Pulsed laser evaporation of boron/carbon pellets: Infrared spectra and quantum chemical structures and frequencies for BC$_2$

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Pulsed laser evaporation of pellets pressed from boron and graphite powder gave a new 1:4 doublet at 1232.5 and 1194.6 cm$^{-1}$ in addition to the carbon cluster absorptions reported previously. The 1232.5 cm$^{-1}$ band dominated boron 10 experiments. The new bands increased as carbon cluster bands decreased with increasing B/C ratio in the pellet and with increasing laser power. Augmented coupled cluster and full-valence complete active space SCF (CASSCF) calculations predict the global minimum BC$_2$ structure to be an asymmetric triangle: however, the vibrationally averaged structure will be an isosceles triangle with a strong symmetric B–C$_2$ stretching frequency near 1200 cm$^{-1}$. The calculated boron-10/boron-11 frequency ratio (1.0323) is in excellent agreement with the observed ratio (1.0317), and confirms assignment of the 1194.6 cm$^{-1}$ band to the BC$_2$ ring. Calculations predict linear BCC to be less stable by 6.2±2 kcal/mol and to absorb in the 2000–2050 cm$^{-1}$ range: the barrier towards rearrangement to the cyclic structure is very low (1.1 kcal/mol). Linear BCC was not detected in these experiments. Computed energetics explain why BC$_2$ is abundant in B/C experiments, but absent in B+C$_2$H$_2$ experiments.

INTRODUCTION

Carbon clusters have attracted considerable recent interest because of their role in soot formation, flame chemistry, and astrophysics. The early work involving carbon vaporized from graphite has recently been supplemented by pulsed laser evaporation and the formation of small carbon clusters including C$_4$, C$_5$, C$_6$, and C$_c$ in solid argon have been discussed. Reassignment of the various bands of C$_n$ (n=4–9) involved was suggested on the basis of quantum chemical calculations and has since been proven experimentally to be correct (see Refs. 4 and 7 and references herein). Boron cluster studies, on the other hand, have been limited to B$_2$ and B$_3$. Mixed boron/carbon clusters have received little attention as well. The diatomic BC has only been characterized by electron spin resonance spectroscopy in noble gas matrices. An early report of BCC has recently been suggested by Knight to instead describe the symmetrical CBC species. Early ab initio calculations suggest that linear BCC is more stable than linear CBC. Pulsed laser evaporation of boron for matrix reactions with small molecules such as O$_2$, H$_2$O, and N$_2$ has been employed in this laboratory. It was therefore decided to pulse laser evaporate mixed boron/carbon samples in search of mixed boron/carbon clusters. Natural isotopic boron provides vibrational spectroscopic evidence for the inclusion of boron in a mixed cluster.

COMPUTATIONAL METHODS

All of the calculations were carried out using either the ACES II or SIRIUS/ABACUS program systems running on either the CRAY Y-MP 8/864 at the San Diego Supercomputer Center, or an IBM RS/6000/350 workstation at the same institution. Geometry and harmonic frequency calculations were carried out at the full-valence (i.e., 11 electrons in 12 orbitals) complete active space SCF (CASSCF) level with the cc-pVDZ (correlation-consistent valence double zeta plus polarization) basis set. Some calculations were also attempted in which the lowest external orbital was included in the active space as well. Additionally, geometries and harmonic frequencies were also determined using the CCSD(T) method, which is an augmentation of the coupled cluster with all singles and doubles (CCSD) method with a quasiperturbative estimate for connected triple excitations. Analytical gradients were used throughout in these calculations. The basis sets used here were both cc-pVDZ and the Huzinaga-Dunning triple-zeta plus two polarization (TZ2P) basis set.

EXPERIMENTAL METHODS

The experimental methods for laser ablation of solids for matrix infrared spectroscopy have been discussed previously. Pellets (13 mm diam×2 mm thick) were pressed (10 tons) from mixtures of natural boron and graphite powder (Aldrich) with different compositions and from mixed enriched boron-10 and graphite. Boron powder was prepared by crushing boron pieces (Aldrich or Eagle-Pitcher) in the pellet press. Several attempts to prepare boron/amorphous carbon-13 pellets were not successful; however, a boron/graphite/amorphous carbon-13 pellet with B/C=5/1 was ablated with limited success. These pellets were laser ablated for 2–4 h by focused YAG fundamental ranging from 20–50 mJ/pulse at the target. In-
Infrared spectra were recorded on a Nicolet 5-DXB Fourier transform instrument at 2 cm\(^{-1}\) resolution and frequency accuracy ±0.5 cm\(^{-1}\).

**EXPERIMENTAL RESULTS**

Laser ablation of carbon/boron targets for matrix infrared examination of new species will be described.

**Carbon**

A graphite target was used to characterize carbon species that might be produced with mixed B/C samples. Infrared spectra contained dominant carbon cluster bands at 2164.2 (C\(_3\)), 2038.9 (C\(_2\)), 1999.1 (C\(_4\)), 1952.6 (C\(_5\)), and 1543.4 cm\(^{-1}\) (C\(_6\)) that have been observed in similar experiments and weaker carbon cluster bands at 1446.5 and 1197.9 cm\(^{-1}\).\(^{d}\)

**Boron/carbon**

Ablation of a 1/1 molar ratio B/C pellet produced the strong carbon cluster absorptions in the 2200-1800 cm\(^{-1}\) region described above and new shoulders appeared at 1899.7 and 1194.6 cm\(^{-1}\) on 1894.6 and 1197.9 cm\(^{-1}\) carbon cluster bands. A new band was also observed at 1602.0 cm\(^{-1}\) in the water region. The laser power was kept low (20 mJ/pulse) to minimize total carbon ablation. It was clear that carbon clusters dominated the spectrum from a B/C=1/1 target, and that the boron concentration must be increased to produce new binary species.

Increasing the boron concentration to a molar ratio B/C=2.5/1 decreased the carbon cluster band intensities significantly as shown in Table I. In the 1350-1150 cm\(^{-1}\) region the 1194.6 cm\(^{-1}\) absorption with a 1232.5 cm\(^{-1}\) counterpart dominated the 1197.9 cm\(^{-1}\) band. Three experiments were run with B/C=5/1 pellets using different laser powers. The first employed 40 mJ/pulse at the sample; the carbon cluster absorptions were decreased and the 1194.6 cm\(^{-1}\) band was increased relative to the carbon cluster absorptions. Annealing this sample to 25±1 K increased C\(_3\), C\(_9\), C\(_6\) and 1197.9 cm\(^{-1}\) bands and decreased C\(_1\) and the 1194.6 cm\(^{-1}\) band. Further increasing the laser power to 45 mJ/pulse with the same B/C=5/1 pellet produced the spectrum illustrated in Fig. 1(a). The major band at 1194.6 cm\(^{-1}\) was further enhanced and exhibited a new low frequency shoulder at 1188.7 cm\(^{-1}\) and the 1232.5 cm\(^{-1}\) counterpart exhibited a similar shoulder at 1226.6 cm\(^{-1}\). Bands for \(^{10}\)BO\(_2\) were observed at 1299.3, 1282.8, and 1274.6 cm\(^{-1}\). The 1197.9 cm\(^{-1}\) band was not detected and C\(_3\) and C\(_4\) bands were reduced further.

Another experiment was run with still higher laser power (50 mJ/pulse) focused to give a bright yellow-white flash from the target. Spectra recorded on a Nicolet 60 SXR at 0.5 cm\(^{-1}\) resolution revealed the sharp boron isotopic doublet at 1232.5±0.1 and 1194.6±0.1 cm\(^{-1}\) (\(A = 0.01\) and 0.04, respectively) and carbon cluster band intensities were reduced even further. The sample was photolyzed for 30 min by the full output of a 175-W mercury arc; the boron doublet decreased by 25%. The sample was annealed to 30±1 K, and the boron doublet decreased another 30% while the 1899.7 cm\(^{-1}\) band increased.

A similar \(^{10}\)B/C = 5/1 pellet gave the spectrum in Fig. 1(b). The 1232.5 cm\(^{-1}\) band and 1226.6 cm\(^{-1}\) satellite dominated. Weak \(^{10}\)BO\(_2\) bands at 1347.6 and 1322.3 cm\(^{-1}\) and a weak 1197.9 cm\(^{-1}\) band were observed. Again the same carbon cluster bands were observed in the 2200-1700 cm\(^{-1}\) region along with the 1899 7 cm\(^{-1}\) feature.

A boron carbide/graphite pellet (1/1 by weight) was prepared and ablated. Weak bands were observed at 1197.9 and 1194.6 cm\(^{-1}\) along with the same carbon cluster bands and a weak band at 1899 cm\(^{-1}\).

The species ablated from a B/C=5/1 pellet were code-
posed with Ar/O₂=400/1 sample. This experiment gave
more intense ¹¹BO₂ and ¹⁰BO₂ absorptions and the absorp-
tions reported above with the same intensities. Weak CO
and CO₂ absorptions were observed without any enhance-
ment.

Finally, a B/C = 5/1 (carbon-12 graphite and amor-
phous carbon-13) pellet was ablated in several exper-
mits. The mixed carbon isotopic sextet for C₃ was ob-
cm⁻¹ as reported previously, but no new bands could be
observed. This soft pellet did not withstand ablation as well
as the boron–graphite pellets.

Boron

The ablation of pure natural boron into condensing
argon, reported previously, produced only traces of BO₂ at
1274.6 cm⁻¹, BOB at 1420.5 cm⁻¹, and B₂N₂ at 1912.7
cm⁻¹ with no bands in the 1250–1150 cm⁻¹ region. This
experiment has been repeated several times, and no new
absorptions were observed that could be due to boron
clusters. It is clear that boron vapor species are very dif-
ferent from graphite vapor species.

DISCUSSION

The new boron-carbon species produced here will be charac-
terized from matrix infrared experiments and quantum
chemical calculations.

Infrared spectrum of BC₂

The new 1194.6 cm⁻¹ band clearly requires both boron
and carbon and it is favored over carbon cluster species as
the boron concentration in the pellet is increased and as the
laser power is increased. Table I further shows that the
cluster size decreases and total carbon cluster ab-
sorbance decreases with increasing boron concentration in
the pellet and with increasing laser power used to ablate
the pellet. It is clear that vaporization of graphite and bor-
on are a very different in terms of elemental cluster forma-
tion. The new 1:4 doublet at 1232.5 and 1194.6 cm⁻¹ in
natural boron/graphite experiments [Fig. 1 (a)] demon-
strates that one boron atom is involved in the vibrational
mode, and that these bands are due, respectively, to
¹⁰BC₆ and ¹¹BC₆ species. The observation of a dominant
1232.5 cm⁻¹ band from boron-10 enriched graphite pellets
[Fig. 1 (b)] confirms this assignment. Unfortunately,
carbon-13 substitution in the product was not successful,
so the number of carbon atoms in the new BC₆ species
cannot be definitively determined by experiment.

Vibrational analysis and the boron isotopic shift, how-
ever, provide helpful information. The boron 10/11 iso-
topic frequency ratio 1232.5/1194.6 = 1.031 73 shows more
boron dependence than the harmonic diatomic BC ratio
(1.02562). The B–C vibration in a linear B–C≡C• mole-
cule is expected to exhibit an isotopic ratio near the BC
diatomic. On the other hand, B vibrating between two C
atoms in the ν₂ (antisymmetric) stretching mode of open
C–B–C or B against C₂ in the ν₂ (symmetric) stretching
mode of acute triangular B–C₂ would show more B iso-
topic dependence than in an isolated B–C vibration. Apex
angle calculations for symmetrical structures are compat-
ible with assignment of the ¹⁰RC₆ and ¹¹RC₆ bands to ν₂ of
an open C–B–C molecule with a valence angle near 130° or
to ν₂ of a triangular B–C₂ molecule with an apex angle near
50°.

The hydrogen atom-addition 12-electron molecules have been observed and characterized by quantum chemical
calculations. The linear H–B–C≡C molecule is dominated by a strong ν(C≡C) mode at 1993.2 cm⁻¹
whereas the HBC₂ (C₂B) ring species exhibits the strongest
band at 1122.7 cm⁻¹ for the symmetric B–C₂ fundamental.
Clearly, the present BC₆ band at 1194.6 cm⁻¹ is strongly
suggestive of a triangular BC₆ species. Quantum chemical
calculations were done to determine structure and the
infrared spectrum of the most stable BC₆ species.

Total energies, geometries, and harmonic frequencies
for the various structures at the CASSCF level are given in
Table II. From the results there, it is obvious that, for
linear geometries, the molecule prefers a BCC arrangement
to a CBC arrangement, as suggested earlier by Thomson. Hence, the suggestion of Knight et al. that the species
observed earlier is CBC does not appear to be correct.

The large energy difference between the CBC and BCC
arrangements is presumably due to the relatively weak BC
bond as compared to the relatively strong CC bond. The
²Σ⁺ state of BCC is quite stable and a local minimum at
this level of theory.

A structure that would combine the strong double CC
bond with two BC bonds would be a cyclic BC₂ ring, com-
parable to the ground state structure of the isoelectronic
C₂⁺ molecule. Because there is no Jahn–Teller effect in
the present case, however, the potential surface looks qual-
itatively different from C₂⁺. The linear ²Σ⁺ state of BCC
correlates with a ²A′ state for the bent geometry, which
corresponds to both ²A₂ and ²B₂ states at C₆g symmetry,
which in turn correlate with the ²Σ⁺ and ²Σ⁺ states of
CBC, respectively. Both the ²B₂ and ²A₂ states are found to
be much more stable than their state correlation limits in
Dₖh symmetry, but, contrary to C₂⁺ (Ref. 30) the ²A₁
state is much more stable than the ²B₂ one. Surprisingly,
however, although ²B₂ is a local minimum, ²A₁ is a saddle
point with respect to antisymmetric stretching. Allowing
the molecule to become asymmetric lowers the energy by
only 0.27 kcal/mol, leading finally to a ²A' state which is
the global minimum at this level of theory, and lies 3.58
cal/mol below the linear structure.

The symmetry breaking of the ²A₁ state to ²A' seems
anomalous. A possible qualitative rationale may be found
by inspection of the bond lengths. In BCC, both the BC
double bond and CC bonds are approximately at their optimum length
for double bonds: Actually the BC bond order is somewhat
lower than two and the CC bond order somewhat greater
than two due to resonance. In the ²A₁ state, the CC bond
length is comparable, but the BC bonds are stretched con-
siderably. The ²A' state, on the other hand, contracts one
of the BC bonds toward its double-bond length at the ex-
 pense of the other. Note that the C₂₀ and C₁₈ structures

have bond lengths quite close to the corresponding moieties in HBC$_2$($^1A_1$) and HBCC($^1\Sigma^+$).\(^{29}\)

A variety of methods were tested as to whether or not they produced the symmetry breaking for the $C_{2v}$ stationary point, including SCF, MP2,\(^{31}\) CCSD,\(^{25}\) QCISD,\(^{32}\) QCISD(T)\(^{32}\) (i.e., quadratic configuration interaction with and without the quasiperturbative triple excitations), and CCSD(T). With the exception of MP2 (which produced a clearly spurious bending frequency of more than 5000 cm$^{-1}$), all methods consistently produced a small imaginary antisymmetric stretching frequency. An attempt to include the lowest-lying external orbital in the reference space, as seen in Table II, again produced an imaginary frequency: this has been seen before with linear molecules [e.g., C$_3$ (Ref. 34) and HOC$^+$ (Ref. 35)] and is an artifact of the basis set. Again the $^2A_1$ state breaks symmetry, although the energy difference is even smaller now (0.09 kcal/mol). Possibly the $^2A_1$ state may turn out to be a minimum when functions are included in the basis set. At any rate, the issue is somewhat academic from the practical point of view. Once the zero-point energies are added in, the $^2A_1$ structure is slightly lower in energy at all levels of theory; in other terms, the $r_e$ structure may be asymmetric. In the TZ2P basis set the linear structure lies 6.2 kcal/mol above the linear form at the CCSD(T) level, but this result can be regarded as uncertain by about 2 kcal/mol because of basis set incompleteness.

Can the linear form be observed? It is close enough in energy, and has an intense IR band. However, at the 11/12 CASSCF level, we find the transition state between linear and cyclic forms to be low enough (barrier height 1.12 kcal/mol). Possibly the $^2A_1$ state may turn out to be a minimum when functions are included in the basis set. At any rate, the issue is somewhat academic from the practical point of view. Once the zero-point energies are added in, the $^2A_1$ structure is slightly lower in energy at all levels of theory; in other terms, the $r_e$ structure may be asymmetric. In the TZ2P basis set the linear structure lies 6.2 kcal/mol above the linear form at the CCSD(T) level, but this result can be regarded as uncertain by about 2 kcal/mol because of basis set incompleteness.

In order to investigate the basis set effect, we have performed CCSD(T) calculations with the TZ2P basis set. Linear BCC now has a very small imaginary bending frequency: this has been seen before with linear molecules [e.g., C$_3$ (Ref. 34) and HOC$^+$ (Ref. 35)] and is an artifact of the basis set. Again the $^2A_1$ state breaks symmetry, although the energy difference is even smaller now (0.09 kcal/mol). Possibly the $^2A_1$ state may turn out to be a minimum when functions are included in the basis set. At any rate, the issue is somewhat academic from the practical point of view. Once the zero-point energies are added in, the $^2A_1$ structure is slightly lower in energy at all levels of theory; in other terms, the $r_e$ structure may be asymmetric. In the TZ2P basis set the linear structure lies 6.2 kcal/mol above the linear form at the CCSD(T) level, but this result can be regarded as uncertain by about 2 kcal/mol because of basis set incompleteness.

Can the linear form be observed? It is close enough in energy, and has an intense IR band. However, at the 11/12 CASSCF level, we find the transition state between linear and cyclic forms to be low enough (barrier height 1.12 kcal/mol from the linear side at the CASSCF/cc-pVDZ level) that any linear BCC formed under the present experimental circumstances would easily relax to the cyclic ground state. At elevated temperatures, however, this situation might be different: again we see an analogy with C$_3^+$.\(^{30}\)

Our best levels of theory then predict as the principal absorption for BC$_2$: 1213 cm$^{-1}$ (CASSCF/cc-pVDZ) and

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**Table II. Computed total energies (Hartree), geometries (Å), and harmonic frequencies (cm$^{-1}$, IR intensities in km/mol) for various structures of BC$_2$.**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Total Energy (Hartree)</th>
<th>Geometry (Å)</th>
<th>Harmonic Frequencies (cm$^{-1}$, IR Intensities in km/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2\Sigma^+$</td>
<td>-100.204 176</td>
<td>$r_{NC} = 1.4411$</td>
<td>1792($a_z$,1182), 915($a_t$), 47($n_4$,41)</td>
</tr>
<tr>
<td>$^2B_2$</td>
<td>-100.300 497</td>
<td>$r_{NC} = 1.4215$, $r_{BC} = 1.4625$</td>
<td>1533($b_y$,496), 1418($a_1$,13), 991($a_2$,28)</td>
</tr>
<tr>
<td>$^2\Sigma^+$</td>
<td>-100.227 035</td>
<td>$r_{NC} = 1.4468$</td>
<td>859($&gt;10^3a_x$), 918($a_y$), 163($n_y$)</td>
</tr>
<tr>
<td>$^2A'$</td>
<td>-100.345 667</td>
<td>$r_{NC} = 1.3043$, $r_{BC} = 1.4652$, $r_{CC} = 1.6758$</td>
<td>1682($a_x'$,1213($a_x'$,61),287($a'$,106)</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>-100.345 242</td>
<td>$r_{CC} = 1.2979$, $r_{CH} = 1.5469$</td>
<td>1722($a_1$), 1143($a_1$,102), 277($b_2$)</td>
</tr>
<tr>
<td>(TS)</td>
<td>-100.338 155</td>
<td>$r_{CC} = 1.3093$, $r_{NC} = 1.4111$, $r_{BC} = 2.4198$</td>
<td>1851($a'3$,177), 1281($a'$,19), 166($a'$)</td>
</tr>
<tr>
<td>$^2\Sigma^+$</td>
<td>-100.393 969</td>
<td>$r_{NC} = 1.4071$, $r_{CC} = 1.3057$</td>
<td>1977($a_x2.81$), 1124($a_3$), 170($a'_2$)</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>-100.361 419</td>
<td>$r_{CC} = 1.2977$, $r_{BC} = 1.5477$</td>
<td>1726($a_1$), 1151($a_1$), 233($b_2$)</td>
</tr>
<tr>
<td>CCSD(T)/TZ2P</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2\Sigma^+$</td>
<td>-100.622 076</td>
<td>$r_{CC} = 1.2824$, $r_{NC} = 1.3761$</td>
<td>2025($a_x$,601), 1172($a_3$), 38i($\pi_3$)</td>
</tr>
<tr>
<td>$^2A'$</td>
<td>-100.631 949</td>
<td>$r_{NC} = 1.4537$, $r_{BC} = 1.5983$</td>
<td>1718($a'$,0.5),1190($a'$,83),273($a'1.41$)</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>-100.631 803</td>
<td>$r_{CC} = 1.2775$, $r_{NC} = 1.5154$</td>
<td>1738($a_1$,3), 1164($a_1$,107)</td>
</tr>
<tr>
<td>CCSD(T)/cc-pVDZ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2A'$</td>
<td>-100.536 019</td>
<td>$r_{NC} = 1.3050$, $r_{BC} = 1.4460$, $r_{CC} = 1.6982$</td>
<td></td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>-100.536 916</td>
<td>$r_{CC} = 1.3016$, $r_{NC} = 1.5402$</td>
<td></td>
</tr>
<tr>
<td>$^2\Sigma^+$</td>
<td>-100.328 234</td>
<td>$r_{CC} = 1.3019$, $r_{NC} = 1.3942$</td>
<td></td>
</tr>
</tbody>
</table>

$^b_2$ frequency not computed due to SCF convergence problems at displaced geometry.
1190 cm\(^{-1}\) [CCSD(T)/TZ2P]. The latter is in excellent agreement with the experimental IR band at 1194.6 cm\(^{-1}\). Isotopic shifts provide additional corroboration: The CASSCF/cc-pVDZ value is 39.1 cm\(^{-1}\), which corresponds to a \(^{10}\)B/\(^{11}\)B ratio of 1.0323, in excellent agreement with the experimental ratio of 1.0317. It appears established at this stage that the 1194.6 cm\(^{-1}\) band belongs to cyclic BC\(_2\).

The 1899.0 cm\(^{-1}\) band does not seem to be due to linear BCC, however. Both CASSCF/cc-pVDZ and CCSD(T)/TZ2P place the most intense band of BCC significantly higher. Additionally, the log isotope shift is 0.0*0.5 cm\(^{-1}\). So linear BCC does not seem to be present, which is consistent with the low 2\(\Sigma^+\) to \(2\Delta^1\) barrier height.

**Reaction mechanism**

Two experimental observations contribute to understanding the reaction mechanism. The first is that pulsed-laser evaporation of boron produces boron atoms as a product BC, is enhanced under low carbon concentration conditions, and high laser power conditions which favor small carbon ring species.\(^{22}\) Analogous to the reaction of B and C\(_2\)H\(_2\), which produced experimental evidence for cyclic BC\(_2\), they do not rule out the presence of linear BCC, although no evidence was found here for linear BCC. However, the low barrier between the \(2\Sigma^+\) and \(2\Delta^1\) states suggests that any BCC formed by axial approach of B to C\(_2\) will rearrange to cyclic BC\(_2\).

**Energetics**

It was impossible to force convergence of the SCF procedure in the cc-pVTZ basis set to the desired solution for the \(2\Delta^1\) state. As the energy difference between \(2\Delta^1\) and \(2\Delta^1\) is on the order of 0.1 kcal/mol anyway (which is negligible compared with the other errors inherent in the treatment), we have computed the CCSD(T)/cc-pVTZ total energy at the CCSD(T)/cc-pVTZ geometry for the \(2\Delta^1\) state instead. (The core electrons were frozen and pure spherical functions.)

\[
\Delta (D_e) = 4.2333n_{\text{pair}} - 1.1027n_\sigma + 0.8575n_\pi, \quad (2)
\]

where the coefficients are specific for the cc-pVTZ basis set and \(n_{\text{pair}}\), \(n_\sigma\), and \(n_\pi\) represent the numbers of electron pairs, \(\sigma\) bonds, and \(\pi\) bonds, respectively. We find that this increases to 113.5 kcal/mol. Using the previously calculated \(\Sigma D_e\) value\(^{30}\) of 401.8 kcal/mol for HBC\(_2\), we find that \(\Sigma D_e(BC_2)\) = 288.3 kcal/mol. Because of the uncertainty in the \(\eta\)-particle treatment for BCC\(_2\), we affix an uncertainty of 4 to 5 kcal/mol to this latter value.

Considering the \(\Sigma D_e\) values of 405.4 (Ref. 36) and 476.6 (Ref. 29) kcal/mol, respectively, for C\(_2\)H\(_2\) and B\(_2\)H\(_2\), it becomes clear why BC\(_2\) was not observed in the B+C\(_2\)H\(_2\) experiments. On the other hand, since \(D_\Delta = 6.32\) eV (or 145.8 kcal/mol) for C\(_2\),\(^{17}\) the reaction B+C\(_2\)→BC\(_2\) is quite significantly exothermic (by 142.5 kcal/mol), which explains the abundance of BC\(_2\) in the present experiments.

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