

Ab initio study of the molecules BC and B₂C

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The potential energy surface for the B₂C molecule and the potential energy curve for the ground state of BC have been investigated using full-valence complete active space SCF (CASSCF), augmented coupled cluster [CCSD(T)] and multireference treatments. The ground state of B₂C is an extraordinarily stable ring ($\Sigma D_e = 261.6 \pm 1$ kcal/mol) with two 2-electron π systems. The first excited state is linear BCB ($^1\Sigma_g^+$), which is essentially biconfigurational due to a $(4\sigma_g) - (3\sigma_u)$ near degeneracy. Anharmonic spectroscopic constants were obtained from quartic force fields at the CCSD(T) level with a correlation-consistent basis set of [4s3p2d1f] quality. A severe Fermi resonance exists between the bending and symmetric stretching modes. All computed intensities are fairly weak. Spectroscopic constants for BC using elaborate multireference techniques were very well reproduced using the CCSD(T) method with a spin-restricted Hartree-Fock reference configuration, but not with an unrestricted Hartree-Fock reference. This suggests that even moderate levels of spin contamination that do not significantly affect relative energies may have a detrimental effect on computed spectroscopic constants.

INTRODUCTION

Considerable interest has been aroused recently by neoceramic materials in the {B,C,N} "magic triangle" of elements. Special cases of mixed {B,C,N} compounds are the ultrahard materials boron carbide (BC), carbon nitride¹ and β -boron nitride.^{2,3} The covalent solid carbon nitride has generated a lot of interest recently¹ while boron carbide has potential in such diverse applications as control rods in nuclear fission reactors (e.g., Ref. 4), target tiles in nuclear fusion reactors (e.g., Refs. 5,6) and protective coating of carbon fiber materials against atomic oxygen in spacecraft.⁷

The precursors of these materials in surface coating are the B_mC_nN_n clusters. Among the heteronuclear clusters, B_mN_n clusters have been given the most attention, notably for BN,⁸ B₂N,^{9,10} BN₂,^{10,11} B₃N,^{12,13} B₂N₂,¹⁴ and BN₃.¹³ In the C_mN_n family, the CN radical is of course very well characterized,¹⁵ while the C₂N and CN₂ radicals recently have been the subject of considerable study (Ref. 16 and references therein), as is the case for cyanogen (C₂N₂).^{17,18} By contrast, much less information is available on the B_mC_n clusters. The available material is basically limited to *ab initio* calculations^{19,20} and an electron spin resonance study²¹ in noble gas matrix on BC, and a combined *ab initio* experimental characterization of BC₂.²² To the authors' knowledge, nothing at all is known on B₂C, except that it has been detected in laser mass spectra of boron carbide²³ and that some small basis set Hartree-Fock calculations have been performed on the linear forms BBC and BCB.²⁴ The purpose of this paper is therefore to present an accurate *ab initio* study of BC and B₂C, including anharmonic force fields for their respective ground states.

METHODS

Since both the BBC and BCB structures of the B₂C molecule have singlet ground states that are essentially bicon-

figurational (*vide infra*), single configuration SCF methods are essentially useless when it comes to predicting the relative energy of different structures and states for B₂C. Therefore full-valence CASSCF (complete active space SCF) calculations²⁵ were carried out instead, in which the variationally optimized wave function is a linear combination of all configuration state functions (CSFs, i.e., symmetry- and spin-adapted linear combinations of Slater determinants) that can be generated by arranging 10 valence electrons in 12 valence orbitals. Since higher angular momentum polarization functions are essentially intended for external correlation effects and are thus not necessary at this level, the basis set used for the CASSCF calculations was Dunning's correlation-consistent²⁶ valence double zeta plus polarization set, which is a [3s2p1d] contraction of a (9s4p1d) primitive set. Optimizations and harmonic frequency calculations were carried out using analytical second derivatives.

For the ground state of B₂C, which we will see below to have relatively small nondynamical correlation effects, further calculations were carried out using the CCSD(T) method,²⁷ which is the coupled cluster method²⁸ with all single and double excitations (CCSD)^{14,29} augmented by a quasiperturbative estimate for the effect of triple excitations.²⁷ For systems dominated by a single reference configuration, this method has been shown to yield correlation energies very close to the full configuration interaction (FCI) limit.^{30,31}

A quartic force field was calculated at the CCSD(T) level using Dunning's cc-pVTZ (correlation consistent valence triple zeta plus polarization) basis set,²⁶ which is a [4s3p2d1f] contraction of a (10s5p2d1f) primitive set. Pure spherical harmonics were used and (1s)-like core orbitals constrained to be doubly occupied. A grid was generated of all points required to generate all nonvanishing quadratic, cubic, and quartic force constants in symmetry

TABLE I. Computed total energies (E_h), geometries (Å), harmonic frequencies (cm⁻¹), and (in parentheses) infrared intensities (km/mol) for B₂C, and anharmonic spectroscopic constants (cm⁻¹) for BC at different levels of theory.

CASSCF[10/12]/cc-pVDZ		
BC(⁴ Σ ⁻)	-62.405 96	$R_{BC}=1.5225$ 1131(σ ,30)
B ₂ C(¹ Σ _g ⁺)	-87.178 88	$R_{BC}=1.3942$ 1863(σ_u ,274),1101(σ_g),204(π_u ,15×2)
B ₂ C(³ Σ _u ⁺)	-87.170 19	$R_{BC}=1.3888$ 1886(σ_u ,318),1123(σ_g),163(π_u ,5×2)
B ₂ C(¹ A ₁)	-87.197 05	$R_{BC}=1.4257,R_{BB}=1.6580$ 1424(a_1 ,31),1259(b_2 ,27),663(a_1 ,4)
B ₂ C(³ B ₂)	-87.174 50	$R_{BC}=1.4153,R_{BB}=1.9796$ 1354(a_1 ,0.6),373(a_1 ,3),1477(b_2 ,59)
B ₂ C(¹ Σ ⁺)	-87.098 18	$R_{BC}=1.4044,R_{BB}=1.5605$ 1629(σ ,71),900(σ ,7),202(π ,2×2)
B ₂ C(³ Σ ⁺)	-87.086 92	$R_{BC}=1.4012,R_{BB}=1.5575$ 1624(σ ,105),904(σ ,1),211(π ,1×2)
UHF-CCSD(T)/TZ2P ^a		
BC(⁴ Σ ⁻)	-62.556 11	$R_{BC}=1.5027$ 1083(σ ,43)
B ₂ C(¹ A ₁)	-87.410 46	$R_{BC}=1.4069,R_{BB}=1.5962$ 1433(a_1 ,5),1237(b_2 ,8),753(a_1 ,2)
CASSCF/ACPF/cc-pVTZ		
BC(⁴ Σ ⁻)	-62.539 50	$R_{BC}=1.5072$ $\omega_e=1143.6,\omega_e x_e=10.2,\alpha_e=0.016$ 28
UHF-CCSD(T)/cc-pVTZ		
BC(⁴ Σ ⁻)	-62.533 95	$R_{BC}=1.5078$ $\omega_e=1092.3,\omega_e x_e=28.2,\alpha_e=0.024$ 13
RHF-CCSD(T)/cc-pVTZ ^b		
BC(⁴ Σ ⁻)	-62.534 16	$R_{BC}=1.5015$ $\omega_e=1147.9,\omega_e x_e=10.2,\alpha_e=0.016$ 72
B ₂ C(¹ A ₁)	-87.377 54	$R_{BC}=1.4142,R_{BB}=1.6031$ 1428(a_1),1228(b_2),748(a_1)
RHF-CCSD(T)/cc-pVQZ ^c		
BC(⁴ Σ ⁻)	-62.545 56	
B ₂ C(¹ A ₁)	-87.399 01	

^aCore correlation included and Cartesian d functions used for technical reasons.

^bCCSD(T)/cc-pVTZ atomic energies: B-24.598 04, C-37.780 64 E_h .

^cCCSD(T)/cc-pVQZ atomic energies: B-24.600 77, C-37.786 41 E_h .

adapted internal coordinates. This required a total of 55 points. (Generally, grids in symmetry coordinates require more points than those in internal coordinates, but the individual geometries have higher symmetry on the average and thus require less CPU time.) Step sizes used were 0.01 Å and radian. The force field thus obtained was transformed to Cartesian coordinates using the program INTDER by Allen. The subsequent anharmonic vibrational analysis was performed using standard second order rovibrational perturbation theory^{32,33} with the aid of the SPECTRO program.^{34,35}

In order to obtain infrared intensities that include external correlation, CCSD(T) gradient calculations were carried out with the Huzinaga–Dunning TZ2P (triple zeta plus two polarization functions) basis set.^{36,37} For computational reasons, the $1s$ core electrons were correlated and Cartesian polarization functions were used in these calculations.

Since the small size and well-defined ground state ($X^4\Sigma^-$) of the BC molecule allow for more advanced calculations, the above methods were supplemented here with multireference averaged coupled pair functional (ACPF)³⁸ results based on a full-valence CASSCF reference wave function. Anharmonic spectroscopic constants for this system were generated by a Dunham analysis³⁹ on a sixth-order polynomial fitted through 11 points around the minimum (a step size of 0.01 bohr was used). Additionally, since this is an open-shell system, both UHF-CCSD(T)²⁷ and RHF-CCSD(T)^{40,41} calculations were performed on this system—that is, both unrestricted Hartree–Fock and spin-restricted Hartree–Fock reference configurations were used.

Finally, in order to obtain accurate total atomization energies, CCSD(T) single-point calculations were carried out with the cc-pVQZ (correlation consistent polarized valence

quadruple zeta) basis set,²⁶ which is a $[5s4p3d2f1g]$ contraction of a $(12s6p3d2f1g)$ primitive set.

The CASSCF geometry optimizations and frequencies were obtained using the SIRIUS/ABACUS package on an IBM RS/6000 model 365 workstation at LUC. The CCSD(T) gradient calculations were performed using ACES II⁴² on an IBM RS/6000 model 350 workstation at SDSC. All other calculations (such as the single-point CCSD(T) and ACPF calculations) were run using the MOLECULE/SWEDEN/TITAN program system^{43,44} with the SEWARD integral package^{45,46} running on the Cray Y-MP/864 and Cray C90/8128 computers at SDSC.

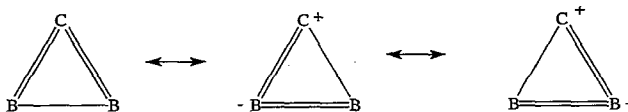
RESULTS AND DISCUSSION

For BC, it is well known from previous *ab initio* studies that the ground state is $X^4\Sigma^-$, with a $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^1(1\pi)^2$ occupation scheme. We will therefore focus exclusively on that state. Computed UHF-CCSD(T) spectroscopic constants with the cc-pVTZ basis set are given in Table I. The \mathcal{S}_1 diagnostic,⁴⁷ which is a measure for the importance of nondynamical correlation, has a value of 0.10; one of the largest we have seen and which (based on our previous experience with BN) should render CCSD(T) results essentially useless. And indeed, the computed ω_e of 1092 cm⁻¹ is no less than 52 cm⁻¹ lower than the result obtained at the ACPF level using a full-valence CASSCF reference, and the anharmonicity constant $\omega_e x_e$ is almost a factor of 3 too high. (A large deviation is also seen in the rotation-vibration coupling constants α_e .) Peculiarly, the computed equilibrium bond distances are in almost perfect agreement.

However, since the expectation value of the S^2 operator indicates substantial spin contamination ($\langle S^2 \rangle \approx 4.0$) it is possible that the high \mathcal{S}_1 is an artifact of the latter. In order to investigate this, we have repeated the calculation with an RHF reference wave function, and as Table I shows, this resolves the discrepancy almost completely. The computed ω_e is now 1148 cm^{-1} , only 4 cm^{-1} higher than the CASSCF/ACPF result. Both $\omega_e x_e$ and α_e are now in almost perfect agreement between the two methods. This result also helps explain the relatively poor agreement between UHF-CCSD(T)/TZ2P and experiment that was obtained for BNN(²II),¹¹ where spin contamination is also high. We expect ω_e to be correct to about $\pm 10 \text{ cm}^{-1}$. Taking into account the average overestimation of double bond lengths at the CCSD(T)/cc-pVTZ level of $0.006\text{--}7 \text{ \AA}$, we give a best estimate for r_e of $1.495 \pm 0.002 \text{ \AA}$.

B₂C. Computed spectroscopic constants at various levels of theory are again given in Table I. The valence occupation scheme for BCB(¹ Σ_g^+) is $(3\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(4\sigma_g)^2(3\sigma_u)^0$. The $(4\sigma_g)$ HOMO here corresponds to a symmetric combination of two lone-pair orbitals, where the antisymmetric combination ($3\sigma_u$) is nearly degenerate with it in energy. It is hardly surprising that, under these circumstances, the wave function for BCB(¹ Σ^+) is almost biconfigurational, and that a single-configuration SCF treatment produces essentially meaningless results. The situation is effectively the same as for a low-spin coupling in a degenerate orbital; the “high-spin” case, which corresponds here to the $^3\Sigma_u^+$ state $\cdots(4\sigma_g)^1(3\sigma_u)^1$, is found to be only slightly higher in energy. The situation is similar for BBC(¹ Σ^+) and BBC(³ Σ^+), with a $(6\sigma) \rightarrow (7\sigma)$ near degeneracy. Here, too, the $^3\Sigma^+$ state is found to be only slightly above the $^1\Sigma^+$ state. As predicted in Thomson’s twenty-year old SCF study,²⁴ BCB(¹ Σ^+) is indeed more stable than BBC(¹ Σ^+). However, neither is in fact the lowest energy structure.

The true global minimum is actually is a C_{2v} -symmetric cyclic structure with a ¹ A_1 ground state and the valence occupation scheme $\cdots(3a_1)^2(2b_2)^2(4a_1)^2(1b_1)^2(5a_1)^2$. Inspection of the computed geometry quickly shows that both BC and BB bond distances are near the optimal values for double bonds. The electronic structure is then probably best described as the resonance



which involves *two* aromatic systems with two electrons each—a “conventional” one with the occupation scheme $(1b_1)^2(1a_2)^0(2b_1)^0$ and an “in-plane” aromatic system (as is well known in carbon clusters⁴⁸) with the occupation scheme $(5a_1)^2(3b_2)^0(6a_1)^0$. This makes the molecule rather unique among neutral triatomics; isoelectronic ions would be B_2N^+ or B_3^- . On the triplet surface, too, the cyclic structure (³ B_2 state) is found to be the lowest in energy, although the separation with the $^3\Sigma_u^+$ state is much smaller than the ¹ A_1 –¹ Σ_g^+ separation.

Summarizing, it is fairly clear that only the ¹ A_1 state is

TABLE II. CCSD(T)/cc-pVTZ quartic force field for B₂C (¹ A_1). Units are aJ, Å, and degree.

$F_{11}=F_{22}$	6.564 50
F_{12}	0.409 23
$F_{13}=F_{23}$	1.553 04
F_{33}	3.117 11
$F_{111}=F_{222}$	−34.749 76
$F_{211}=F_{221}$	−1.311 46
$F_{311}=F_{322}$	−1.253 01
F_{321}	−4.945 76
$F_{331}=F_{332}$	−9.338 52
F_{333}	−28.722 61
$F_{1111}=F_{2222}$	158.059 21
$F_{2111}=F_{2221}$	−0.058 86
F_{2211}	6.294 60
$F_{3111}=F_{3222}$	−7.671 42
$F_{3211}=F_{3221}$	10.348 21
$F_{3311}=F_{3322}$	0.258 76
F_{3321}	27.767 88
$F_{3331}=F_{3332}$	44.099 85
F_{3333}	186.660 85

important for our further spectroscopic investigation. This is fortunate, since this state has fairly limited multireference character: the \mathcal{S}_1 diagnostic⁴⁷ is found to be only 0.035, which indicates a system that has some multireference character, but should still be tractable at the CCSD(T) level.

As seen from Table I, both CASSCF/cc-pVDZ and CCSD(T)/TZ2P calculations predict all three bands of B₂C(¹ A_1) to be fairly weak. (It is worth noting here that there is only very weak coupling between the symmetric stretching and bending modes.) It could be argued that it is all the more important to have accurate predictions in such a case, and we have therefore calculated a quartic force field at the CCSD(T)/cc-pVTZ level. The internal coordinate force field can be found in Table II, while predicted spectroscopic constants using second-order vibrational perturbation theory are given in Table III for ¹¹B₂C, ¹¹BC¹⁰B, and ¹⁰B₂C. One feature is immediately conspicuous: the severe Fermi resonance between the bending and symmetric stretching vibrations. The resulting states are essentially 50:50 mixtures between (100) and (020) states; therefore both bands would probably be observed. One of both Fermi states has a very pronounced isotopic effect: for the other state and the remaining two fundamentals, differences between harmonic and anharmonic isotopic shifts are only on the order of 3 and 1 cm^{-1} , respectively. Regarding the geometry, we know from experience⁴⁹ that CCSD(T)/cc-pVTZ will overestimate the length of double bonds by $0.006\text{--}7 \text{ \AA}$, and that of single bonds by about 0.002 \AA . From the computed r_0 geometry of $r_0=1.421 \text{ \AA}$ and $\theta_0=69.2^\circ$, we then propose a best estimate for the geometry of B₂C of $r_0=1.414 \text{ \AA}$ and $\theta=69.5^\circ$, which we expect to be accurate to within $\pm 0.002 \text{ \AA}$ and 0.3° .

Thermochemistry. From the energies in Tables I and III, we can obtain accurate total atomization energies using the correction formula published by Martin,⁴⁹ which has the form

$$\Delta E = n_\sigma a_\sigma + n_\pi b_\pi + n_{\text{pair}} c_{\text{pair}}$$

TABLE III. Anharmonic spectroscopic constants (cm⁻¹) for B₂C and some isotopomers.

	¹¹ B ¹¹ B ¹² C	¹¹ B ¹⁰ B ¹² C	¹⁰ B ¹⁰ B ¹² C
$r_0(\text{B}_1, \text{C})$	1.4210	1.4210	1.4212
$r_0(\text{B}_2, \text{C})$	1.4210	1.4212	1.4212
θ_0	69.2361	69.2461	69.2557
ω_1	1427.82	1448.51	1465.91
ω_2	1228.11	1245.38	1265.98
ω_3	747.65	762.47	776.88
F_{13}	-56.79	-61.42	-66.30
$\nu_1(\text{deperturbed})$	1404.76	1424.92	1442.03
ν_2	1203.84	1220.65	1240.55
ν_3	719.05	732.56	745.68
$2\nu_3$	1461.58	1489.21	1515.41
$\nu_1(\text{corr})$	1348.00	1366.25	1382.12
X_{11}	-5.38	-5.68	-5.54
X_{12}	-22.06	-21.89	-22.83
X_{13}	-2.54	-2.57	-2.76
X_{22}	-9.60	-9.87	-10.01
X_{23}	11.92	11.89	12.04
X_{33}	-16.64	-17.29	-17.92
ZPE (kcal/mol)	4.83	4.91	4.98
A_e	1.598 79	1.631 23	1.654 92
B_e	1.191 59	1.246 51	1.310 17
C_e	0.682 74	0.706 58	0.731 25
$\alpha 1a$	0.011 25	0.012 00	0.011 74
$\alpha 2a$	0.022 72	0.022 47	0.024 05
$\alpha 3a$	-0.032 04	-0.032 50	-0.034 35
$\alpha 1b$	0.002 71	0.002 63	0.003 35
$\alpha 2b$	-0.010 49	-0.010 32	-0.011 76
$\alpha 3b$	0.025 39	0.026 42	0.028 85
$\alpha 1c$	0.002 33	0.002 53	0.002 81
$\alpha 2c$	0.000 01	0.000 01	-0.000 06
$\alpha 3c$	0.009 77	0.010 16	0.010 57
$10^6 D_J$	5.161 6	5.522 7	6.202 0
$10^6 D_{JK}$	21.232 8	21.177 5	23.733 9
$10^6 D_K$	-12.221 9	-12.251 2	-14.751 0
$10^6 d_J$	2.200 8	2.361 2	2.679 6
$10^6 d_K$	1.974 5	2.228 5	1.725 5
$10^6 R_6$	-0.394 0	-0.427 9	-0.497 2
$10^{10} H_J$	-0.293 9	-0.354 2	-0.389 2
$10^{10} H_K$	17.526 5	18.237 5	20.438 8
$10^{10} H_{JK}$	5.180 1	5.784 2	6.445 4
$10^{10} H_{KJ}$	-18.064 6	-19.230 6	-21.672 8
$10^{10} h_J$	-0.144 7	-0.175 1	-0.193 1
$10^{10} h_{JK}$	0.902 3	1.060 3	1.212 0
$10^{10} h_K$	-0.051 8	-0.066 5	-0.475 1

in which n_σ , n_π , and n_{pair} represent the number of σ bonds, π bonds, and lone pairs, respectively, and a , b , and c are constants specific to the basis set, electron correlation, and level of theory for the reference geometry. More specifically, these constants are obtained by a fitting procedure in which calculated binding energies are adjusted to obtain best agreement with experimental values for a series of well-characterized molecules. Full details are given in Ref. 49. For CCSD(T)/cc-pVTZ energies at a CCSD(T)/cc-pVTZ reference geometry, $a = -0.706$, $b = 0.784$, and $c = 3.798$ kcal/mol;⁴⁹ for CCSD(T)/cc-pVQZ energies, these constants become $a = -0.089$, $b = 0.668$, and $c = 1.277$ kcal/mol.⁴⁹ There is some ambiguity involved here, in that it is not very clear whether the two high-spin coupled electrons in the π orbital should be counted as one π bond, but in view of the rather large uncorrected D_e value (97.6 kcal/mol with the

cc-pVTZ and 99.4 kcal/mol with the cc-pVQZ basis set), we are inclined to assert that they should be. With the cc-pVTZ basis set, the corrected D_e is then found to be 97.6 kcal/mol, with an expected accuracy of ± 1 to 2 kcal/mol. (The agreement between uncorrected and corrected values results from a fortuitous cancellation between a and b , and the fact that no new electron pairs are formed in the molecule.) With the cc-pVQZ basis set, however, the value increases to 100.0 kcal/mol, with an expected error of ± 0.5 to 1 kcal/mol. This rather large D_e value is somewhat less than that for BN⁸ but shows that a boron-carbon bond can be fairly strong. From the calculated ω_e and $\omega_e x_e$ in Table I, we find a zero-point energy (ZPE) of 1.63 kcal/mol [both at the CAS-ACPF and RHF-CCSD(T) levels], which finally leads to $D_0(\text{BC}) = 98.3$ kcal/mol.

The same calculation for B₂C shows that it is surprisingly strongly bound: with the cc-pVTZ basis set, the corrected ΣD_e is found to be no less than 258.6 kcal/mol, a value that is similar to the very strongly bound B₂N molecule. With the cc-pVQZ basis set, this value even increases to 261.6 kcal/mol, with an expected error of 0.5 to 1 kcal/mol. For species with more than one multiple bond, this kind of difference between the corrected cc-pVTZ and cc-pVQZ results is by no means unusual.⁴⁹ Using the anharmonic zero-point energy (ZPE) in Table III, we find $\Sigma D_0 = 256.8 \pm 1$ kcal/mol.

Given the low D_e of B₂,⁵⁰ it is obvious that the thermodynamically preferred channel for fragmentation would be $\text{B}_2\text{C}(^1A_1) \rightarrow \text{BC}(^4\Sigma^-) + \text{B}(^2P)$. Since the reaction from ground state to ground state is spin-forbidden, however, it is possible that dissociation actually goes to $\text{C}(^3P) + \text{B}_2(^3\Sigma_u^-)$.

The only experimental observations with which we can correlate these data, so far, are the mass spectrometric experiments of Becker and Dietze,²³ who describe the cluster distribution in a laser plasma of boron carbide. They find B₂C⁻, followed closely by BC₂, to be by far the most abundant small cluster in the anion spectrum (the most abundant cluster overall is BC₄⁻), while B₂C⁺ is among the most abundant species in the cation spectrum. Since cation and anion spectra are quite different, the relative abundances are probably more a function of the relative stabilities of the ions than of the neutral species: it is then readily seen why B₂C⁻ (isoelectronic with the very stable molecules C₃⁺, BC₂, and B₂N) will be more prominent than B₂C⁺ (isoelectronic with B₃).

CONCLUSIONS

The ground state of B₂C is an extraordinarily stable ring ($\Sigma D_e = 261.6 \pm 1$ kcal/mol) with two 2-electron π systems. Second lowest in energy is linear BCB ($^1\Sigma_g^+$), which is essentially biconfigurational due to a $(4\sigma_g) - (3\sigma_u)$ near degeneracy. Best estimates for the spectroscopic constants are $\omega_1 = 1428$, $\omega_2 = 1228$, and $\omega_3 = 748$ cm⁻¹; $\nu_1(\text{deperturbed}) = 1405$, $\nu_2 = 1204$, and $\nu_3 = 719$ cm⁻¹; $r_0(\text{BC}) = 1.414$ Å, and $\theta_0 = 69.5^\circ$. A severe Fermi resonance exists between $2\omega_3$ and ω_1 ; best estimates for the Fermi levels are 1462 and 1348 cm⁻¹.

Best estimates for the molecular constants of BC($^4\Sigma^-$) are $D_e = 100.0 \pm 1$ kcal/mol, $\omega_e = 1147.9 \pm 10$, $\omega_e x_e$

= 10.2, $\alpha_e = 0.01672 \text{ cm}^{-1}$, and $r_e = 1.495 \pm 0.002 \text{ \AA}$. Computed spectroscopic constants using elaborate multireference methods are well reproduced at the CCSD(T) level with an RHF, but not with a UHF, reference, implying that moderate levels of spin contamination may not substantially affect relative energies but may compromise the quality of computed spectroscopic constants.

Note added in proof. After acceptance of this article, we discovered Knudsen cell experimental values for ΣD_0 (B₂C) = 254 kcal/mol [G. Verhaegen, F. E. Stafford, and J. Drowart, *J. Chem. Phys.* **40**, 1622 (1964)] and 260 ± 10 kcal/mol [G. Verhaegen, F. E. Stafford, M. Ackerman, and J. Drowart, technical report quoted in previous reference], in agreement with our computed value of 256.8 ± 1 kcal/mol. These authors note that substantial resonance energy is present, which they estimate at about 20% of the total atomization energy. The same references list D_0 (BC) = 106 and 105 ± 10 kcal/mol, respectively, substantially higher than our computed value of 98.3 ± 1 kcal/mol; this is probably not significant, however, given the large experimental uncertainty. Additionally, the following experimental spectroscopic constants are given for BC ($X^4\Sigma^-$) in W. T. M. L. Fernando, L. C. O'Brien, and P. F. Bernath, *J. Chem. Phys.* **93**, 8482 (1990); $r_e = 1.4916(34) \text{ \AA}$, $\alpha_e = 0.01733(46) \text{ cm}^{-1}$; compared to our RCCSD(T)/cc-pVTZ computed values of 1.5015 \AA and 0.01672 cm^{-1} . The error in the bond distance is somewhat bigger than the expected overestimation of a double bond length by 0.006–0.007 Å at this level of theory.⁴⁹

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¹C. M. Niu, Y. Z. Lu, and C. M. Lieber, *Science* **261**, 334 (1993).

²A. Meller, in *Gmelin's Handbook of Inorganic Chemistry*, 8th ed., 3rd supplement: Boron compounds (Springer, Berlin, 1988).

³J. J. Pouch and S. A. Alterovitz, *Synthesis and Properties of Boron Nitride* (Trans Tech, Zürich, 1990).

⁴F. Kaminaga, S. Sato, and Y. Okamoto, *J. Nucl. Sci. Tech.* **29**, 121 (1992).

⁵J. P. Coad, B. Farmery, J. Linke, and E. Wallura, *J. Nucl. Mater.* **200**, 389 (1993).

⁶T. Shikama, M. Fujitsuka, H. Araki, T. Noda *et al.*, *J. Nucl. Mater.* **191**, 611 (1992).

⁷B. M. Swinyard, *J. Spacecr. Rockets* **28**, 730 (1991).

- ⁸J. M. L. Martin, T. J. Lee, G. E. Scuseria, and P. R. Taylor, *J. Chem. Phys.* **97**, 6549 (1992).
- ⁹J. M. L. Martin, J. P. François, and R. Gijbels, *J. Chem. Phys.* **90**, 6469 (1989).
- ¹⁰L. Andrews, P. Hassanzadeh, T. R. Burkholder, and J. M. L. Martin, *J. Chem. Phys.* **98**, 922 (1993).
- ¹¹J. M. L. Martin and P. R. Taylor, *Chem. Phys. Lett.* (in press).
- ¹²Z. Slanina, J. M. L. Martin, J. P. François, and R. Gijbels, *Chem. Phys. Lett.* **201**, 54 (1993).
- ¹³J. M. L. Martin, Z. Slanina, J. P. François, and R. Gijbels, *Mol. Phys.* (in press).
- ¹⁴J. M. L. Martin and P. R. Taylor (unpublished).
- ¹⁵K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ¹⁶J. M. L. Martin and P. R. Taylor, *Chem. Phys. Lett.* (submitted).
- ¹⁷P. Botschwina and J. Flugge, *Chem. Phys. Lett.* **180**, 589 (1991); (E) **210**, 495 (1993).
- ¹⁸P. Botschwina, *J. Chem. Phys.* **99**, 6217 (1993).
- ¹⁹G. Hirsch and R. J. Buenker, *J. Chem. Phys.* **87**, 6004 (1988).
- ²⁰N. Oliphant and L. Adamowicz, *Chem. Phys. Lett.* **168**, 1126 (1990).
- ²¹L. B. Knight Jr., S. T. Cobranchi, J. T. Petty, E. Earl, D. Feller, and E. R. Davidson, *J. Chem. Phys.* **90**, 690 (1989).
- ²²J. M. L. Martin, P. R. Taylor, J. T. Yustein, T. R. Burkholder, and L. Andrews, *J. Chem. Phys.* **99**, 12 (1993).
- ²³S. Becker and H. J. Dietze, *Int. J. Mass Spectrosc. Ion Proc.* **82**, 287 (1988).
- ²⁴C. Thomson, *J. Chem. Phys.* **58**, 216 (1973).
- ²⁵B. O. Roos, *Adv. Chem. Phys.* **69**, 399 (1987).
- ²⁶T. H. Dunning Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ²⁷K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- ²⁸R. J. Bartlett, *J. Phys. Chem.* **93**, 1697 (1989).
- ²⁹G. D. Purvis III and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
- ³⁰T. J. Lee, A. P. Rendell, and P. R. Taylor, *J. Phys. Chem.* **94**, 5463 (1990).
- ³¹G. E. Scuseria and T. J. Lee, *J. Chem. Phys.* **93**, 5851 (1990).
- ³²H. H. Nielsen, *Rev. Mod. Phys.* **22**, 90 (1951).
- ³³J. K. G. Watson, in *Vibrational Spectra and Structure: A Series of Advances*, edited by J. R. Durig (Elsevier Scientific, Amsterdam, 1977), p. 1.
- ³⁴J. F. Gaw, A. Willetts, W. H. Green, and N. C. Handy, in *Advances in Molecular Vibrations and Collision Dynamics*, edited by J. M. Bowman (JAI, Greenwich, 1990).
- ³⁵A. Willetts, J. F. Gaw, W. H. Green Jr., and N. C. Handy, SPECTRO 2.0, a second-order rovibrational perturbation theory program.
- ³⁶S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ³⁷T. H. Dunning, Jr., *J. Chem. Phys.* **55**, 716723 (1971).
- ³⁸R. J. Gdanitz and R. Ahlrichs, *Chem. Phys. Lett.* **143**, 413 (1988).
- ³⁹J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).
- ⁴⁰G. E. Scuseria, *Chem. Phys. Lett.* **176**, 27 (1991).
- ⁴¹J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
- ⁴²J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, D. E. Bernholdt, and R. J. Bartlett, ACES II, an ab initio program system.
- ⁴³J. Almlöf, C. W. Bauschlicher Jr., 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, MOLECULE/SWEDEN, an electronic structure program system.
- ⁴⁴T. J. Lee, A. P. Rendell, and J. E. Rice, TITAN, a set of electronic structure programs.
- ⁴⁵R. Lindh, SEWARD, a vectorized two-electron integral package.
- ⁴⁶R. Lindh, U. Ryu, and B. Liu, *J. Chem. Phys.* **95**, 5889 (1991).
- ⁴⁷T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem. Symp.* **23**, 199 (1990).
- ⁴⁸K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).
- ⁴⁹J. M. L. Martin, *J. Chem. Phys.* (in press).
- ⁵⁰M. Dupuis and B. Liu, *J. Chem. Phys.* **68**, 2902 (1978).