

Potential constants of borane carbonyl^{a)}

Llewellyn H. Jones

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87545

Robert C. Taylor

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48106

Robert T. Paine

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87545

(Received 22 August 1978)

The vibrational spectra of several isotopic species of BH_3CO in neon matrices at 10°K have been observed. A number of combination bands have also been observed, leading to an assignment of most of the fundamental harmonic frequencies of these isotopic species. A least squares normal coordinate treatment, without constraints, has estimated a set of potential constants. We can conclude that the CO bond in BH_3CO is slightly stronger than that of free CO. The interaction coordinates suggest that unimolecular dissociation of the B-C bond proceeds initially toward $\text{BH}_3^- + \text{CO}^+$ but reverts to $\text{BH}_3 + \text{CO}$ before dissociation.

INTRODUCTION

In discussing the bonding of metal carbonyls, one is often concerned with the effect which bonding to the metal has on the CO group. We know that π bonding of the metal d electrons to the antibonding pi orbitals of the CO groups weakens the CO bonds. At the same time it is believed that sigma bonding alone would strengthen the CO bond as the lone pair of electrons on the carbon, which are used in sigma bond formation, are slightly antibonding¹ in free CO. Thus, it is of interest to find an example of a carbonyl which forms a single M-C sigma bond free of back pi bonding to evaluate the effect of sigma bonding. Borane carbonyl appears to be the best example of such a molecule, though there is the possibility of hyperconjugation² which may put some H electron density into the CO antibonding π orbitals. Previous estimates of the force field of borane carbonyl have appeared³⁻⁵ with rather different results, particularly for the CO bond strength. The first of these³ was from the infrared spectrum of the gas phase using frequencies for some isotopically enriched species (¹⁰B, D). Unfortunately the gas phase absorption bands are rather asymmetric and not suitable for locating the band center under the available resolution. Another report,⁴ which appeared at about the same time, was based on Raman spectra of the liquid for which the bands are rather broad. In neither case were ¹³C or ¹⁸O isotope shifts available so a number of constraints were introduced to derive the potential function.

In this work we have prepared a number of isotopically enriched borane carbonyls and have observed most of the fundamental frequencies of ten isotopic species. The spectra were recorded in a low temperature, rare gas matrix so that sharp peaks could be attained and accurate isotope shifts determined.

EXPERIMENTAL SECTION

Standard high vacuum gas handling techniques were used for the manipulation of the volatile compounds. The purities of the starting materials, diborane and carbon monoxide, were verified by mass and infrared spectra of gaseous samples. The ¹⁰B₂H₆ was obtained from the reduction of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ by LiAlH_4 .⁶ Boron-10 enriched diborane was obtained in a similar fashion from ¹⁰BF₃ · O(C₂H₅)₂ which was generated thermally from CaF₂ · ¹⁰BF₃ complex (Oak Ridge National Laboratory). The ¹⁰B₂D₆ was obtained from the action of NaBD₄ (Alpha) on polyphosphoric acid. The diborane was subjected to triple vacuum trap to trap distillation prior to use. The carbon monoxide ¹³CO (94% ¹³C) was obtained from Los Alamos Scientific Laboratory and the ¹²C¹⁸O sample was obtained from Bio Rad Laboratories.

The borane carbonyl samples of varying isotopic constitution were all prepared in the same fashion using the technique described by Carter.⁷ Typically, a 10 mmol sample of diborane was condensed into a 25 ml high pressure, stainless steel bomb fitted with a high pressure valve and gauge. The carbon monoxide was then condensed onto the diborane in a five- to tenfold excess. The bomb was closed and allowed to warm to room temperature. After twelve hours the volatile products were fractionated through traps cooled to -96°, -160°, and -196°C. The borane carbonyls were retained at -160° and stored at -196°C.

For all the low temperature matrices a Displex model 202S closed cycle refrigerator with CsI windows was used. The BH_3CO was mixed with neon or argon at a ratio of $\frac{1}{1000}$ in a liter bulb kept at dry ice temperature to inhibit decomposition. The mixture was deposited slowly (several min. per Torr l) through a metering valve onto a cold CsI window. The spectra were observed in transmission. Such matrices prepared with argon exhibited splitting of the degenerate fundamentals suggesting significant distortion of the BH_3CO molecule in the matrix. However, the size of the BH_3CO mole-

^{a)}This work performed under the auspices of the U. S. Department of Energy.

TABLE I. Observed vibrational frequencies (in cm^{-1}) for various isotopic species, $^i\text{H}_3^j\text{B}^k\text{C}^l\text{O}$, in neon matrices at 10°K .

i	1	1	1	1	1	1	2	2	2	2
j	11	10	11	10	11	10	11	10	11	10
k	12	12	13	13	12	12	12	12	13	13
l	16	16	16	16	18	18	16	16	16	16
ν_1	2379.5 ^a	2384.0 ^a	2382.0 ^a	2383.7 ^a	2383.1 ^a	...	1682.3 ^a	1699.8 ^a	1681.5 ^a	1696.5 ^a
ν_2	2167.4	2168.5	2118.1	2119.8	2120.6	...	2171.0	2171.8	2121.4	...
ν_3	1072.7	1083.3	1073.3	1083.3	1072.8	1083.2	863.8	884.3	863.5	883.5
ν_4	698.4	713.6	694.8	710.5	690.6	705.9	628.8	633.7	625.4	630.5
ν_5	2435.3	2447.4	2434.5	2447.1	2435.3	2447.7	1831.4	1847.5	1831.7	1847.8
ν_6	811.4	...	808.0	...
ν_7	810.3	819.6	802.1	811.4	809.2	818.4	709.7	718.8	701.0	710.0
ν_8	312.1	312.1	307.3	...	309.5	...	263.2	...	261.4	...
$\nu_1 + \nu_4$					3078.8					
$\nu_2 + \nu_3$			3190.9 ^c	3199.0			3032.5	3055.0	2984.3 ^c	
$\nu_2 + \nu_4$	2867.5 ^c	2884.9			2815.3	2829.0	2800.7	2806.4	2749.0	
$\nu_2 + \nu_5$							3990.8 ^c			
$\nu_2 + \nu_7$	2973.4	2983.2	2915.5 ^c	2926.5	2925.7	2935.9				
$\nu_2 + \nu_8$	2478.3		2422.0		2426.2		2433.5 ^c			
$2\nu_3$	2133.0 ^c	2152.4	2133.8	2159.4	2135.0		1753.0 ^a		1752.2 ^a	
$\nu_3 + \nu_4$			1758.8	1787.2					1499.2	
$\nu_3 + \nu_5$							2693.1		2692.1 ^c	
$\nu_2 + \text{Q}^b$	2182.9		2132.8		2134.0		2186.0		2136.6	
$\nu_3 + \nu_6$	2170.3 ^c	2180.6	2170.4 ^c				1671.2			
$\nu_4 + \nu_5$			3135.2 ^c							
$\nu_4 + \nu_6$									1437.0	
$\nu_4 + \nu_7$			1495.1 ^c						1322.8	
$\nu_5 + \nu_8$	2746.3	2756.5	2740.5 ^c	2749.3	2743.4		2091.9	2108.0	2088.7 [?]	
$2\nu_6$	2190.7 ^c		2191.9 ^c				1598.8	1602.8		
$\nu_6 + \nu_7$	1898.9				1909.7		1516.8 ^c		1504.6	
$\nu_6 + \nu_8$	1404.9		1405.4				1074.4 ^c			
$2\nu_7$	1614.8 ^c	1633.3					1416.1 ^c		1400.4	
$\nu_7 + \nu_8$	1111.6	1121.0	1099.3 ^c	1109.1	1107.6	1117.0	966.2	975.3	954.6	964.4
$2\nu_8$	626.0 ^c		616.4		619.4		527.9		521.4	

^aObserved in Raman spectrum of neon matrix.

^bQ is a transition whose origin is not yet clear (see text).

^cOvertone or combination band used in establishing anharmonicity.

cule with C_{3v} symmetry is about right to fit into a neon matrix in place of four neon atoms in a tetrahedral array, with the CO group aligned along a C_3 axis. Therefore, we deposited BH_3CO in a neon matrix at about 9°K and were pleased to find that the degenerate modes were not split though the BCO bending mode is somewhat broader than the other fundamentals. This indicates that the BH_3CO is not significantly distorted from C_{3v} symmetry in a neon matrix. We consequently studied all the isotopic species (BH_3CO , BD_3CO , $\text{BH}_3^{13}\text{CO}$, BH_3^{18}O , and $\text{BD}_3^{13}\text{CO}$) in neon matrices. The natural abundance of boron (80% ^{11}B , 20% ^{10}B) was satisfactory for assigning most of the ^{10}B and ^{11}B fundamentals. Some uncertainties were clarified by studying BH_3CO with ~50% ^{10}B and 50% ^{11}B .

The spectra were observed on a Perkin-Elmer 180 spectrometer. Raman spectra were also studied primarily to observe the symmetric B-H stretch which is very weak in the infrared. Rather thick deposits on a copper block at 10°K were required for the Raman study. We used a mixture $\text{Ne}/\text{BH}_3\text{CO} = \frac{200}{1}$ and deposited about 100 Torr l over about 5 cm^2 of the block.

Spectral observations and frequency assignments

As discussed later, BH_3CO has C_{3v} symmetry and thus has four A_1 type frequencies and 4 E type frequencies. We have observed most of the fundamentals for ten isotopic species together with a number of combination bands. Table I lists the frequencies observed in neon matrices and Table II the frequencies of solid films. Parts of the spectrum of the normal species are shown in Fig. 1. We hoped to observe enough combination bands to determine the various anharmonicity corrections, X_{ij} , in the energy level expression

$$G_{v_1, v_2} = \sum \omega_i(v_i + d_i/2) + \sum_{i < j} X_{ij}(v_i + d_i/2)(v_j + d_j/2).$$

However, in the neon matrix relatively few combinations and overtones were observable. In order to supplement these data we also observed spectra of the pure solids at 10°K . Most of these data are listed in Table III. Though the anharmonicity corrections are not necessarily the same in matrix and pure solid, such an assumption should be a reasonable approximation and was used.

The earlier work^{3,4} has been of great help in assign-

TABLE II. Infrared absorption frequencies (in cm^{-1}) for solid films of ${}^1\text{H}_3{}^1\text{B}{}^1\text{C}{}^1\text{O}$ at 10°K .

i	1	1	1	1	1	1	2	2	2	2
j	11	10	11	10	11	10	11	10	11	10
k	12	12	13	13	12	12	12	12	13	13
l	16	16	16	16	18	18	16	16	16	16
ν_1	2377.7	2382.0	2375.6	2381.2	2379.0	...	1687.1	1698.0
ν_2	2185.1	...	2134.8	2136.5	2123.4	...	2187.9	...	2138.6	...
ν_3	1078.1	1089.2	1077.8	1088.7	1077.5	1091.5	868.0	...	868.5	889.0
ν_4	693.1	707.9	688.7	703.7	686.0	697.0	622.7	...	620.0	...
ν_5	{2425.7 2440.5	2436.0	2423.0	...	2426.0	...	1824.0	1839.0	1842.2	...
ν_6	{1105.8 1112.2	...	1106.3	...	1107.5	...	814.1	...	810.9	812.2
ν_7	{817.3 822.3	826.7	809.4	818.6	816.0	825.0	710.6	720.4	701.5	711.5
ν_8	314.5	...	308.1	713.4	722.2	703.5	713.5
$2\nu_1$	4734.3 ^a		4730.7 ^a				274.5
$\nu_1 + \nu_2$	4556.9 ^a	4562.3	4507.4	4511.2						
$\nu_1 + \nu_4$							2313.0			
$\nu_1 + \nu_5$	4751.2 ^a	4764.8	4751.9 ^a	4766.8						
$\nu_1 + \nu_7$	3194.0 ^a	3207.4								
$\nu_1 + \nu_8$	2699.0									
$2\nu_2$	4344.4 ^a		4246.0 ^a							
$\nu_2 + \nu_4$	2875.2	2888.9								
$\nu_2 + \nu_5$	{4602.0 4617.3	4629.9	4552.7	4563.0	4581.1					
$\nu_2 + \nu_6$							3004.3 ^a			
$2\nu_3$				2143.7	2162.6					
$\nu_3 + \nu_4$	1761.6 ^a	1785.6								
$\nu_3 + \nu_5$	3505.0?									
$\nu_3 + \nu_6$			2174.7				1679.0			
$\nu_3 + \nu_7$	1890.8 ^a	1906.7								
$\nu_3 + \nu_8$	1391.7 ^a									
$2\nu_4$	1373.7 ^a	1401.7								
$\nu_4 + \nu_5$	{3121.0 3136.0									
$\nu_4 + \nu_6$	1803.9 ^a	1822.4								
$\nu_4 + \nu_7$	1509.0	1533.2								
$2\nu_5$	4816.0 ^a		4816.0	4834.4						
$\nu_5 + \nu_6$	3556.0						{2630.5 2640.6 ^a		2638.4	
$\nu_5 + \nu_7$	3255.0	3266.3								
$\nu_6 + \nu_8$	1422.6	1426.9								
$2\nu_7$	{1629.4 1637.0	1648.4	1614.4							
$\nu_7 + \nu_8$	1128.1	1136.7	1106.4							

^aOvertone or combination used to establish anharmonicity.

ing the fundamental frequencies. We shall discuss them individually.

ν_1 . This is mainly the symmetrical BH stretch and is very weak in the infrared so we have relied primarily on the Raman shifts for the assignments. As noted previously,⁴ for BD_3CO there is a strong Fermi resonance of ν_1 with $2\nu_3$. We find this to be true for both ${}^{11}\text{BD}_3{}^{12}\text{C}{}^{16}\text{O}$ and ${}^{11}\text{BD}_3{}^{13}\text{C}{}^{16}\text{O}$. For the ${}^{10}\text{B}$ species resonance is somewhat weaker. As seen in Table I we have observed ν_1 and $2\nu_3$ for ${}^{11}\text{BD}_3{}^{12}\text{C}{}^{16}\text{O}$ and ${}^{11}\text{BD}_3{}^{13}\text{C}{}^{16}\text{O}$ and ν_1 for the ${}^{10}\text{B}$ species. The Fermi perturbation can be described by the relation⁸

$$\pm D_{\nu, \nu'} = \frac{1}{2} [(\delta^2 + 4W_{\nu, \nu'}^2)^{1/2} - \delta]. \quad (1)$$

Where δ is the separation of unperturbed levels, ν and ν' , $W_{\nu, \nu'}$ is the Fermi interaction constant ($\int \psi_{\nu'}^0 W \psi_{\nu} d\tau$), and $\pm D$ is the displacement of the observed levels from their unperturbed positions. If we know the anharmonic

TABLE III. Fermi interaction constant and unperturbed frequencies in cm^{-1} for ν_1 and $2\nu_3$ of BD_3CO .

	${}^{11}\text{BD}_3{}^{12}\text{C}{}^{16}\text{O}$	${}^{11}\text{BD}_3{}^{13}\text{C}{}^{16}\text{O}$	${}^{10}\text{BD}_3{}^{12}\text{C}{}^{16}\text{O}$	${}^{10}\text{BD}_3{}^{13}\text{C}{}^{16}\text{O}$
W	35.3	35.3	(35.3) ^a	(35.3) ^a
$(\nu_1)_0$	1716.1	1715.1	1718.1	1716.7
$(2\nu_3)_0$	1719.2	1718.6	1759.9	1758.3

^aAssumed the same as the ${}^{11}\text{B}$ values.

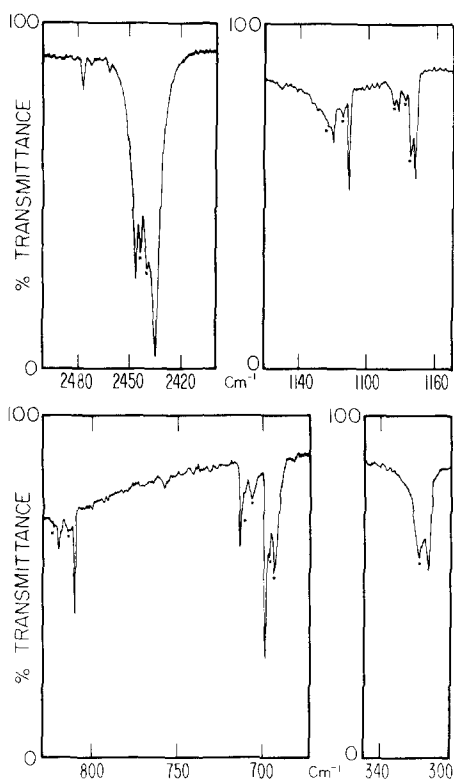


FIG. 1. Neon matrix of BH_3CO : 1000/1 $10^\circ\text{K} \sim 4 \mu\text{mole}$ $\text{BH}_3\text{CO}/\text{cm}^2$. Absorptions labeled with * are believed to arise from aggregates of interacting BH_3CO molecules.

nicity constant, X_{33} , we can calculate the "unperturbed" values for $(2\nu_3)_0$. With this information and the observed values from Table I for ν_1 and $2\nu_3$ of the $^{11}\text{BD}_3\text{CO}$ species we can calculate W and the unperturbed values of $(\nu_1)_0$. Assuming W is the same, we can then calculate the values of $(\nu_1)_0$ for the ^{10}B species. For the H species X_{33} is found to be about -6.4 cm^{-1} . Using the usual relation $X_{ij}^2 = [\omega_i^2 \omega_j^2 / \omega_i^2 \omega_j^2] X_{ij}^2$, we find $X_{33} = -4.2$ for $^{11}\text{BD}_3\text{CO}$ and -4.35 for $^{10}\text{BD}_3\text{CO}$. We are then able to calculate the results listed in Table III.

ν_2 . This is primarily the CO stretching mode and gives rise to the strongest band in infrared absorption. There is no problem in assigning the ν_2 peaks; however, there are combination bands in this region which complicate the structure somewhat. In Fig. 2 we show this region for the normal species. The major peaks shown here have been assigned except for that at 2183 cm^{-1} . This poses an anomaly as an analogous peak occurs for all ^{11}B isotopic species at about 15 cm^{-1} above the ν_2 fundamental. There is no combination of internal modes which would fall in such a position for the different isotopic species. We have assigned it as a combination of $\nu_2 + Q$ where Q is 15 cm^{-1} for all species. One might speculate that it arises from a combination of ν_2 with a phonon mode of the neon lattice or with a translational or librational mode of BH_3CO in the neon lattice. However, in an argon matrix a similar strong band occurs at $\nu_2 + 15$ which tends to rule out the matrix material as contributing to such a band. Another thought was that this band may arise from a dimer, or aggregate of sev-

eral BH_3CO molecules, as it comes near the frequency for pure, solid BH_3CO (see Table II). However, dilution does not affect its relative intensity; thus, at neon/ $\text{BH}_3\text{CO} = 5000/1$ this band at 2183 cm^{-1} is just as intense relative to ν_2 as at a ratio of $1000/1$. This seems to rule out aggregates as an explanation; for the present we must consider this band unexplained.

ν_3 and ν_4 . These A_1 modes are easily assigned by comparison with previous work^{3,4} and the expected isotope shifts.

ν_5 . This is primarily antisymmetric BH stretch and is readily assigned to the strong absorptions in the 2400 cm^{-1} region for BH and 1800 cm^{-1} for BD.

ν_6 . The assignment of this mode, which is an antisymmetric HBH deformation, gave problems. It was originally thought to give rise to some relatively strong peaks slightly over 1100 cm^{-1} for the H species. This would be in agreement with the assignments of Taylor⁴ from the Raman spectra. However, the relatively large isotope shifts for $^{10}\text{B}/^{11}\text{B}$, $^{12}\text{C}/^{13}\text{C}$, and $^{16}\text{O}/^{18}\text{O}$ for this absorption rule out its assignment as ν_6 ; instead, it is more satisfactorily assigned as the combination $\nu_7 + \nu_8$ for which the isotope shift is in close agreement. The fundamental ν_6 has been observed for BD_3CO and $\text{BD}_3^{13}\text{CO}$ as a weak band at 811.4 and 808.0 cm^{-1} , respectively. Apparently for the H species ν_6 is weaker than $\nu_7 + \nu_8$ and lost in the latter. Its assignment in the H species can be approximated from the pure solid spectra for which $\nu_7 + \nu_8$ is well shifted from the ν_6 region. From this observation and the solid-matrix shift for the deuterium species we estimate $\nu_6 \approx 1105.5 \text{ cm}^{-1}$ for $^{11}\text{BH}_3\text{CO}$ in a neon matrix.

ν_7 and ν_8 . There is no problem in the assignment of these two E modes— BH_3 rock and BCO bend, respectively.

We should point out that there are spurious bands near the sharp peaks of ν_7 , ν_3 , and $\nu_7 + \nu_8$. We believe these arise from aggregates since they decrease in intensity with respect to the nearby sharp peaks for more dilute matrices.

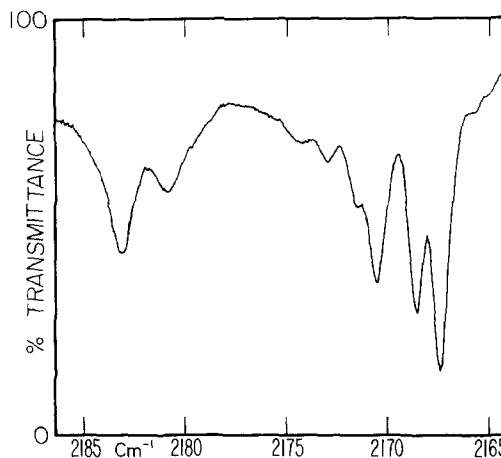


FIG. 2. Neon matrix of BH_3CO : 1000/1 $10^\circ\text{K} \sim 0.8 \mu\text{mole}$ $\text{BH}_3\text{CO}/\text{cm}^2$.

TABLE IV. Anharmonic corrections for $H_3^{11}B^{12}C^{16}O$ and harmonic frequencies for ${}^4H_3{}^4B^4C^1O$ in cm^{-1} .

X_{ij}		X_{23}		X_{36}		X_{56}					
X_{11}	-10.5	X_{23}	-1.0	X_{36}	-8.0	X_{56}	-13.0				
X_{12}	-5.8	X_{24}	+1.7	X_{37}	-6.0	X_{57}	0.0				
X_{13}	0.0	X_{25}	-15.0	X_{38}	-3.0	X_{58}	-1.3				
X_{14}	0.0	X_{26}	+3.0	X_{44}	-6.0	X_{66}	-10.0				
X_{15}	-60.0	X_{27}	-4.7	X_{45}	+4.0	X_{67}	-6.7				
X_{16}	0.0	X_{28}	-3.0	X_{46}	+4.8	X_{68}	0.0				
X_{17}	-6.0	X_{33}	-6.4	X_{47}	-1.8	X_{77}	-2.5				
X_{18}	0.0	X_{34}	-9.0	X_{48}	+3.5	X_{78}	-10.0				
X_{22}	-12.5	X_{35}	-5.1	X_{55}	-33.0	X_{88}	+1.0				
$i-j-k-l$	\rightarrow	1-10-12-16	1-11-12-16	2-10-12-16	2-11-12-16	1-10-13-16	1-11-13-16	2-10-13-16	2-11-13-16	1-10-12-18	1-11-12-18
ω_1		2474.5 25.0 ^a	2469.4 25.0	1767.9 0.25	1765.5 1.0	2474.0 0.0	2471.9 25.0	1766.3 0.25	1764.3 1.0	2475.0 0.0	2473.1 25.0
ω_2		2215.9 100.0	2214.7 100.0	2214.6 100.0	2213.6 100.0	2165.5 0.0	2163.6 100.0	2162.3 0.0	2162.2 100.0	2168.1 1.0	2166.3 100.0
ω_3		1123.9 25.0	1112.6 25.0	911.3 1.0	889.9 1.0	1123.8 25.0	1113.1 25.0	910.3 1.0	889.4 25.0	1123.7 0.0	1112.7 25.0
ω_4		719.2 6.0	703.6 6.0	639.0 6.0	633.9 6.0	716.1 6.0	699.9 6.0	635.7 6.0	630.5 6.0	711.3 6.0	695.6 6.0
ω_5		2600.0 25.0	2586.7 25.0	1934.9 25.0	1917.5 25.0	2599.5 0.0	2585.6 25.0	1935.1 25.0	1917.7 25.0	2600.2 0.0	2586.5 25.0
ω_6		1156.8 0.0	1155.3 1.0	839.5 0.0	838.7 11.0	1157.3 0.0	1155.9 0.0	836.7 0.0	835.1 11.0	1157.5 0.0	1156.0 0.0
ω_7		853.6 25.0	843.8 25.0	743.5 25.0	733.9 25.0	844.8 25.0	834.9 25.0	734.2 25.0	724.7 25.0	852.2 25.0	842.5 25.0
ω_8		321.8 11.0	321.7 11.0	270.5 0.0	270.2 11.0	316.7 0.0	316.6 11.0	268.4 0.0	268.3 11.0	319.1 0.0	319.0 11.0

^aThe numbers below the frequencies are the partial weights used in the least squares potential constant calculations. They are equal to $1/(\Delta\nu)^2$ where $\Delta\nu$ is the estimated error in observed frequency. Total weight = $[1/(\Delta\nu_i)^2] \cdot [1/\lambda_i]$.

TABLE V. Symmetry coordinates^{a,b} for BH₃CO of C_{3v} symmetry.

A_1	$S_1 = \frac{1}{\sqrt{3}} (d_1 + d_2 + d_3)$
	$S_2 = r$
	$S_3 = [b(\alpha_1 + \alpha_2 + \alpha_3) - (\beta_1 + \beta_2 + \beta_3)]/[3(1 + b^2)]^{1/2}$
	$S_4 = R$
E	$S_5 = \frac{1}{\sqrt{6}} (2 d_1 - d_2 - d_3)$
	$S_6 = \frac{1}{\sqrt{6}} (2 \alpha_{23} - \alpha_{12} - \alpha_{13})$
	$S_7 = \frac{1}{\sqrt{6}} (2 \beta_1 - \beta_2 - \beta_3)$
	$S_8 = \gamma$

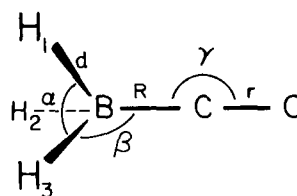
^a b is a constant = $-3 \sin \beta_0 \cos \beta_0 / \sin \alpha_0$.

^bThe internal coordinates given are, of course, displacements ($d_1 = \Delta d_1$).

From the observation of overtones and combination bands many of the anharmonicity corrections have been estimated. This has made it possible to estimate the harmonic fundamental frequencies from the usual relationship

$$\omega_i = \nu_i - X_{ij}(1 + d_i) - \sum_{j < i} X_{ij} \frac{d_j}{2}.$$

Unfortunately, for most X_{ij} , experimental data were not

FIG. 3. Internal coordinates of BH₃CO.

available for all the isotopic species. Therefore use was made of the standard approximation $X_{ij}^k = X_{ij}^l \nu_i^k \nu_j^k / \nu_i^l \nu_j^l$ to provide the missing values. Two of the anharmonicity corrections were estimated from high resolution work, namely X_{28} ^{9a} and X_{48} ^{9b}. The ones estimated from our neon matrix studies are X_{23} , X_{24} , X_{25} , X_{27} , X_{33} , X_{35} , X_{36} , X_{38} , X_{45} , X_{46} , X_{47} , X_{58} , X_{67} , X_{77} , X_{78} , and X_{88} . Other constants were transferred from observations on the pure solid; namely, X_{11} , X_{12} , X_{15} , X_{17} , X_{22} , X_{26} , X_{34} , X_{37} , X_{44} , X_{55} , X_{56} , and X_{66} . A number of values were assigned as 0.0 as there was no consistent information concerning them; these are X_{13} , X_{14} , X_{16} , X_{18} , X_{57} , and X_{68} .

The estimated anharmonic corrections, X_{ij} , for the normal species and harmonic frequencies, ω_i , for all species are listed in Table IV.

Normal coordinate calculations

The first structure determination on BH₃CO was by Bauer¹⁰ who confirmed that the molecule had C_{3v} symmetry and gave approximate values for molecular parameters. The most recent parameters are those determined from microwave studies by Venkatachar,

TABLE VI. Symmetry potential constants calculated for BH₃CO.

		A_1				E	
		Harmonic ν	Observed ν			Harmonic ν	Observed ν
F_{11}	BH	3.50 ^a (15) ^b	3.25	F_{55}	BH	3.58(5)	3.10
F_{22}	CO	19.24(13)	18.67	F_{66}	α	0.365(15)	0.31
F_{33}	α (HBH)	0.63(14)	0.58	F_{77}	β (HBC)	0.412(57)	0.39
F_{44}	BC	2.85(30)	2.76	F_{88}	γ (BCO)	0.502(69)	0.52
F_{12}	BH, CO	0.07(62)	0.22	F_{56}	BH, α	-0.18(73)	0.00
F_{13}	BH, α	-0.34(54)	-0.26	F_{57}	BH, β	0.2(18)	0.00
F_{14}	BH, BC	0.51(110)	0.26	F_{58}	BH, γ	0.0(11)	0.03
F_{23}	CO, α	-0.46(11)	-0.46	F_{67}	α, β	0.07(19)	0.11
F_{24}	CO, BC	0.45(11)	0.60	F_{68}	α, γ	-0.05(22)	0.02
F_{34}	α, BC	-0.31(19)	-0.28	F_{78}	β, γ	-0.226(83)	-0.21
Compliance (Harmonic)							
	C_{11}	0.31(8)	C_{55}	0.30(10)			
	C_{22}	0.0530(7)	C_{66}	2.93(59)			
	C_{33}	1.76(9)	C_{77}	3.46(20)			
	C_{44}	0.31(8)	C_{88}	2.68(35)			
	C_{12}	0.003(3)	C_{56}	0.18(57)			
	C_{13}	0.15(21)	C_{57}	-0.2(19)			
	C_{14}	-0.04(10)	C_{58}	-0.1(14)			
	C_{23}	0.04(1)	C_{67}	-0.5(22)			
	C_{24}	-0.005(2)	C_{68}	0.1(19)			
	C_{34}	0.16(1)	C_{78}	1.51(39)			

^aThe units for force constants are mdyne/Å for stretch, mdyne·Å·rad⁻² for bend and millidynes/radian for stretch bend. For compliance constants the units are inverted.

^bStandard deviations in parentheses in units of last decimal place given.

TABLE VII. Deviations of observed from calculated harmonic frequencies for ${}^1\text{H}_3\text{B}^{13}\text{C}^{16}\text{O}$.

$i-j-k-l \rightarrow$	16-12-10-1	16-12-10-2	16-12-11-1	16-12-11-2	16-13-10-1	16-13-10-2	16-13-11-1	16-13-11-2	18-12-10-1	18-12-11-1
$\Delta\omega_1^a$	0.3	-7.0	-2.1	-4.5	[2474.0] ^b	-8.6	0.6	-5.7	[2474.2]	1.6
$\Delta\omega_2$	0.1	0.1	-0.2	-0.3	[2164.4]	[2162.7]	0.0	0.1	1.0	0.1
$\Delta\omega_3$	-0.1	-1.0	0.1	-0.5	0.0	-1.9	0.7	-0.9	[1123.5]	0.5
$\Delta\omega_4$	0.0	-1.8	1.2	-1.2	0.0	-1.9	0.8	-1.2	1.0	2.4
$\Delta\omega_5$	1.1	-0.3	0.1	-0.1	[2598.9]	-0.1	-1.0	0.1	[2598.9]	-0.1
$\Delta\omega_6$	[1150.8]	[839.5]	5.5	-0.5	[1149.3]	[835.8]	[1148.2]	-0.1	[1150.6]	[1149.6]
$\Delta\omega_7$	0.1	-0.2	0.0	-0.1	0.1	-0.1	-0.1	0.0	0.0	0.0
$\Delta\omega_8$	0.4	[272.0]	0.3	-1.6	[316.2]	[268.8]	0.5	-0.4	[318.3]	0.7

^aThe units of $\Delta\omega_i$ are obs-calc cm^{-1} .^bNumbers in brackets are calculated values which were not observed.

*et al.*¹¹; $r_{\text{CO}} = 1.135 \pm 0.01 \text{ \AA}$, $R_{\text{BC}} = 1.534 \pm 0.01 \text{ \AA}$, $d_{\text{BH}} = 1.221 \pm 0.001 \text{ \AA}$, $\angle\text{HBC} = 103.70 \pm 0.06^\circ$, and $\angle\text{HBH} = 114.50 \pm 0.15^\circ$. Symmetry coordinates for this molecule were given previously by Taylor⁴ and later by McNaught¹² who also gave explicit expressions for the symmetry G matrix elements. Since other authors have not all used the same set, and also to clarify the numbering of the normal modes, we reproduce the symmetry coordinates used in Table V. The internal coordinates are defined in Fig. 3. Elements of the symmetry G matrices were evaluated using the computer program of Schachtschneider¹³ and also from the expressions of McNaught¹²; agreement was found within normal round-off error.

Force constants were determined using a standard iterative least squares procedure which fitted all isotopic frequencies in a given class simultaneously. The principal program used was that of Schachtschneider¹³ but parallel calculations were made using an independently written program at The University of Michigan with a laboratory designation of JACO-3D. Essentially identical results were obtained from the two programs, the refined values of the force constants agreeing well within the calculated dispersions of the constants with one or two exceptions. The exceptions were not considered serious and involved off-diagonal force constants which were not well determined, as judged by the magnitude of their dispersions. The discrepancies are attributed to small differences in convergence limits and the different method of damping used in the two programs. Weighting factors used in the refinement were proportional to $1/(\Delta\nu)^2\lambda$ where $\Delta\nu$ is the estimated uncertainty in the observed frequency. The values of $1/(\Delta\nu)^2$ are listed in Table IV. They do not include the uncertainties in anharmonicities, but do give a reasonable estimate of how well the isotope shifts are known which are the most important quantities in the least squares calculations. A zero weight was used for all frequencies where the experimental band was not observed with confidence (the values listed in the table in those cases have been estimated from isotope shifts). The exclusion of such frequencies left 32 frequencies in the A_1 class and 27 in the E class actually used in the refinement of the 10 symmetry force constants in each class.

Inasmuch as previous force constant analyses utilized experimental (anharmonic) frequencies, the present calculations were extended to fit these as well. Because of uncertainties in some of the anharmonicity corrections, it turned out that the experimental frequencies could be fitted nearly as well as the harmonic, judged solely in terms of the average deviations of the calculated results. However, the primary force constants based on the harmonic values should be more meaningful than those calculated from the observed frequencies. With one exception (F_{88}), the principal harmonic force constants ranged from 2%–15% higher than the anharmonic values. The interaction constants, of course, differed over a much larger range, particularly those which were not well determined.

Symmetry force constants determined from both the experimental and harmonic frequencies are listed in Table VI. Compliance constants obtained by inversion

TABLE VIII. Symmetry eigenvectors for fundamental modes of $^{11}\text{B}^{1}\text{H}_3^{12}\text{C}^{16}\text{O}$.

A_1				
ν , cm^{-1}	L_{BH}	L_{CO}	L_{α}	L_{BC}
2471.5	0.99 ^a	-0.02	-0.21	-0.03
2214.9	-0.05	-0.38	0.11	0.25
1112.5	-0.13	-0.04	-1.13	-0.12
702.4	0.05	-0.02	0.03	-0.31
E				
ν , cm^{-1}	L_{BH}	L_{α} (HBH)	L_{β} (HBC)	L_{γ} (BCO)
2586.6	1.06	0.07	-0.07	0.06
1149.8	0.04	1.31	0.40	-0.07
843.8	-0.06	-0.54	0.73	-0.36
321.4	-0.03	-0.04	0.35	0.38

^aUnits for L are such that $LL^T = G$.

of the F matrices are included in the same table. As can be seen from Table VI, interaction constants involving the B-H stretching coordinate uniformly were rather poorly determined both in the A_1 and E classes. The deviations of calculated frequencies from those of Table IV are given in Table VII.

The potential energy distribution showed very little mixing of coordinates in the normal modes and consequently is not given here. A description of the normal modes can be gleaned from the eigenvectors listed in Table VIII for the normal species. The changes for isotopic species are not great.

DISCUSSION

The CO stretching force constant found here (19.24 $\text{mdyn}/\text{\AA}$) appears to be slightly greater than that of free CO (19.02 $\text{mdyn}/\text{\AA}$),¹⁴ but less than that of CO^+ (19.80 $\text{mdyn}/\text{\AA}$).¹⁴ A recent theoretical treatment¹⁵ of borane carbonyl indicates that "The CO bond of BH_3CO is somewhat stronger than in free CO," in agreement with our findings. Also, their calculations¹⁵ indicate that there is electron transfer from the MO of BH_3 to the antibonding 2π MO of CO, the previously postulated² hyperconjugative stabilization of the molecule which weakens the CO bond. Thus the CO bond tends toward that of CO^+ due to the B-C sigma bonding but the donation of BH_3 electrons to the CO antibonding π orbital counteracts this effect, leaving a CO bond only slightly stronger than in free CO.

The theoretical calculations of Ermler *et al.*¹⁵ also indicate a B-C bond considerably weaker than a good single bond. We find a B-C force constant of 2.85 $\text{mdyn}/\text{\AA}$ which is weaker than expected for the usual single bond (4-6 $\text{mdyn}/\text{\AA}$ for C-C, C-N, etc.),¹⁶ though it is somewhat stronger than the very weak N-F bond in ONF ($F_{\text{NF}} = 2.2$ $\text{mdyn}/\text{\AA}$).¹⁷ The actual B-C force constant for a simple sigma bond may be even less than 2.85 $\text{mdyn}/\text{\AA}$ since this includes the $\text{H}\cdots\text{C}$ hyperconjugative interaction if it exists.¹⁸

The interaction coordinates¹⁹ are of interest in discussing the bonding. For example, we find $(\text{CO})_{\text{BC}}$

$= -0.013$ and $(\alpha)_{\text{BC}} = 0.4$. Thus, when the BC bond is stretched a small amount for minimum energy the CO bond tends to contract by 1.3% of that amount. Thus, it appears to tend toward CO^+ rather than neutral CO. This suggests that near equilibrium the B-C bonding electrons tend to stay more with the boron atom than to move out with the CO group; or perhaps this is equivalent to an initial dissociative process toward $\text{BH}_3 + \text{CO}^+$. At greater displacement of the B-C bond, of course, the process must cross over into dissociation toward $\text{BH}_3 + \text{CO}$.

The interaction of the B-C stretch with the HBH angle, α , expressed as $(\alpha)_{\text{BC}}$, indicates that a slight stretch of the B-C bond tends to open up the HBH angles for minimum energy. This could arise from two effects: the hyperconjugation tends to pull the hydrogens toward the carbon; the BH_3 group may have a larger HBH angle than found in BH_3CO .

The BH, BH interaction is apparently very small—negligible within one standard deviation. The work of Ermler, *et al.*¹⁵ suggests a strong B-H bond, yet the force constant of 3.5 $\text{mdyn}/\text{\AA}$ is considerably less than for the C-H bond of methane (5.5 $\text{mdyn}/\text{\AA}$).

One other interaction of interest is the $(\alpha)_{\text{CO}}$ coordinate, 0.8 $\text{rad}/\text{\AA}$, which tells us that stretching the CO bond tends to open up the HBH angles for minimum energy. This is reasonable if one considers the hyperconjugation as analogous to back π bonding in metal carbonyls; stretching the CO bond lowers the energy of its antibonding π orbitals making them more available for accepting the BH electrons. Most of the other interactions calculated are too poorly determined to be meaningful.

In general, the experimental results are consistent with the most recent theoretical results¹⁵ though the correlations cannot be considered unique.

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¹⁸Actually, we do not know what the force constant for a good B-C single bond should be; it may, in fact, be less than that for C-C, C-N, etc.

- ¹⁹Ref. 14, pp. 29-30.