

# Fourier transform emission spectroscopy: The $B^4\Sigma^- - X^4\Sigma^-$ transition of BC

W. T. M. L. Fernando, L. C. O'Brien,<sup>a)</sup> and P. F. Bernath<sup>b)</sup>  
*Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

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The gas-phase emission spectrum of BC was recorded using a high resolution Fourier transform spectrometer. The BC radical was produced by sputtering in a composite-wall hollow cathode discharge lamp. The  $\Delta v = 0$  vibrational sequence of the  $B^4\Sigma^- - X^4\Sigma^-$  transition near 5590 Å was rotationally analyzed. A set of spectroscopic constants were derived for the 0-0, 1-1, 2-2, and 3-3 vibrational bands, including  $r_e = 1.491\ 16(34)$  Å for the  $X^4\Sigma^-$  state and  $r_e = 1.460\ 23(29)$  Å for the  $B^4\Sigma^-$  state.

## INTRODUCTION

The simplest boron and carbon containing compound, BC, was first observed by Verhaegen, Stafford, and Drowart<sup>1</sup> in 1964. They studied the vapor in equilibrium with solid  $B_4C$  with a mass spectrometer and found several boron-carbon molecules. The atomization energy of 106 kcal/mol for BC was measured by them. The first spectroscopic study of BC was carried out by Knight *et al.*<sup>2</sup> in rare gas matrices by electron spin resonance. Their results confirmed that the ground state is  $X^4\Sigma^-$ , in agreement with theoretical predictions.

A number of *ab initio* theoretical calculations are available for BC. Kourba and Ohrn<sup>3</sup> reported the potential energy curves for number of electronic states and predicted the ground state to be  $^4\Sigma^-$ . Other calculations were carried out by Mitin *et al.*<sup>4</sup> and by Hirsch and Buenker.<sup>5</sup> The calculations of Hirsch and Buenker are particularly extensive with potential energy curves and spectroscopic constants for the ground and low-lying excited states of BC and  $BC^+$ . They also compared the properties of BC with the isoelectronic  $C_2^+$  molecule. An extensive theoretical treatment of BC was also carried out by Knight *et al.*<sup>2</sup> for comparison with the ESR experiment. The most recent calculation was done by Oliphant and Adamowicz<sup>6</sup> in order to provide a theoretical  $r_e$  value in the ground electronic state for comparison with our experimental value.

Presented here is the first electronic spectrum of BC: the  $B^4\Sigma^- - X^4\Sigma^-$  electronic transition near 5590 Å. The BC spectrum was recorded in emission from a composite-wall hollow cathode lamp with a high resolution Fourier transform spectrometer.

## EXPERIMENTAL METHODS

The composite-wall hollow cathode was made by pressing a 3:1 mixture of copper and  $B_4C$  powders. The cathode used for BC was similar to the one recently used to record the infrared electronic transitions of SiC.<sup>7</sup> A slow flow of argon gas was maintained through the lamp. The discharge was operated at a pressure of 1.2 Torr and a current of 400 mA. The emission from the lamp was imaged into the entrance

aperture of the National Solar Observatory Fourier transform spectrometer at Kitt Peak.

In our preliminary work, the 2800–11 000 Å interval was surveyed using different bandpass filters (Corion). Two cooled RCA 31034 photomultiplier detectors were used. About 22 scans were coadded with two hours of integration for each spectral interval. A set of lines near 17 900  $cm^{-1}$  with a *P* head and an *R* branch was seen in one of the scans. However the signal-to-noise ratio for these lines was poor. As a result the expected spin splittings were not very well resolved and the first few lines of the *P* and *R* branches were not observed in the spectrum. At this point in the analysis the molecule was identified as BC but the location of the band origin was not certain.

In order to find the band origin and to better see the spin splittings the spectrum was recorded for a second time under similar conditions. Using a prism monochromator the spectral interval was limited to 17 300–18 900  $cm^{-1}$ . Photomultiplier detectors were used and 46 scans were coadded. Spectral lines in this scan were quite strong and a doublet splitting was seen for most of the lines. However this spectrum contained a large number of  $C_2$  lines from the  $d^3\Pi_g - a^3\Pi_u$  (Swan system) transition. Many of the BC lines, particularly the weak lines, were blended and, again, the first *P* and *R* lines were not obvious in the spectrum.

Finally, the spectrum was recorded for a third time with similar conditions but in this case the hollow cathode was operated for several hours before the spectrum was recorded. This helped clean the cathode and eliminated the  $C_2$  emission. Intensities of the lines in this spectrum were slightly better than the first experiment and the first *P* and *R* lines were found.

The spectrometer resolution was 0.05  $cm^{-1}$  and the observed BC linewidths were 0.1  $cm^{-1}$ , slightly larger than the expected Doppler width of about 0.07  $cm^{-1}$ . The spectra were calibrated with line positions of singly ionized argon measured by Norlen.<sup>8</sup> The absolute accuracy of the  $Ar^+$  lines is better than  $\pm 0.001\ cm^{-1}$ .

## RESULTS AND DISCUSSION

The interferograms were transformed by G. Ladd of the National Solar Observatory. The line positions in the spectra were determined using a data reduction program called PC-DECOMP developed by J. Brault. To determine the peak

<sup>a)</sup> Current Address: Food and Drug Administration, Division of Drug Analysis, St. Louis, Missouri 63101.

<sup>b)</sup> Alfred P. Sloan Fellow, Camille and Henry Dreyfus Teacher-Scholar.

positions a Voigt line shape function was fitted to the lines.

Lines associated with 0-0, 1-1, 2-2, and 3-3 bands in the  $\Delta v = 0$  vibrational sequence were measured and assigned. These bands show the characteristic rotational structure of a  $\Sigma-\Sigma$  transition. The head is in the *P* branch of the blue-degraded bands and the rotational analysis was straightforward. Figure 1 shows the *P* head of the 0-0 band while Fig. 2 gives a portion of the *R* branch of the same band.

Line centers obtained from the first experiment were fit to a  ${}^1\Sigma^- - {}^1\Sigma^-$  energy level expression ignoring the partially resolved spin splittings. Since the first *P* and *R* lines were not found in this spectrum, there were three possible assignments for the band origin resulting in three different possible  $r_e$  values. The experimental  $r_e$  values were compared with the calculated values by Hirsch and Buenker<sup>5</sup> (1.5012 Å) and Davidson<sup>2</sup> (1.521 Å) in order to find the correct assignment. This comparison between experiment and theory was ambiguous. Oliphant and Adamowicz<sup>6</sup> performed another theoretical calculation and found a ground state  $r_e = 1.491$  Å. This third theoretical value agrees with value of Hirsch and Buenker's and with one of the possible experimental values (1.488 Å). Ultimately, the third spectrum that we recorded provided an unambiguous rotational assignment. Table I compares theoretical and experimental  $B_e$  and  $r_e$  values for the ground state. The experimental and best theoretical values are in excellent agreement.

The electronic configuration of BC in its ground  ${}^4\Sigma^-$  state is

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 \quad (1)$$

and the potential energy curve dissociates to  $B(^2P) + C(^3P)$ . The  $B^4\Sigma^-$  excited state can be obtained by promoting an electron from the  $4\sigma$  to the  $5\sigma$  orbital. The band origin predicted by Hirsch and Buenker<sup>5</sup> (17 900  $\text{cm}^{-1}$ ) is in embarrassingly good agreement with the experimental value of 17 904.8622(14)  $\text{cm}^{-1}$ .

In order to fit the rotational line positions the effective Hamiltonian, as described by Brown *et al.*<sup>9</sup> for a  ${}^4\Sigma$  state,

$$\mathbf{H}_{\text{eff}} = \mathbf{H}_{\text{rot}} + \mathbf{H}_{\text{cd}} + \mathbf{H}_{\text{sr}} + \mathbf{H}_{\text{ss}} \quad (2)$$

was used where

BC  $B^4\Sigma^- - X^4\Sigma^-$

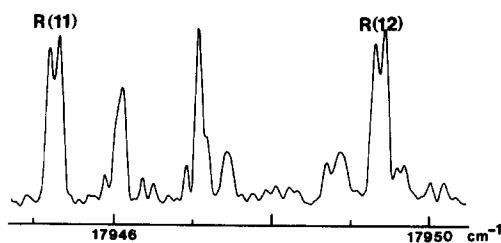


FIG. 2. A portion of *R* branch of the 0-0 band of BC. The doublet structure is caused by the spin-spin interaction. The weaker unmarked features belong to  $C_2$ .

$\mathbf{H}_{\text{rot}} = \mathbf{B}\mathbf{N}^2$ , the rotational kinetic energy,

$\mathbf{H}_{\text{cd}} = -\mathbf{D}\mathbf{N}^4$ , the centrifugal distortion energy,

$\mathbf{H}_{\text{sr}} = \gamma\mathbf{N}\cdot\mathbf{S}$ , the spin-rotation interaction,

and

$\mathbf{H}_{\text{ss}} = 2/3\lambda(3S_z^2 - S^2)$ , the spin-spin interaction.

The  $4 \times 4$  Hamiltonian matrix for a  ${}^4\Sigma^-$  state was derived with Hund's case (a) basis functions and reduced to two  $2 \times 2$  matrices by making the *e/f* parity transformation. These matrix elements are provided in Table II. The data were fit by diagonalizing the Hamiltonian matrices and adjusting the spectroscopic parameters in a least-squares procedure.

In a  ${}^4\Sigma^-$  state each rotational level  $N(\geq 2)$  is split into four spin components and several transitions between different  $N$  and  $J$  levels are possible. The selection rule  $\Delta J = 0, \pm 1$  results in 24 branches for a  ${}^4\Sigma^- - {}^4\Sigma^-$  transition. However, for the higher  $N$  transitions there are four strong *P* and *R* branches ( $P_1, P_2, P_3, P_4, R_1, R_2, R_3$  and  $R_4$ ) in agreement with the general selection rule  $\Delta J = \Delta N = \pm 1$ . The energy level diagram for a  ${}^4\Sigma^- - {}^4\Sigma^-$  transition is given in Fig. 3.

If the spin-rotation parameter  $\gamma$  is small in both electronic states of BC then the fine structure is determined by spin-spin interaction which has only diagonal matrix elements:

$$E_{\text{ss}} = 2/3\lambda [3\Sigma^2 - S(S+1)]. \quad (3)$$

Thus  ${}^4\Sigma_{1/2}$  and  ${}^4\Sigma_{-1/2}$  ( $\Omega = 1/2$ ) have same energy

TABLE I. Comparison of experimental and theoretical molecular constants for the  $X^4\Sigma^-$  state of BC.

	$r_e$ (Å)	$B_e$ ( $\text{cm}^{-1}$ )
This work	1.491 16	1.320 41
Kouba and Ohm <sup>a</sup>	1.665	1.069
Hirsch and Buenker <sup>b</sup>	1.501	1.3028
Knight <i>et al.</i> <sup>c</sup>	1.521	1.2691
Oliphant and Adamowicz <sup>d</sup>	1.491	1.3207

<sup>a</sup> Reference 3.

<sup>b</sup> Reference 5.

<sup>c</sup> Reference 2.

<sup>d</sup> Reference 6.

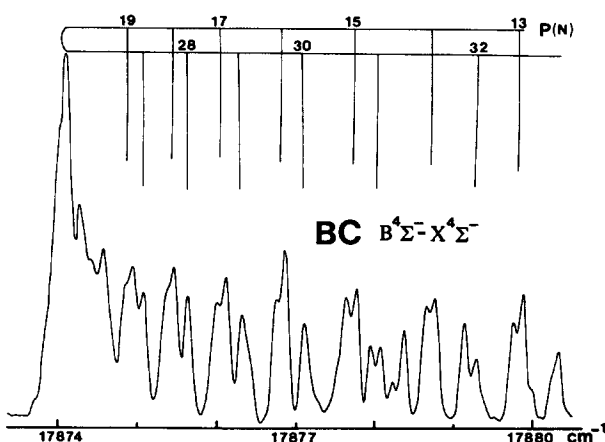


FIG. 1. A portion of the 0-0 band of BC near the *P* bandhead.

TABLE II. Matrix elements for a  ${}^4\Sigma^-$  state (upper/lower sign for  $e/f$  parity).<sup>a</sup>

$ 3/2\rangle$	$ 1/2\rangle$
$B(y^2 - 1)$	$-B\{3(y^2 - 1)\}^{1/2}$
$-D\{(y^2 - 1)^2 + 3(y^2 - 1)\}$	$D\{3(y^2 - 1)\}^{1/2}(2x + 5/2 \mp 2y)$
$-3/2\gamma + 2\lambda$	$\gamma/2\{3(y^2 - 1)\}^{1/2}$
$-B\{3(y^2 - 1)\}^{1/2}$	$B(x + 13/4 \mp 2y)$
$D\{3(y^2 - 1)\}^{1/2}(2x + 5/2 \mp 2y)$	$-D\{7y^2 - 3 + (x + 13/4)^2 \mp 4y(x + 13/4)\}$
$\gamma/2\{3(y^2 - 1)\}^{1/2}$	$-\gamma(7/2 \mp y)$
	$-2\lambda$

$${}^a x = J(J + 1), y = (J + 1/2).$$

( $-2\lambda$ ) while  ${}^4\Sigma_{3/2}$  and  ${}^4\Sigma_{-3/2}$  are also unsplit ( $+2\lambda$ ). Therefore, only doublets can be expected under the resolution used in this experiment. The separation between the two peaks in the doublet is approximately given by the difference in the spin-spin interaction parameters  $4\Delta\lambda$  in the two electronic states. For a given  $N$ , two lines from each branch ( $P_1 + P_4$  and  $P_2 + P_3$  or  $R_1 + R_4$  and  $R_2 + R_3$ ) combine to make the doublet.

The intensity formulas given by Kovacs<sup>10</sup> and its corrections<sup>11</sup> were used to assign the two lines in the doublet (i.e., determine which line is  $R_1 + R_4$  and which is  $R_2 + R_3$ ). The calculated intensity of the  $R_1 + R_4$  line is slightly greater than that of the  $R_2 + R_3$  line. The two lines in the doublet are labeled to match the experimental and calculated intensities. This intensity pattern was also observed for the unblended  $P$

branch lines. The agreement between the predicted and observed relative intensities was not very good, presumably because of interactions with other states.

The measured line positions are reported in Table III. Each band was fit separately to the  ${}^4\Sigma^-$ - ${}^4\Sigma^-$  fitting program. The spin-spin interaction parameter  $\lambda$  was estimated ( $0.0284 \text{ cm}^{-1}$ ) from Ref. 3 and used as the initial guess of the fit for the 0-0 band.

For the 0-0 band, all the parameters ( $B$ ,  $D$ , and  $\lambda$ ) were varied for both electronic states and the  $\gamma$ 's were set to zero. Many of the doublets in the  $P$  branch are not resolved or are blended. The weights for these lines in the fit are adjusted to reflect the blending and the intensity of the lines.

The 1-1, 2-2, and 3-3 bands were fit by fixing the ground state  $\lambda$  to the  $v = 0$  value. For the 2-2 and 3-3 bands the values for  $D'$  and  $D''$  were linearly extrapolated with the usual formula

$$D_v = D_e + \beta_e(v + 1/2) \quad (4)$$

using  $D_0$  and  $D_1$  values. The lines in 3-3 band were very weak. Most of the  $P$  branch lines were blended with  $C_2$  lines and except for a few  $R$  branch lines, the spin doubling was not resolved. For the 3-3 band only a band origin and the rotational constant  $B$  for both electronic states were varied. The molecular constants extracted from the fits are given in Table IV. The equilibrium rotational constants obtained by fitting the  $B_v$  values of Table IV are reported in Table V. The equilibrium bond lengths calculated from the  $B_e$  values are reported in Table V.

The spin-spin parameters ( $\lambda$ 's) of Table IV are effective values. As usual  $\lambda = \lambda^{(1)} + \lambda^{(2)}$  where the "true" spin-spin interaction energy ( $\lambda^{(1)}$ ) is small relative to the second-order spin-orbit interaction energy ( $\lambda^{(2)}$ ). The microscopic form of the spin-orbit Hamiltonian

$$H = \sum a_i l_i s_i \quad (5)$$

connects a  ${}^4\Sigma^-$  state to other electronic states. The  $4\sigma^2 5\sigma^1 1\pi^2$  configuration of the  $X^4\Sigma^-$  state and the  $4\sigma^1 5\sigma^2 1\pi^2$  configuration of the  $B^4\Sigma^-$  each give rise to  ${}^4\Sigma^-$ ,  ${}^2\Sigma^+$ ,  ${}^2\Sigma^-$ , and  ${}^2\Delta$  states. Within a  $\sigma^1 \pi^2$  configuration the  ${}^4\Sigma^-$  and  ${}^2\Sigma^+$  states are connected by the  $1_x s_z$  part of the  $H_{so}$  operator. Application of second-order perturbation theory results in the equation<sup>12</sup>

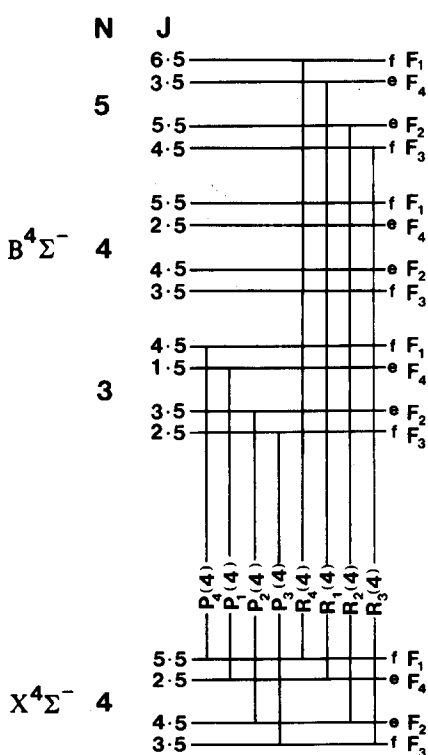
FIG. 3. Energy level diagram for a  ${}^4\Sigma^-$ - ${}^4\Sigma^-$  transition.

TABLE III. Observed line positions of the  $B^4\Sigma^- - X^4\Sigma^-$  transition of BC (in  $\text{cm}^{-1}$ ).

$N$	$R_1 + R_4$	O-C <sup>a</sup>	$R_2 + R_3$	O-C	$P_1 + P_4$	O-C	$P_2 + P_4$	O-C
0-0 Band								
0	17 907.610	-9	...					
1	17 910.482	-8	17 910.514	3	17 902.233	-16	...	
2	17 913.475	8	17 913.395	-8	17 899.736	-28	17 899.869	48
3	17 916.566	12	17 916.462	-3	17 897.374	-8	17 897.313	-14
4	17 919.759	5	17 919.643	-9	17 895.117	7	17 895.020	-6
5	17 923.074	8	17 922.950	-6	17 892.964	12	17 992.852	-0
6	17 926.497	5	17 926.385	9	17 890.895	-13	17 890.799	-1
7	17 930.041	9	17 929.912	0	17 889.002	22	17 888.866	0
8	17 933.685	2	17 933.554	-6	17 887.185	18	17 887.048	-1
9	17 937.441	-7	17 937.320	-4	17 885.478	7	17 885.359	11
10	17 941.331	3	17 941.203	2	17 883.897	5	17 883.771	5
11	17 945.316	-5	17 945.191	-1	17 882.427	-1	17 882.318	17
12	17 949.418	-8	17 949.294	-1	17 881.094	12	17 880.956	3
13	17 953.640	-5	17 953.516	4	17 879.853	-1	17 879.729	6
14	17 957.970	-5	17 957.847	4	17 878.740	-3	17 878.619	7
15	17 962.414	-6	17 962.295	9	17 877.748	-2	17 877.606	-11
16	17 966.973	-5	17 966.839	-3	17 876.874	-2	17 876.731	-11
17	17 971.633	-15	17 971.518	6	17 876.124	3	17 875.985	-1
18	17 976.428	-2	17 976.299	5	17 875.470	-14	17 875.362	14
19	17 981.334	6	17 981.202	12	17 874.970	4	17 874.841	11
20	17 986.338	5	17 986.203	5	17 874.577	9	17 874.430	-2
21	17 991.456	3	17 991.325	6	17 874.296	6	17 874.170	17
22	17 996.684	-4	17 996.538	-15	17 874.132	-0	17 873.966	-29
23	18 002.036	-3	18 001.920	20	17 874.113	18	17 873.955	-2
24	18 007.504	6	18 007.347	-11	17 874.179	0	17 874.023	-17
25	18 013.075	5	18 012.946	14	17 874.380	-4	17 874.232	-13
26	18 018.746	-10	18 018.594	-23	17 874.661	-49	17 874.557	-15
27	18 024.551	-3	18 024.410	-5	17 875.098	-62	17 875.026	10
28	18 030.459	-6	18 030.839	14	17 875.666	-66	17 875.628	36
29	18 036.514	24	18 036.407	58	17 876.425	-1	17 876.293	7
30					17 877.290	46	17 877.106	3
31					17 878.218	33	17 878.032	-13
32					17 879.270	19	17 879.121	11
33							17 880.293	-6
1-1 Band								
0	18 028.302	-6	...					
1	18 031.186	29	18 031.186	17	18 023.014	19	...	
2	18 034.110	-3	18 034.030	-2	18 020.569	15	18 020.647	9
3	18 037.165	-18	18 037.068	-5	18 018.215	-0	18 018.129	-23
4	18 040.373	5	18 040.246	3	18 015.975	-15	18 015.879	-9
5	18 043.638	-31	18 043.539	4	18 013.894	12	18 013.785	24
6	18 047.082	-6	18 046.948	3	18 011.908	16	18 011.754	-6
7	18 050.619	-4	18 050.471	-5	18 010.031	11	18 009.868	-13
8	18 054.243	-32	18 054.117	-7	18 008.284	15	18 008.126	3
9	18 058.050	7	18 057.894	5	18 006.630	-7	18 006.476	-12
10	18 061.230	2	18 061.783	12	18 005.125	-1	18 004.975	0
11	18 065.933	3	18 065.776	4	18 003.729	-8	18 003.577	-5
12	18 070.052	4	18 069.889	1	18 002.474	6	18 002.299	-12
13	18 074.285	2	18 074.122	-0	18 001.323	-2	18 001.154	-8
14	28 078.630	-4	18 078.488	16	18 000.322	24	18 000.135	-2
15	18 083.102	0	18 082.916	-23	17 999.390	-5	17 999.211	-22
16	18 087.694	8	18 087.548	26	17 998.627	12	17 998.424	-28
17	18 092.388	1	18 092.224	2	17 997.976	16	17 997.795	1
18	18 097.207	3	18 097.037	0	17 997.407	-20	17 997.238	-24
19	18 102.131	-5	18 101.969	-1	17 997.007	-12	17 996.841	-12
20	18 107.183	-3	18 107.004	-14	17 996.774	39	17 996.552	-16
21	18 112.351	-0	18 112.170	-13	17 996.612	37	17 996.382	-26
22	18 117.610	-24	18 117.440	-24				
23	18 123.024	-8	18 122.853	-9				
24	18 128.542	-4	18 128.362	-14				
25	18 134.187	10	18 134.037	31				
26	18 139.935	11	18 139.784	31				
27	18 145.778	-10	18 145.645	29				
28	18 151.756	-12	18 151.614	18				

TABLE III (continued).

<i>N</i>	$R_1 + R_4$	O-C <sup>a</sup>	$R_2 + R_3$	O-C	$P_1 + P_4$	O-C	$P_2 + P_4$	O-C
2-2 Band								
1	18 152.231	-43	18 152.343	49	18 144.206	-15	...	
2	18 155.190	-13	18 155.100	-35	18 141.880	64	18 141.880	4
3	18 158.262	14	18 158.150	-6	18 139.510	-9	18 139.493	31
4	18 161.409	-4	18 161.297	-10	18 137.350	9	18 137.224	-30
5	18 164.723	25	18 164.599	14	18 135.254	-30	18 135.206	24
6	18 168.127	23	18 167.992	7	18 133.321	-28	18 133.173	-64
7	18 171.614	-16	18 171.486	-20	18 131.515	-22	18 131.386	-34
8	18 175.283	8	18 175.156	7	18 129.798	-52	18 129.729	1
9	18 179.054	12	18 178.916	4	18 128.230	-56	18 128.182	22
10	18 182.904	-24	18 182.789	-8	18 126.901	53	18 126.762	43
11	18 186.934	-0	18 186.802	0	18 125.567	33	18 125.425	22
12	18 191.052	-10	18 190.933	6	18 124.321	-24	18 124.221	8
13	18 195.316	8	18 195.174	2	18 123.273	-11	18 123.129	-20
14	18 199.679	5	18 199.545	8	18 122.297	-52	18 122.168	-44
15	18 204.158	-3	18 204.015	-7	18 121.565	25	18 121.339	-63
16	18 208.768	1	18 208.628	0	18 120.864	6	18 120.715	-6
17	18 213.477	-15	18 213.346	-6	18 120.352	48	18 120.171	5
18	18 218.316	-21	18 218.207	10	18 119.875	-5	18 119.725	-15
19	18 223.297	-5	18 223.154	-7	18 119.582	-1	18 119.387	-55
20	18 228.376	-11	18 228.242	-3	18 119.437	21	18 119.259	-15
21	18 233.583	-8	18 233.430	-19	18 119.383	5	18 119.195	-42
22	18 238.908	-7	18 238.767	-7				
23	18 244.354	-6	18 244.208	-9				
24	18 249.905	-19	18 249.769	-12				
25	18 255.587	-21	18 255.458	-6				
26	18 261.399	-13	18 261.269	1				
27	18 267.344	9	18 267.193	2				
28	18 273.380	1	18 273.265	30				
29	18 279.516	-28	18 279.398	-1				
30	18 285.848	20	18 285.710	26				
31	18 292.242	8	18 292.111	22				
32	18 298.777	17	18 298.655	41				
3-3 Band								
4	18 282.769	-23	18 282.769	79				
5	18 286.026	-36	18 286.026	74	18 256.877	-50	18 256.877	49
6	18 289.443	-11	18 289.271	-68	18 254.973	-58	18 254.973	50
7	18 292.878	-91	18 292.878	29	18 253.226	-34	18 253.226	80
8	18 296.550	-56	18 296.550	67	18 251.615	-1	18 251.615	118
9	18 300.302	-63	18 300.302	63	18 250.095	-4	18 250.095	118
10	18 304.266	20	18 304.066	-53	18 248.679	-29	18 248.679	96
11	18 308.252	4	18 308.078	-41	18 247.466	20	18 247.466	147
12	18 312.291	-83	18 312.291	48	18 246.308	-4	18 246.308	125
13	18 316.552	-68	18 316.552	64	18 245.248	-58	18 245.248	72
14	18 320.911	-78	18 320.911	55	18 244.355	-75	18 244.355	57
15	18 325.402	-76	18 325.402	58	18 243.623	-60	18 243.623	72
16	18 330.061	-29	18 329.944	-11	18 242.953	-114	18 242.953	20
17	18 334.796	-27	18 334.710	22	18 242.423	-158	18 242.423	-24
18	18 339.671	-7	18 339.566	24	18 242.143	-85	18 242.143	51
19	18 344.567	-88	18 344.567	49	18 241.918	-88	18 241.918	48
20	18 349.770	17	18 349.607	-9	18 241.796	-121	18 241.796	16
21	18 354.991	19	18 354.852	17				
22	18 360.293	-20	18 360.217	41				
23	18 365.829	52	18 365.657	18				
24	18 371.323	-39						

<sup>a</sup>O-C correspond to the observed minus calculated line positions (in  $10^{-3} \text{ cm}^{-1}$ ) using the spectroscopic constants of Table IV.

$$\lambda^{(2)} = a_{\pi}^2 / 6 \{ E(^2\Sigma^+) - E(^4\Sigma^-) \}, \quad (6)$$

where  $a_{\pi} (= \langle \pi | a_i | \pi \rangle)$  is the molecular analog of the atomic spin-orbit parameter  $\zeta$ .

In the case of the  $X^4\Sigma^-$  state of BC there is another important contribution to  $\lambda^{(2)}$  from another low lying configuration,  $4\sigma^2 1\pi^3$ , which gives rise to the  $a^2\Pi$  state. This  $a^2\Pi$  state is calculated<sup>5</sup> to lie only  $4600 \text{ cm}^{-1}$  above the

TABLE IV. Molecular constants for the  $B^4\Sigma^- - X^4\Sigma^-$  transition of BC (in  $\text{cm}^{-1}$ ).

Constant	$v = 0$	$v = 1$	$v = 2$	$v = 3$
		$X^4\Sigma^-$		
$B_v$	1.311 730(52)	1.295 05(12)	1.276 40(10)	1.262 72(31)
$10^6 D_v$	7.600(46)	9.16(25)	10.720 <sup>a</sup>	12.280 <sup>a</sup>
$10^2 \lambda$	2.82 (33)	2.82 <sup>b</sup>	2.82 <sup>b</sup>	2.82 <sup>b</sup>
		$B^4\Sigma^-$		
$T_{uv}$	17 904.8622(14)	18 025.5754(22)	18 146.7638(26)	18 268.250(12)
$B_v$	1.369 140(52)	1.354 32(12)	1.337 49(10)	1.324 88(29)
$10^6 D_v$	7.273(47)	8.73(22)	10.187 <sup>a</sup>	11.644 <sup>a</sup>
$10^2 \lambda$	-4.57(34)	-6.23(14)	-4.80(17)	-4.57 <sup>b</sup>

<sup>a</sup> Extrapolated from  $v = 0$  and 1 values.<sup>b</sup> Fixed to the  $v = 0$  value.

ground state. Furthermore the  $5\sigma$  and  $1\pi$  orbitals are nominally  $p\sigma$  and  $p\pi$  orbitals for which a pure precession relationship is a reasonable approximation. The  $1^+s^-$  part of  $H_{80}$  can, therefore, connect the  $X^4\Sigma^-$  and the  $a^2\Pi$  state. The  $^4\Sigma_{3/2}$  component interacts with the  $^2\Pi_{3/2}$  while the  $^4\Sigma_{1/2}$  component interacts with the  $^2\Pi_{1/2}$  state and the application of second-order perturbation theory results in the expression

$$\lambda^{(2)} = a_\pi^2 / 12 \{ E(^2\Pi) - E(^4\Sigma^-) \}. \quad (7)$$

The molecular  $a_\pi$  value is not known for BC but  $\zeta = 11 \text{ cm}^{-1}$  for the B atom and  $\zeta = 29 \text{ cm}^{-1}$  for the C atom.<sup>12</sup> Assuming that the corresponding  $1\pi$  molecular orbital is a simple linear combination of atomic orbitals then  $a_\pi \approx (\zeta_C + \zeta_B) / 2 = 20 \text{ cm}^{-1}$ . From the *ab initio* calculations of Hirsch and Buenker<sup>5</sup>  $E(^2\Sigma^+) - E(X^4\Sigma^-) = 13\,300 \text{ cm}^{-1}$  while  $E(a^2\Pi) - E(X^4\Sigma^-) = 4600 \text{ cm}^{-1}$ . Therefore Eq. (6) contributes  $0.005 \text{ cm}^{-1}$  to  $\lambda$  while Eq. (7) contributes  $0.007 \text{ cm}^{-1}$  for a total of  $0.012 \text{ cm}^{-1}$  compared to the observed value of  $\lambda = 0.027 \text{ cm}^{-1}$  for the  $X^4\Sigma^-$ . Considering the approximations made in this semiempirical estimate, the agreement is satisfactory.

For the excited  $B^4\Sigma^-$  state the value of  $\lambda = -0.046$

TABLE V. Equilibrium molecular constants for BC in the  $X^4\Sigma^-$  and  $B^4\Sigma^-$  states (in  $\text{cm}^{-1}$ ).

Constant	$X^4\Sigma^-$	$B^4\Sigma^-$
$B_e$	1.320 41(61)	1.376 93(55)
$\alpha_e$	0.017 33(46)	0.015 53(40)
$r_e$ (Å)	1.491 16(34)	1.460 23(29)

$\text{cm}^{-1}$  is more difficult to rationalize. By interchanging the assignment of the spin doublets it is possible to obtain a positive value of  $\lambda$  in the excited  $B^4\Sigma^-$  state but the variance of the fit is degraded by a factor of 2. The excited state configurations of BC are probably too mixed for any semiempirical estimate to have any meaning.

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