mg 3p$_y$ and B 2s orbitals, respectively. Thus, this molecule is far from ionic. Note that we added diffuse functions to account for this involvement of the Mg 3p orbitals in the bonding.

We report a $\Delta H_f{}^{298.15}$ value of 194 ± 5 kcal mol^{-1} for $MgB_2(\tilde{X}^1A_1)$, where the error bar is conservative and includes cited errors[19] in $\Delta H_f{}^{298.15}$ for B and Mg as well as covering residual errors in the calculations and the approximate statistical mechanical treatment.

We finish by noting that we performed CIS/6-311+G(3df) calculations at the RCCSD(T)/aVQZ optimized geometry but that these had the $^3B_1$ (and its corresponding open-shell $^1B_1$ state) lower in energy that the $^1A_1$ state. We conclude that CIS calculations will not be adequate for this species and that detailed calculations aimed at determining spectroscopic transition energies will have to be of CASMP2 or CASSCF + MRCI quality.

Acknowledgment. The authors are grateful to the EPSRC for the award of computer time at the Rutherford Appleton Laboratories under the auspices of the Computational Chemistry Working Party (CCWP), which enabled these calculations to be performed. E.P.F.L. is grateful to the Research Grant Council (RGC) of the Hong Kong Special Administration Region for support. We are also grateful to a referee who suggested that we ought to consider multireference behavior in more detail, to obtain more reliable energy differences.

References and Notes

(1) Nagamatsu, J.; Nakagawa, N.; Muranaka, T.; Zenitani, Y.; Akimitsu, J. *Nature (London)* **2001**, *410*, 63.

(2) Ivanovskii, A. L. *Phys. Solid State* **2003**, *45*, 1829.

(3) Amoruso, S.; Bruzzese, R.; Spinelli, N.; Velotta, R.; Wang, X.; Ferdeghini, C. *Appl. Phys. Lett.* **2002**, *80*, 4315.

(4) Ashfold, M. N. R.; Claeyssens, F.; Fuge, G. M.; Henley, S. J. *Chem. Soc. Rev.* **2004**, *33*, 23.

(5) Preppernau, B. L.; Miller, T. A. In *Glow Discharge Spectroscopies*; Marcus, R. K., Ed.; Plenum Press: New York, 1993.

(6) Amoruso, S.; Bruzzese, R.; Spinelli, N.; Velotta, R.; Vitiello, M.; Wang, X. *Phys. Rev. B* **2003**, *67*, 224503.

(7) Kim, J.; Singh, R. K.; Newman, N.; Rowell, J. M. *IEEE Trans. Appl. Superconduct.* **2003**, *13*, 3238.

(8) Erkoç, Ş. *Int. J. Mod. Phys. C* **2003**, *14*, 483.

(9) Gaussian 03, Frisch, M. J. et al. Gaussian Inc.: Pittburgh, 2003.

(10) Hampel, C.; Peterson, K.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1.

(11) MOLPRO is a package of ab initio programs written by Werner, H.-J.; Knowles, P. J. with contributions from Almlöf, J. Amos, R. D.; Berning, A.; Deegan, M. J. O.; Eckert, F.; Elbert, S. T.; Hampel, C.; Lindh, R.; Meyer, W.; Nicklass, A.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.; Mura, M. E.; Pulay, P.; Schuetz, M.; Stoll, H.; Thorsteinsson, T.; Cooper, D. L.

(12) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053.

(13) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **2985**, *115*, 259.

(14) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803.

(15) Knowles, P. J.; Werner, P. J. *Chem. Phys. Lett.* **1988**, *145*, 514.

(16) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 23.

(17) Hirsch, G.; Bruma, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys. Lett.* **1977**, *52*, 442.

(18) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, 1974; p 17.

(19) Chase, M. W., Jr. *NIST-JANAF Themochemical Tables*, 4th ed.; J. Phys. Chem. Ref. Data, Monograph 9, 1998.