9106 *J. Phys. Chem. A* **1998,** *102,* 9106−9108

Electronic Absorption Spectra of BC, BC$^-$, BC$_2$, and BC$_2^-$ in Neon Matrices

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Received: July 16, 1998; In Final Form: September 9, 1998

The electronic absorption spectra of BC, BC$_2$ and their anions were detected in 5 K neon matrices. After mass-selected co-deposition of BC$^-$ with excess of neon, an absorption system with origin at 622.7(2) nm is observed and assigned to the A $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$ electronic transition of BC$^-$. Irradiation of the matrix leads to photodetachment, and the known B $^4\Sigma^- \leftarrow$ X $^4\Sigma^-$ electronic transition of BC, as well as a new one C $^4\Pi \leftarrow$ X $^4\Sigma^-$ with origin at 291.0(2) nm, are observed. Measurements with mass-selected BC$_2^-$ lead to the identification of the A $^1\Pi \leftarrow$ X $^1\Sigma^+$ electronic transition of linear BC$_2^-$ at 432.2(2) nm. Subsequent neutralization leads to the appearance of two new systems with origin at 851.4(2) and 1587.8(2) nm of either linear and/or cyclic BC$_2$. In the infrared the ν_1 band of linear BC$_2^-$ was observed at 1936.3(1.0) cm^{-1} and after irradiation the ν_2 band of cyclic BC$_2$ at 1196.8(1.0) cm^{-1}.

Introduction

Boron-carbon compounds are of technical importance because of their outstanding hardness. Although early studies on boron- and carbon-containing molecules by mass spectrometry showed their strong bonding character,[1] these species have only recently been investigated in more detail. The first spectroscopic investigation on BC was by ESR in rare gas matrices[2] and confirmed the $^4\Sigma^-$ ground-state symmetry predicted by CI calculations.[3,4] These and other calculations on the BC molecule provided the energies and vibrational frequencies in the ground and several electronic excited states.[5,6] Only one electronic transition of BC, B $^4\Sigma^- \rightarrow$ X $^4\Sigma^-$ near 559 nm, has been observed in the gas phase by Fourier transform emission spectroscopy.[7]

Calculations on BC$_2$ in the ground state have been carried out. These predict a cyclic structure to lie 26 ± 8 kJ/mol below the linear geometry.[8] An infrared band at ~1194 cm^{-1} observed in an argon matrix has been shown to belong to the ν_2 vibration of the cyclic symmetric BC$_2$ species.[8,9] No spectroscopic data exist for the anions BC$^-$ and BC$_2^-$. According to calculations, both BC$^-$ and linear BC$_2^-$ have $^1\Sigma^+$ ground states.[10,11]

In this study absorption systems in the visible region have been detected, which are assigned to the A $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$ transition of BC$^-$ and the A $^1\Pi \leftarrow$ X $^1\Sigma^+$ transition of linear BC$_2^-$. A new electronic transition of BC of C $^4\Pi \leftarrow$ X $^4\Sigma^-$ symmetry has also been observed in the UV and two transitions of BC$_2$ in the near-infrared.

Experimental Section

BC$^-$ and BC$_2^-$ were generated in a cesium sputter source that has been used to produce carbon anions.[12] A solid boron carbide target was sputtered by Cs$^+$ ions with ~1 keV kinetic energy to produce the carbon- and boron-containing anions, which were extracted and accelerated to 50 eV through an electrostatic lens system. A quadrupole filter selected the ions of interest with a mass resolution of 1−2 amu. These anions were then co-deposited with an excess of neon on a rhodium-coated sapphire plate held at 5 K. After a deposition of ~4 h, an absorption spectrum was measured in the range of 220−1100 nm by a waveguide approach, and in the infrared using a Fourier transform spectrometer with a single reflection arrangement. To study the mass-selected neutral species, the anions trapped in the neon matrix were irradiated with a medium-pressure mercury lamp resulting in electron detachment.

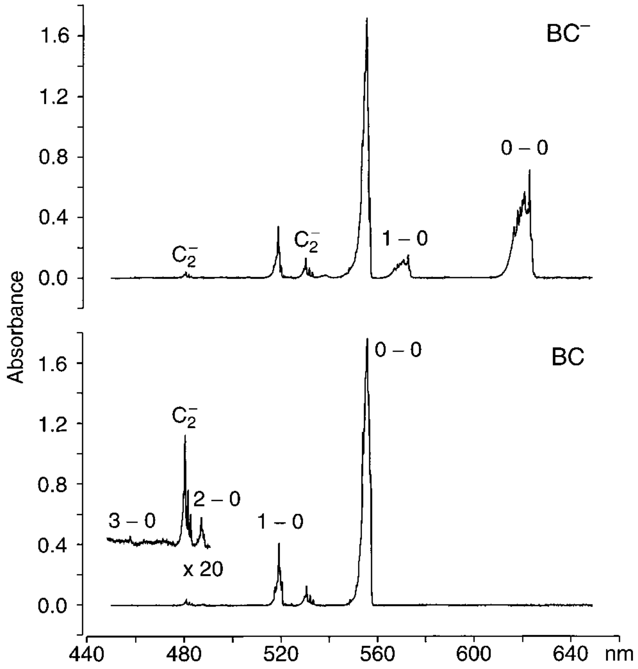

Figure 1. Spectrum observed after 4 h co-deposition of BC$^-$ with neon to form a 5 K matrix (upper trace). The B $^4\Sigma^- \leftarrow$ X $^4\Sigma^-$ transition of BC and the A $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$ transition of BC$^-$ as well as C$_2^-$ absorptions are apparent. The lower trace shows the spectrum after irradiation ($\lambda \geq$ 305 nm) of the matrix.

Results and Discussion

Electronic Transitions of BC$^-$ and BC. The upper trace of Figure 1 shows the recorded spectrum in the 450−650 nm range after 4 h co-deposition of mass-selected BC$^-$ with neon. In addition to new bands the known [7] B $^4\Sigma^- \leftarrow$ X $^4\Sigma^-$ transition of BC with 0−0 band at 555 nm is apparent. Also present are

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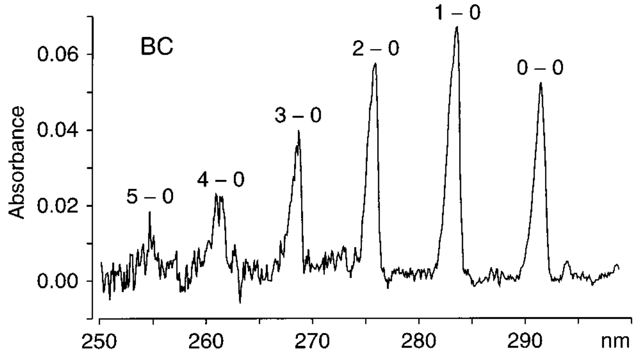

Figure 2. C $^4\Pi \leftarrow$ X $^4\Sigma^-$ transition of BC observed after irradiation ($\lambda \geq 305$ nm) of the matrix obtained by 4 h co-deposition of BC$^-$ with neon.

TABLE 1: Peak Maxima of the Observed Transitions of BC, BC$_2$, and BC$_2^-$ in a Neon Matrix ($\lambda \pm 0.2$ nm) and Suggested Vibrational Assignment (Those in Parentheses Are Tentative). In the Case of BC$^-$ the Wavelength of the Sharp Zero-Phonon Line Is Given

	transition	λ (nm)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	assignment
BC$^-$	A $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$	622.7	16 055	0	$0 \leftarrow 0$
		572.5	17 462	1407	$1 \leftarrow 0$
BC	B $^4\Sigma^- \leftarrow$ X $^4\Sigma^-$	555.3	18 003	0	$0 \leftarrow 0$
		518.7	19 274	1271	$1 \leftarrow 0$
		487.1	20 524	2521	$2 \leftarrow 0$
		457.8	21 837	3834	$3 \leftarrow 0$
	C $^4\Pi \leftarrow$ X $^4\Sigma^-$	291.0	34 354	0	$0 \leftarrow 0$
		283.0	35 325	971	$1 \leftarrow 0$
		275.4	36 300	1946	$2 \leftarrow 0$
		268.2	37 275	2921	$3 \leftarrow 0$
		261.0	38 303	3949	$4 \leftarrow 0$
		254.2	39 327	4973	$5 \leftarrow 0$
BC$_2^-$	A $^1\Pi \leftarrow$ X $^1\Sigma^+$	432.2	23 131	0	0_0^0
		423.1	23 628	497	(2_0^2)
		416.7	23 991	860	3_0^1
		412.9	24 212	1081	$(3_0^1\,2_0^1)$
		405.3	24 666	1535	1_0^1
		392.1	25 496	2365	$1_0^1\,3_0^1$
		381.7	26 191	3060	1_0^2
		370.5	26 983	3852	$1_0^2\,3_0^1$
		361.1	27 685	4554	1_0^3
BC$_2$		851.2	11 745		0_0^0
		1587.8	6 296		0_0^0

TABLE 2: Comparison of the Experimental T_o and Theoretical T_e Excitation Energies of BC, BC$^-$, BC$_2$, and BC$_2^-$

molecule	state	T_o/eV neon matrix	T_o/eV gas phase	T_e/eV calculation
BC	C $^4\Pi$	4.261(3)		4.33[b]
	B $^4\Sigma^-$	2.233(1)	2.218[a]	2.22[b]
BC$^-$	A $^1\Sigma^+$	1.991(1)		
BC$_2$		1.4566(4)		
		0.7809(2)		
BC$_2^-$	A $^1\Pi$	2.869(2)		

[a] Reference 7. [b] Reference 3.

TABLE 3: Comparison of Experimental Vibrational Frequencies (1−0 Spacing) and Calculated Harmonic Vibrational Frequencies ω_e (in cm^{-1}) of BC, BC$^-$, BC$_2$, and BC$_2^-$ in Different Electronic States

		frequency
BC		
X $^4\Sigma^-$	calc[a]	1140
B $^4\Sigma^-$	exp[b]	1271(7)
	calc[a]	1250
C $^4\Pi$	exp[b]	971(24)
	calc[a]	965
BC$^-$		
X $^1\Sigma^+$	calc[c]	1588
A $^1\Sigma^+$	exp[b]	1407(6)

		ν_1	ν_2	ν_3
BC$_2$				
X ^{2}A′	exp[b]		1196.8(1.0)	
	exp[d]		1194.6	
	calc[d]	1682	1213	287
BC$_2^-$				
X $^1\Sigma^+$	exp[b]	1936.3(1.0)		
	calc[c]	1974	218	1051
A $^1\Pi$	exp[b]	1535(11)	249(11)	860(11)

[a] Reference 3. [b] This work, neon matrix. [c] Reference 11. [d] Reference 8, argon matrix.

the absorption bands of C$_2^-$ at 530 and 480 nm.[13] C$_2^-$ is present either because of insufficient mass resolution or as result of fragmentation and recombination processes in the matrix.

The new band system apparent has its 0−0 band at 623 nm, and the first member of the progression is evident at 573 nm. The bands are broad and show multiplet-site structure. These two bands disappear after irradiation of the matrix with a medium-pressure mercury lamp ($\lambda \geq 305$ nm), while the bands due to the neutral BC remain. The resulting spectrum is seen in the lower trace of Figure 1. The use of photon wavelengths above 345 nm leads to no change in the peak intensities of the top spectrum. Thus the electron detachment energy of the species causing the 623 nm absorption lies between 3.6 and 4.1 eV. The stabilization of anions in a neon matrix as a result of solvation is ~1 eV, which implies a gas-phase electron detachment energy ~1 eV lower. This is in reasonable agreement with the 2.8(3) eV electron detachment energy of BC$^-$ estimated experimentally.[14] The separation between the two observed bands is 1407(6) cm^{-1} and corresponds to vibrational excitation in the upper electronic state. In the ground state of BC$^-$ the calculated harmonic frequency (MP2/6-31G(d) with diffuse functions on the terminal atoms [END+]) is around 1600 cm^{-1}.[11] The band system with origin at 623 nm is assigned to the A $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$ electronic transition of BC$^-$.

In addition to the systems in the visible region, another transition in the UV with origin band at 291 nm is observed. This shows an extended vibrational progression, and the bands persist after irradiation (Figure 2) indicating that it is associated with neutral BC. The latter has been calculated to have a $^4\Pi$ excited state at 4.33 eV and $\omega_e \sim 965$ cm^{-1}. The MRD-CI method was used with an augmented Dunning basis.[3] The observed system, with origin band at 4.26 eV and a vibrational frequency (1−0 spacing) of 971(24) cm^{-1}, is therefore attributed to the C $^4\Pi \leftarrow$ X $^4\Sigma^-$ transition of BC. Its intensity is about 25 times smaller than that of the B $^4\Sigma^- \leftarrow$ X $^4\Sigma^-$ electronic transition of BC. A further allowed transition, A $^4\Pi \leftarrow$ X $^4\Sigma^-$, of BC is predicted at 1.15 eV.[3] This could not be detected.

The observed bands with assignments are given in Table 1. The excitation energies are compared to calculations in Table 2. The inferred vibrational frequencies are summarized in Table 3 and compared to calculated harmonic frequencies.

Electronic Transitions of BC$_2^-$ and BC$_2$. The spectrum obtained after BC$_2^-$ was mass-selected and co-deposited with neon at 5 K is shown in Figure 3. An absorption band system with origin at 432 nm and several vibrational progressions is apparent (Table 1). Upon irradiation with a medium-pressure

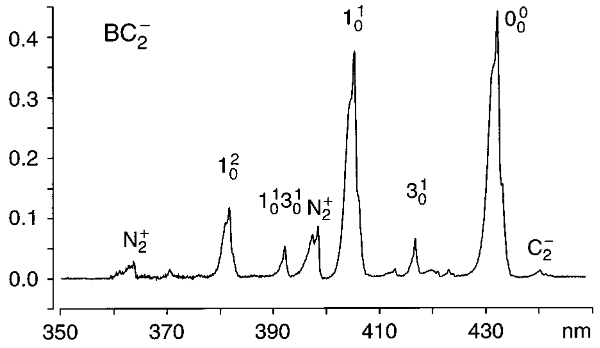

Figure 3. A $^1\Pi \leftarrow X\ ^1\Sigma^+$ transition of BC_2^- observed after growing of a neon matrix with mass-selected BC_2^-.

mercury lamp this transition disappears. This yields an upper limit for the electron detachment energy of 5.4 eV in a neon environment. Isoelectronic to BC_2^- is C_3 with its well-known A $^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ transition at 405.8 nm, nearby to the presently observed band system.[15] Calculations (SCF/3-21G and MP2/6-31G(d)[END+]) predict for BC_2^- also a linear structure with $^1\Sigma^+$ symmetry in the ground state and an electron detachment energy of ~3 eV.[10,11]

The vibrational pattern of the spectrum is characteristic of a linear (or quasi linear) species. A strong progression involving the excitation of the $\nu_1 = 1535(11)$ cm^{-1} mode is seen. The $\nu_3 = 860(11)$ cm^{-1} mode and the combinations with ν_1 are also discernible. The degenerate bending mode ν_2 may be weakly excited with double quanta ($2 \times 249(11)$ cm^{-1}) and the $2_0^1\, 3_0^1$ transition as well. The latter is forbidden but is often weakly apparent in matrix environments, e.g., in the A $^2\Sigma^+ \leftarrow X\ ^2\Pi$ absorption spectrum of CNO in a neon matrix.[16] The inferred vibrational frequencies for the excited state (Table 3) can be compared with the MP2/6-31G(d)[END+] calculated harmonic values for linear BC_2^- in the ground state: $\nu_1 = 1974.2$ cm^{-1}, $\nu_2 = 218$ cm^{-1}, and $\nu_3 = 1050.5$ cm^{-1}.[11]

In the infrared a band is observed at 1936.3 cm^{-1}, which correlates in intensity with the 432 nm electronic transition. This value fits the calculated $\nu_1 = 1974.2$ cm^{-1} fundamental frequency of BC_2^- in the X $^1\Sigma^+$ state.[11] In view of the above, the observed system is assigned to the A $^1\Pi \leftarrow X\ ^1\Sigma^+$ electronic transition of linear BC_2^-.

After irradiation of the matrix with a medium-pressure mercury lamp, the infrared as well as the visible bands disappear. A new infrared absorption at 1196.8 cm^{-1} appears. This fundamental has already been observed in an argon matrix at ~1194 cm^{-1} and was assigned to cyclic BC_2.[8,9] In the near-infrared two new systems with origin bands at 851 nm and at 1588 nm grow. These are presumably due to neutral BC_2. Calculations on BC_2 (by CASSCF/cc-pVDZ as well as CCSD(T)/cc-pVDZ and B3LYP with several basis sets up to cc-pVTZ) show that the asymmetric and the symmetric cyclic structures lie close in energy. Taking into account the zero-point vibrational energy, which is considerably higher than the energy for the interconversion, the ground-state geometry appears symmetric, as experimentally found.[8,9] As the anion BC_2^- is linear, it may be that during its neutralization in the neon matrix at 5 K not all the linear species cyclize, so that both forms could be present. Hopefully theoretical studies of the electronic states of the isomers of BC_2 will help to identify the observed band systems.

Acknowledgment. This work has been supported by the Swiss National Science Foundation (project no. 20-49104.96).

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