Infrared Spectra and Density Functional Calculations of the BCS and $B(CS)_2$ Molecules in Solid Argon

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High-frequency discharge through CS_2/Ar yielded CS, which was co-condensed with laser-ablated boron atoms at 4 K. The BCS and $B(CS)_2$ thiocarbonyl molecules were formed via the reactions of ground-state boron atoms with CS in solid argon. On the basis of isotopic shifts and splittings, absorptions at 881.6 and 860.8 cm^{-1} are assigned to the C−S stretching vibrations of the linear ^{10}BCS and ^{11}BCS molecules. The absorptions at 1772.3/1727.2 and 1021.6/1005.7 cm^{-1} are assigned to the B−C and C−S stretching vibrations of the linear $^{10}B(CS)_2$ and $^{11}B(CS)_2$ molecules, respectively. The BCS molecule has a $^4\Sigma^-$ ground state, and the $B(CS)_2$ molecule has a $^2\Pi_u$ ground state with the bonding similar to the corresponding boron carbonyls.

Introduction

Since the first preparation of carbonyl borane H_3BCO,[1] a number of carbonyl borane compounds have been characterized.[2] Most recently, Willner and co-workers described a new derivative of carbonyl borane, carbonyltris(trifluoromethyl) borane ($(CF_3)_3BCO$), in the gas and solid phases,[3,4] and we combined matrix isolation spectroscopy and quantum chemical calculations to characterize novel boron carbonyl species.[5−7] We identified boron carbonyl species such as OCBBCO and $B_4(CO)_2$ as products from the reactions of laser-evaporated boron atoms with CO in solid argon. Interestingly, the OCB≡BCO molecule exhibits some degree of boron−boron triple bonding.[5] $B_4(CO)_2$, with a four-membered B_4 ring, was characterized as a new $\sigma-\pi$ diradical.[6] The known boron carbonyl compounds suggest that BCO is "isolobal" with a CH group.[7] This isolobal relationship has been applied to predict a set of new aromatic monocyclic boron carbonyl compounds, that mimic the monocyclic aromatic hydrocarbons.[8]

Carbon monoxide and carbon monosulfide are isovalent molecules. Although a large number of binary transition metal as well as main group metal carbonyl compounds have been well studied,[9−11] the analogous thiocarbonyl species have received far less attention, partly because of the lack of the stable molecular CS.[12] The use of CS_2 or its complexes comprises the most important methods of generating thiocarbonyl compounds.[12] However, the synthesis of thiocarbonyls by using CS prepared using microwave discharge has been reported.[13] Recently, we reported the production and spectroscopic characterization of binary transition metal thiocarbonyls: MCS, $M(CS)_2$, and M_2CS (M = Cu, Ag, and Au).[14,15] These carbonyl species were prepared by the reactions of metal atoms with CS molecules generated via high-frequency discharge of CS_2 vapor in excess argon. In this paper, we report a combined matrix isolation infrared spectroscopic and density functional theoretical investigation of boron thiocarbonyls.

Experimental and Computational Methods

The CS molecules were prepared by subjecting CS_2/Ar mixtures to high-frequency discharge with a high-frequency generator (Tesla coil).[16] The tip of the Tesla coil was connected to a copper cap on one end of a quartz tube extending into the vacuum chamber. The other end of the quartz tube was connected to a copper tube with ground potential. Discharge takes place between the cap and the copper tube. CS_2/Ar mixtures were prepared in a stainless steel vacuum line using standard manometric technique. CS_2 was cooled to 77 K using liquid N_2 and was evacuated to remove volatile impurities. Isotopic labeled $^{13}CS_2$ and $C^{34}S_2$ (Isotec, 99%) were used without further purification.

The boron atoms were produced by laser ablation of a bulk boron target. The experimental setup for pulsed laser ablation and matrix isolation FTIR spectroscopic investigation has been described in detail previously.[17] Briefly, the 1064 nm fundamental of a Nd:YAG laser (20 Hz repetition rate and 8 ns pulse width) was focused onto the rotating boron metal target through a hole in a CsI window. The laser-ablated boron atoms were co-deposited with the Tesla coil discharged CS_2/Ar sample onto the 4 K CsI window for 1 h at a rate of 3−5 mmol/h. Infrared spectra were recorded on a Bruker Equinox 55 spectrometer at 0.5 cm^{-1} resolution using a DTGS detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband irradiation using a high-pressure mercury arc lamp.

Density functional theoretical calculations were performed using the Gaussian 03 program.[18] The Becke's three-parameter hybrid functional, with additional correlation corrections due to Lee, Yang, and Parr, was utilized (B3LYP).[19,20] The 6-311+G* basis set was used for B, C, and S atoms.[21,22] Geometries were fully optimized, vibrational frequencies were calculated with analytical second derivatives, and zero-point vibrational energies were derived.

Results and Discussion

Infrared Spectra. Recent studies in our laboratory have shown that CS can be prepared by high-frequency discharge of

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TABLE 1: Infrared Absorptions (cm^{-1}) from Co-deposition of Laser-Ablated Boron Atoms and Discharged CS$_2$/Ar Sample

$^{12}C^{32}S_2$	$^{13}C^{32}S_2$	$^{12}C^{34}S_2$	$^{12}CS_2 + ^{13}CS_2$	$C^{32}S_2 + C^{34}S_2$	assignment
1772.3	1744.3	1771.8	1772.3, 1759.5, 1744.3		$^{10}B(CS)_2$
1727.2	1697.5	1726.7	1727.2, 1713.9, 1697.5		$^{11}B(CS)_2$
1227.0	1209.9	1217.7	1227.0, 1209.9		$S^{10}BCS$
1201.9	1187.9	1192.8	1201.9, 1187.9	1201.9, 1197.3, 1192.8	$S^{11}BCS$
1021.6	1007.2	1011.7	1021.6, 1014.4, 1007.2	1021.6, 1016.6, 1011.7	$^{10}B(CS)_2$
1005.7	992.9	995.8	1005.7, 998.9, 992.9	1005.7, 1000.8, 995.8	$^{11}B(CS)_2$
999.7	987.6	989.1			$^{10}BCS(CS_2)$
976.0	964.7	968.0			$^{11}BCS(CS_2)$
881.6	876.0	872.4	881.6, 876.0	881.6, 872.4	^{10}BCS
860.8	856.0	851.8	860.8, 856.0	860.8, 851.8	^{11}BCS

TABLE 2: Calculated (B3LYP/6-311+G*) Structures (Bond Lengths in Å), Dissociation Energies (with Respect to B (^{2}P) + CO ($^1\Sigma^+$), in kcal/mol), Vibrational Frequencies (cm^{-1}), and Intensities (km/mol) for Different BCS Isomers

	D_0	R_{BC}	R_{CS}	R_{BS}	frequency (intensity)
BCS ($^4\Sigma^-$)	66.2	1.388	1.575		1662.0 (4), 859.8 (25), 343.3 (18)
BCS ($^2A''$)	58.4	1.437	1.566	2.979	1234.6 (1844), 755.2 (276), 283.5 (7)
CBS (2Π)	61.8	1.497		1.626	1400.9 (1), 711.9 (14), 261.8 (32)
CBS ($^4\Sigma^-$)	58.3	1.432		1.636	1433.6 (2), 764.6 (5), 334.1 (1)
B(CS) ($^2A'$)	49.2	1.521	1.792	1.756	1116.4 (24), 819.1 (29), 643.5 (22)
B(CS) ($^4A''$)	39.7	1.416	1.724	2.020	1382.9 (19), 822.9 (6), 308.3 (20)

CS$_2$. Co-condensation of discharged CS$_2$/Ar at 4 K resulted in the formation of strong CS absorption (1270.0 and 1275.0 cm^{-1}), as well as weak (CS)$_2$ (1281.2 cm^{-1}), C$_2$S$_2$ (1180.5 cm^{-1}), C$_3$S$_2$ (2078.2 and 1024.3 cm^{-1}), and S(CS)$_2$ (1051.0 cm^{-1}) absorptions.[16,23] The relative intensities of these fragments depend strongly on the power level of discharge. Generally, the formation of CS dominated at low power level of discharge

As the deposited discharged sample contains a large amount of parent CS$_2$ molecules, we first ran an experiment using a 0.5% CS$_2$ sample without discharge. When the CS$_2$/Ar mixture was co-deposited with boron atoms produced by laser ablation of a natural abundance boron target with a laser power of about 10 mJ/pulse, weak CS absorptions were observed on sample deposition and new absorptions at 1227.0 and 1201.9 cm^{-1} were produced and increased on annealing. The 1227.0 and 1201.9 cm^{-1} bands exhibited approximately 1:4 relative intensities and have been assigned previously to the S^{10}BCS and S^{11}BCS molecules.[24]

New absorptions were observed when the discharged CS$_2$/Ar (0.5%) sample was co-deposited with laser-ablated natural abundance boron atoms. The spectra in selected regions are shown in Figure 1, and the product absorptions are listed in Table 1. Besides the absorptions due to the above-mentioned C$_x$S$_y$ species and the SBCS molecules, new product absorptions at 860.8 and 881.6 cm^{-1} were observed on sample deposition (Figure 1a). The 860.8 and 881.6 cm^{-1} bands slightly increased on annealing to 25 and 30 K, but decreased on broadband irradiation. New product absorptions at 976.0, 999.7, 1005.7, 1727.2, and 1772.3 cm^{-1} were produced and increased on sample annealing (Figure 1b and c). The 976.0 and 999.7 cm^{-1} bands were broad and were eliminated on broadband irradiation (Figure 1d). The 1005.7, 1727.2, and 1772.3 cm^{-1} bands slightly decreased on broadband irradiation and were almost recovered on subsequent annealing to 35 K (Figure 1e). A similar experiment was done using a boron-10 enriched target, and the spectra in selected regions are shown in Figure 2. In the ^{10}B-enriched experiment, only the 881.6, 999.7, and 1772.3 cm^{-1} bands were observed. The 1005.7 cm^{-1} band gave a ^{10}B counterpart at 1021.6 cm^{-1}, which was partly overlapped by the strong C$_3$S$_2$ absorption at 1024.3 cm^{-1} in natural abundance boron experiments.

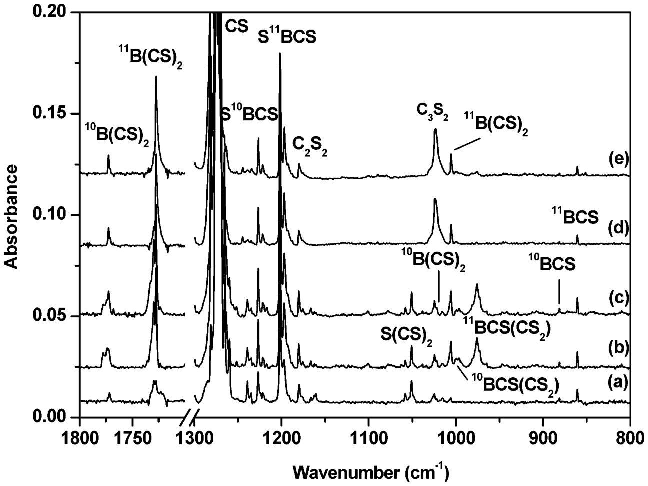

Figure 1. Infrared spectra in the 1800−1700 and 1300−800 cm^{-1} regions from co-deposition of laser-ablated natural abundance boron atoms with discharged CS$_2$/Ar (0.5%) sample. (a) 1 h of sample deposition at 4 K, (b) after annealing to 25 K, (c) after annealing to 30 K, (d) after 20 min of broadband irradiation, and (e) after annealing to 35 K.

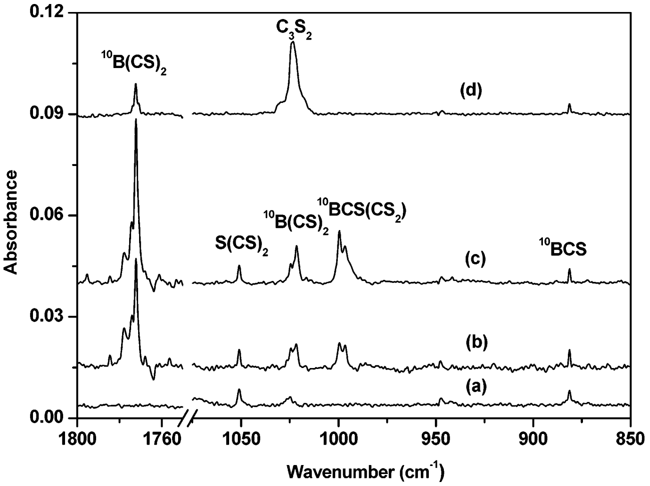

Figure 2. Infrared spectra in the 1800−1750 and 1100−850 cm^{-1} regions from co-deposition of laser-ablated boron-10 atoms with discharged CS$_2$/Ar (0.5%) sample. (a) 1 h of sample deposition at 4 K, (b) after annealing to 25 K, (c) after annealing to 30 K, and (d) after 20 min of broadband irradiation.

The experiments were repeated using the isotopic labeled ^{13}CS$_2$, C^{34}S$_2$, and ^{12}CS$_2$ + ^{13}CS$_2$, C^{32}S$_2$ + C^{34}S$_2$ mixtures. The isotopic counterparts are also listed in Table 1. The spectra in

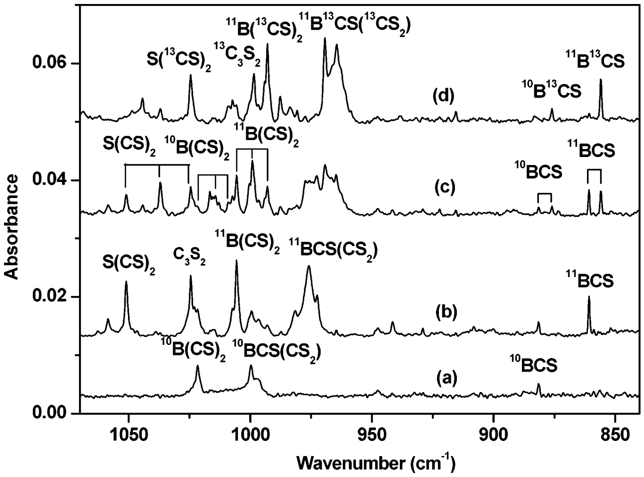

Figure 3. Infrared spectra in the 1070−840 cm^{-1} region from co-deposition of laser-ablated boron atoms with discharged CS_2/Ar sample. Spectra were taken after 30 K annealing. (a) ^{10}B-enriched (97%) target, 0.5% $^{12}CS_2$, (b) natural abundance boron, 0.5% $^{12}CS_2$, (c) natural abundance boron, 0.25% $^{12}CS_2$ + 0.25% $^{13}CS_2$, and (d) natural abundance boron, 0.5% $^{13}CS_2$.

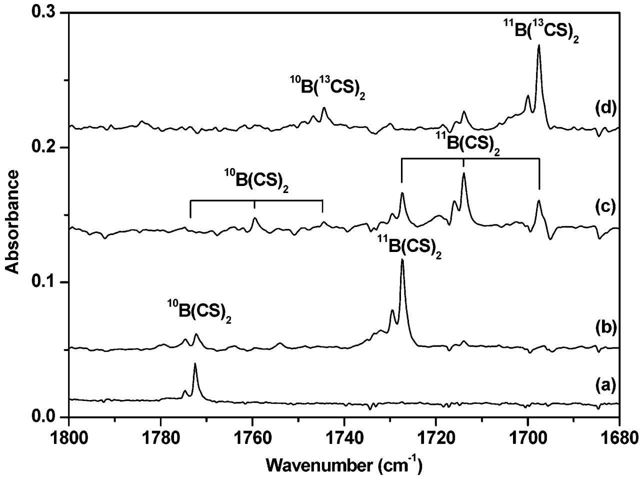

Figure 4. Infrared spectra in the 1800−1680 cm^{-1} region from co-deposition of laser-ablated boron atoms with discharged CS_2/Ar sample. Spectra were taken after 30 K annealing. (a) ^{10}B-enriched (97%) target, 0.5% $^{12}CS_2$, (b) natural abundance boron, 0.5% $^{12}CS_2$, (c) natural abundance boron, 0.25% $^{12}CS_2$ + 0.25% $^{13}CS_2$, and (d) natural abundance boron, 0.5% $^{13}CS_2$.

the 1800−1680 and 1070−840 cm^{-1} regions using different carbon isotopic labeled CS_2 samples after 30 K annealing are illustrated in Figures 3 and 4. Figure 5 shows the spectra in the 1040−840 cm^{-1} region from co-deposition of laser-ablated natural abundance boron atoms with discharged 0.25% $C^{32}S_2$ + 0.25% $C^{34}S_2$/Ar sample.

Calculation Results. To provide insight into the structure and bonding of the experimentally observed reaction products, we have performed density functional calculations. Three BCS structural isomers were considered, and the computational results are given in Table 2. Our DFT/B3LYP calculations predicted the BCS thiocarbonyl structure to have a $^4\Sigma^-$ ground state with the B−C and C−S bond lengths of 1.388 and 1.575 Å. A bent $^2A''$ state BCS with B−C and C−S bond lengths of 1.437 and 1.566 Å and a BCS bond angle of 165.2° lies 7.8 kcal/mol higher in energy than the $^4\Sigma^-$ state. Calculations on the inserted CBS isomer predicted a linear doublet ground state, with a linear quartet state lying 2.6 kcal/mol higher in energy. This insertion isomer is only 4.4 kcal/mol less stable than quartet BCS. We have also considered both quartet and doublet states for the cyclic structural isomer, and we found the doublet state to be more stable, lying 17.0 kcal/mol above the ground state of linear BCS. Calculations were also done on the $B(CS)_2$ and BCS-(CS_2) molecules, and the optimized geometric parameters are shown in Figure 6.

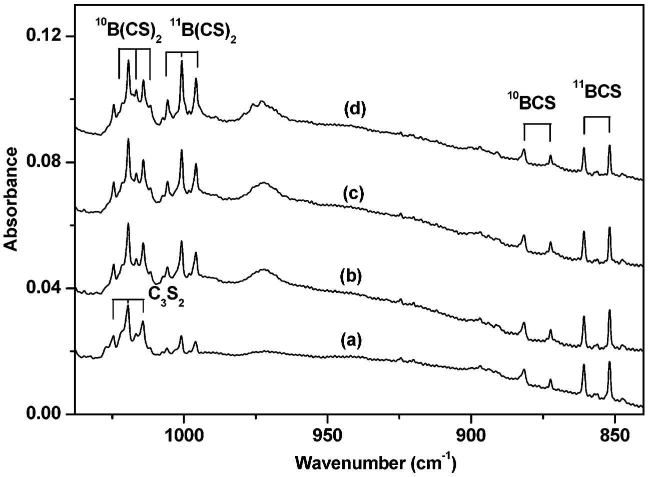

Figure 5. Infrared spectra in the 1040−840 cm^{-1} region from co-deposition of laser-ablated natural abundance boron atoms with discharged 0.25% $C^{32}S_2$ + 0.25% $C^{34}S_2$/Ar sample. (a) 1 h of sample deposition at 4 K, (b) after annealing to 25 K, (c) after annealing to 30 K, and (d) after annealing to 35 K.

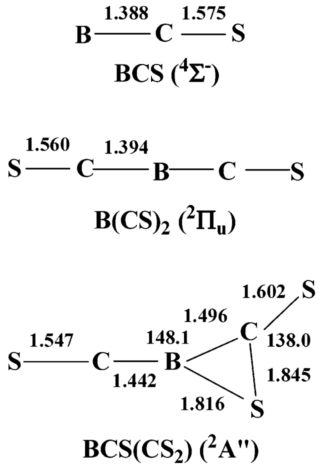

Figure 6. Optimized geometries (bond lengths in Å, bond angles in deg) of the BCS, $B(CS)_2$, and $BCS(CS_2)$ molecules.

TABLE 3: Calculated Harmonic Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) for the $B(CS)_2$ Isotopomers

mode	$^{10}B(CS)_2$	$^{11}B(CS)_2$	$^{11}B(^{13}CS)_2$	$^{11}B(C^{34}S)_2$
σ_u	1837.2 (1767)	1788.8 (1761)	1758.1 (1639)	1788.3 (1753)
σ_g	1537.3 (0)	1537.3 (0)	1483.4(0)	1532.4 (0)
σ_u	1044.0 (328)	1027.7 (290)	1014.7 (303)	1017.3 (286)
π_u	458.9 (15)	449.2 (15)	439.9 (15)	448.8 (15)
σ_g	442.3 (0)	442.3 (0)	440.3 (0)	430.5 (0)
π_g	352.8 (0)	352.8 (0)	340.0 (0)	352.0 (0)
π_u	88.6 (0)	86.8 (0)	86.1(0)	86.1 (0)

BCS. Absorptions at 860.8 and 881.6 cm^{-1} only were observed in the discharge experiments using the natural abundance boron target (19.8% ^{10}B, 80.2% ^{11}B). When the ^{10}B-enriched target was used, only the 881.6 cm^{-1} band was observed. The 881.6 cm^{-1} band is approximately one-fourth the intensity of the 860.8 cm^{-1} band, which clearly indicates that only one boron atom is involved in the molecule. These two bands shifted to 856.0 and 876.0 cm^{-1} with the discharged

$^{13}CS_2$/Ar sample, and to 851.8 and 872.4 cm^{-1} with the discharged $C^{34}S_2$/Ar sample. Only pure isotopic counterparts were observed in the spectra with the mixed $^{12}CS_2 + {}^{13}CS_2$/Ar and $C^{32}S_2 + C^{34}S_2$/Ar samples, which clearly indicate that only one C atom and one S atom are involved in this molecule. Therefore, the 860.8 and 881.6 cm^{-1} bands are assigned to the ^{11}BCS and ^{10}BCS molecules, respectively.

The assignment is strongly supported by theoretical calculations. As noted above, DFT/B3LYP calculations predicted a $^4\Sigma^-$ ground state for BCS with a linear structure. The C−S stretching vibrations for ^{11}BCS and ^{10}BCS were computed at 859.8 and 880.1 cm^{-1}, just −1.0 and −1.5 cm^{-1} from the observed values. The calculated isotopic frequency ratios ($^{10}B/^{11}B = 1.0236$; $^{12}C/^{13}C = 1.0041$ (^{11}B); $^{32}S/^{34}S = 1.0114$ (^{11}B)) are in good agreement with the experimental values ($^{10}B/^{11}B = 1.0242$; $^{12}C/^{13}C = 1.0064$ (^{11}B); $^{32}S/^{34}S = 1.0106$ (^{11}B)). The calculations predicted the C−S stretching mode to have the highest IR intensity (25 km/mol). The B−C stretching mode was predicted at 1662.0 cm^{-1} with a very low IR intensity (<4 km/mol) and could not be observed in the experiment. The doubly degenerate bending vibration was calculated at 343.6 cm^{-1}, which is out of the detection range of the spectrometer.

In transition metal carbonyl compounds, the interactions between metal and ligand CO are dominated by the synergic donation of electrons in σ HOMO of CO to an empty σ orbital of the metal and the back-donation of the metal π electrons to the CO π^* orbital. CS and CO are isovalent molecules, and the bonding in thiocarbonyl compounds is similar to that in carbonyl molecules. The BCS molecule can be regarded as being formed by the interaction of B with CS. The $^4\Sigma^-$ ground state of BCS has an electron configuration of $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(6\sigma)^2(7\sigma)^2(8\sigma)^2(2\pi)^4(9\sigma)^1(3\pi)^2$, which reflects the B $2s^12p^2$ excited state (^{4}P). The three unpaired electrons occupy the 9σ and 3π molecular orbitals. The 9σ molecular orbital is largely B 2s in character and is nonbonding. The doubly degenerate 3π molecular orbitals are largely B 2p in character and comprise B 2p → CS π^* back-bonding. The formation of $^4\Sigma^-$ state BCS from ground-state B (^{2}P) and CS involves B 2s → 2p promotion, which requires about 82.5 kcal/mol promotion energy.[25] This promotion increases the B−CS bonding by decreasing the σ repulsion and increasing the B 2p → CS π^* back-bonding. The π back-donation of B to CS π^* results in the lengthening of the C−S bond from 1.539 Å in free CS to 1.575 Å in BCS. The binding energy of $^4\Sigma^-$ BCS with respect to B (^{2}P) + CS ($^1\Sigma^+$) was calculated to be 66.2 kcal/mol at the B3LYP/6-311+G* level of theory after zero-point energy correction. This binding energy is significantly larger than that of the BCO molecule calculated at the same level (25.9 kcal/mol).[5] The calculated B−C bond length of BCS is about 0.022 Å shorter than that of BCO. As has been discussed,[15] this may be attributed to the energy differences between the σ HOMO and π^* LUMO of CO and CS. The energy level of 7σ HOMO of CS is higher than that of the 5σ HOMO of CO, whereas the energy level of π^* LOMO of CS is lower than that of the π^* LUMO of CO, and, therefore, both the σ donation and the π back-donation are strong in thiocarbonyls relative to those in the corresponding carbonyls.

B(CS)$_2$. Absorptions at 1772.3, 1727.2, 1021.6, and 1005.7 cm^{-1} were only observed in the discharge experiments using the natural abundance boron target. These absorptions can be grouped together on the basis of their growth/decay characteristics measured as a function of changes of experimental conditions. When the ^{10}B-enriched boron target was used, only the 1772.3 and 1021.6 cm^{-1} bands were observed. The relative intensities of the absorptions clearly indicate that only one boron atom is involved in the molecule. The 1772.3 and 1727.2 cm^{-1} bands exhibited very small shifts with the discharged $C^{34}S_2$/Ar sample, but shifted to 1744.3 and 1697.5 cm^{-1} with the discharged $^{13}CS_2$/Ar sample. The isotopic $^{10}B/^{11}B$ ratio of 1.0261 and $^{12}C/^{13}C$ ratios of 1.0160 (^{10}B) and 1.0175 (^{11}B) suggest that these two bands are due to B−C stretching vibrations. The boron isotopic ratio is slightly higher, whereas the carbon isotopic ratios are slightly lower than those of diatomic BC, suggesting that the boron atom is vibrating between two C atoms. In the mixed $^{12}CS_2 + {}^{13}CS_2$ experiments (Figure 4), triplets with approximately 1:2:1 relative intensities were observed for both bands with intermediates at 1759.5 and 1713.9 cm^{-1}, indicating that two equivalent C atoms are involved. The 1021.6 and 1005.7 cm^{-1} bands shifted to 1007.2 and 992.9 cm^{-1} with $^{13}CS_2$, and to 1011.7 and 995.8 cm^{-1} with $C^{34}S_2$. Triplets with approximately 1:2:1 relative intensities were observed for both bands with intermediates at 1014.4 and 998.9 cm^{-1} when a mixed $^{12}CS_2 + {}^{13}CS_2$/Ar sample was used (Figure 3). Similar triplets with intermediates at 1016.6 and 1000.8 cm^{-1} were also observed in the mixed $C^{32}S_2 + C^{34}S_2$ spectra (Figure 5). These band profiles indicate that two equivalent CS subunits are involved. Accordingly, we assign the 1772.3, 1727.2, 1021.6, and 1005.7 cm^{-1} bands to the antisymmetric B−C and C−S stretching vibrations of the $^{10}B(CS)_2$ and $^{11}B(CS)_2$ molecules, respectively. The observation of only one C−S stretching vibration and one B−C stretching vibration implies that the molecule is linear.

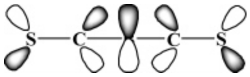

Figure 7. Depiction of the highest occupied molecular orbital (π_u) of B(CS)$_2$.

The assignment is strongly supported by density functional calculations. B(CS)$_2$ was predicted to have a $^2\Pi_u$ ground state with a linear structure (Figure 6). The antisymmetric B−C and C−S stretching vibrational frequencies were calculated at 1788.5 and 1027.9 cm^{-1} for $^{11}B(CS)_2$ with the calculated isotopic frequency ratios in excellent agreement with the experimental ratios. B3LYP calculations produced $^{10}B(CS)_2/^{11}B(CS)_2 =$ 1.0271 and 1.0159, $^{11}B(^{12}CS)_2/^{11}B(^{13}CS)_2 =$ 1.0175 and 1.0128, and $^{11}B(C^{32}S)_2/^{11}B(C^{34}S)_2 =$ 1.0003 and 1.0102 for the B−C and C−S stretching modes, respectively. The experimental values are as follows: $^{10}B(CS)_2/^{11}B(CS)_2 =$ 1.0261 and 1.0175, $^{11}B(^{12}CS)_2/^{11}B(^{13}CS)_2 =$ 1.0158 and 1.0129, and $^{11}B(C^{32}S)_2/^{11}B(C^{34}S)_2 =$ 1.0003 and 1.0099, respectively.

According to our DFT calculations, the ground state of B(CS)$_2$ reflects the B $2p^3$ electron configuration of the B atom. Formation of B(CS)$_2$ from quartet BCS and CS requires BCS $9\sigma \rightarrow 3\pi$ promotion. The molecule is predicted to have a $^2\Pi_u$ ground state with an electron configuration of (core) $(8\sigma_g)^2(7\sigma_u)^2(2\pi_u)^4(2\pi_g)^4(3\pi_u)^3$. As shown in Figure 7, the boron-based p electrons occupy the doubly degenerate $3\pi_u$ MO, which comprises significant B → CS π^* back-bonding. The ground-state B(CS)$_2$ molecule is predicted to be linear with the B−C and C−S bond lengths of 1.394 and 1.560 Å, respectively. The linear geometry is preferred to maximize the boron-to-CS back-bonding. The binding energy of the second CS was computed to be 98.5 kcal/mol, significantly higher than that of the first CS, and also is higher than that of the corresponding B(CO)$_2$ molecule.

Other Absorptions. Broad bands at 999.7 and 976.0 cm^{-1} appeared together on annealing in natural abundance boron experiments. When the ^{10}B-enriched target was used, only the

999.7 cm^{-1} band was observed. The relative intensities of these two bands matched natural isotopic abundance boron and indicate one boron atom involvement in the vibrational mode. These bands were only observed in the discharge experiments and were shifted to 987.6 and 964.7 cm^{-1} with $^{13}CS_2$, and to 989.1 and 968.0 cm^{-1} with $C^{34}S_2$. In the mixed $^{12}CS_2 + {}^{13}CS_2$ experiment, a broad doublet was produced. This doublet suggests that the vibration involves one carbon atom and is slightly perturbed by another nonequivalent carbon atom. The isotopic splitting could not be resolved in the mixed $C^{32}S_2 + C^{34}S_2$ experiment. These bands are tentatively assigned to the CS stretching mode of the $BCS(CS_2)$ molecule. DFT/B3LYP calculation predicted the $BCS(CS_2)$ molecule to have a $^2A''$ ground state with planar C_s symmetry (Figure 6). The C−S stretching mode of $^{11}BCS(CS_2)$ was predicted at 981.7 cm^{-1}.

Besides the boron monocarbonyl and dicarbonyl molecules, diboron species such as BBCO and OCBBCO were observed in the boron and CO reactions.[5−7] The observation of OCBBCO with some boron−boron triple bond character is of particular interest. It is generally known that the electron-deficient nature of boron hinders the formation of boron−boron multiple bonding. Molecules containing boron−boron multiple bonds are extremely rare. The isovalent SCBBCS molecule also was predicted to have a linear $^1\Sigma_g^+$ ground state and exhibits some boron−boron triple bond character. The B−B bond length was predicted to be 1.478 Å, slightly longer than that of OCBBCO,[5] but significantly shorter than those of B−B double-bonded species.[26−28] The OCBBCO molecule was formed from the dimerization of BCO, rather than from reaction of B_2 with CO. This suggests that SCBBCS also might be viable from the dimerization of BCS. However, no evidence was found for the formation of SCBBCS in the present experiments. The $SC^{11}B^{11}BCS$ molecule was predicted to have a strong B−C stretching vibration at 1603.3 cm^{-1}. We note that the BCS absorptions are weak in the experiments, and BCS is expected to be more difficult to diffuse in solid argon matrix than BCO.

Conclusions

Boron thiocarbonyl compounds BCS and $B(CS)_2$ have been studied by matrix isolation infrared absorption spectroscopy and density functional theory calculations. These boron thiocarbonyl species were produced via the reactions of CS produced by high-frequency discharge and boron atoms in solid argon matrix.

The bonding in these boron thiocarbonyl compounds is very similar to that in the corresponding carbonyls and is dominated by the synergic donation of electrons in 7σ HOMO of CS to an empty symmetry matching orbital of boron and the back-donation of the boron π electrons to the CS π^* orbital. The bonding involves significant B s → p promotion. The ground state of BCS was predicted to be $^4\Sigma^-$, which reflects the B $2s^12p^2$ electron configuration of the B atom. The $B(CS)_2$ molecule has a $^2\Pi_u$ ground state. Formation of $B(CS)_2$ from quartet BCS and CS requires BCS $9\sigma \rightarrow 3\pi$ promotion.

The binding energy of $^4\Sigma^-$ BCS with respect to B (^2P) + CS ($^1\Sigma^+$) was calculated to be 66.2 kcal/mol. The binding energy of the second CS was computed to be 98.5 kcal/mol, significantly higher than that of the first CS. These energies are significantly higher than those of the corresponding boron carbonyls.

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