Raman Spectra, Vibrational Assignments, and Force Constants for BH_3CO and BD_3CO

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Raman spectra of BH_3CO and BD_3CO have been obtained for the liquid state at −80°C, and a complete assignment of the sixteen fundamentals of the two molecules has been made with the help of the Teller-Redlich product rule and a normal coordinate treatment. The calculations were carried out using the *FG* method of Wilson, ten symmetry force constants being required to produce a fit with a standard deviation of 0.3% from the observed fundamentals. Extension of the calculations to include the isotopic B^{10} molecules gave results in agreement with the data available.

INTRODUCTION

DESPITE the rather active chemical interest in boron hydrides and their derivatives, the amount of spectroscopic work which has been carried out on these compounds has been disproportionately small. This disparity is particularly marked if one compares the data available on vibrational frequencies, assignments, force constants, molecular parameters, and so on for the derivatives of simple hydrocarbons with the corresponding data for the various boron-hydride derivatives. Experimental difficulties caused by the high reactivities of the boron compounds are responsible to a large degree for this situation; however, if one is willing to work in condensed phases and at low temperatures, a great deal of spectroscopic information can be obtained which can yield significant values for molecular constants and provide a basis for comparisons of chemical properties.

The class of compounds containing the BH_3 group is of particular interest here, from the spectroscopic point of view, as yielding information about the hypothetical simple boron hydride BH_3, and from the chemical point of view, as an example of complex formation through a Lewis acid-base interaction. In the present work, the Raman spectrum of a simple member of this class, BH_3CO, has been obtained, a complete assignment of fundamental frequencies has been made, and a set of valence force constants has been determined which agrees with the experimental data for four isotopic combinations. It is hoped these data will serve as a basis for comparison with other molecules containing the borane group.

Only one previous spectroscopic paper on BH_3CO has appeared, a paper by Cowan[1] reporting the infrared spectrum of the vapor. Five fundamentals reported by him agree with the values found in the present work, two he did not observe, and his assignment of the last appears incorrect. No data for the BD_3CO molecule have been found.

EXPERIMENTAL

Both BH_3CO and BD_3CO were prepared by reaction of B_2H_6 or B_2D_6, respectively, with CO in a sealed tube at several atmospheres pressure. After several days, the tubes were opened and the contents carefully fractionated at low temperatures on the vacuum line. After fractionation, the sample was distilled into the Raman cell which was then sealed off. To reduce thermal decomposition, the vapors were never allowed to come in contact with surfaces warmer than about −50°C during all transfer operations. The spectra obtained showed no bands attributable to diborane or CO which would be produced as decomposition products. The sample of BH_3CO examined was about 1 ml in volume while the BD_3CO was about 0.2 ml. During the exposures, the samples were maintained at approximately −80°C, at which temperature the decomposition occurring in the liquid is negligible. A general description of the apparatus and spectrograph has been given previously.[2] Exposure times varied from ten minutes to three hours using Eastman 103a-J plates. Measurements were made with a comparator directly on the plates and on enlarged tracings made with a Leeds and Northrup microphotometer. The estimated probable error for most lines reported is approximately 1 cm^{-1}.

EXPERIMENTAL RESULTS

The experimentally observed frequencies for BH_3CO are listed in Table I, and those for BD_3CO are listed in Table II. Tracings of spectra of the two substances selected to show the fundamentals most clearly are shown in Figs. 1 and 2. The agreement between the frequencies here reported and those found previously in the infrared of the vapor is very satisfactory, the differences at most amounting to a few cm^{-1} and being well within the normal shifts in frequency observed in the transition from vapor to liquid. Several overtones and combinations were observed on some of the longer exposures on BH_3CO which are not shown in the figure. No bands attributable to diborane or CO were observed in any of the spectra indicating a fairly high purity for the compounds. However, a weak band was observed at 2411 cm^{-1} in the spectrum of the deuterated compound which indicates a small amount of hydrogen to be present.

[1] R. D. Cowan, J. Chem. Phys. 18, 1101 (1950).

[2] G. L. Vidale and R. C. Taylor, J. Am. Chem. Soc. 78, 294 (1956).

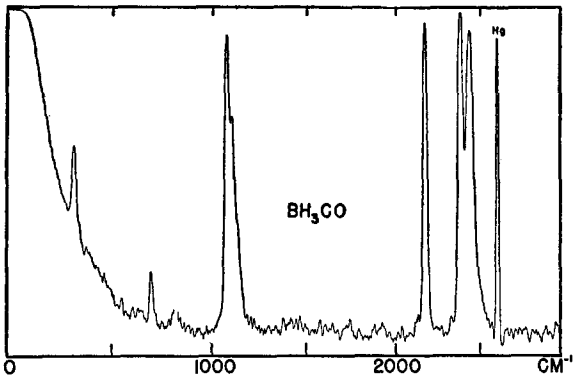

FIG. 1. The Raman spectrum of BH_3CO at −80°C.

ASSIGNMENTS

The BH_3CO molecule has C_{3v} symmetry which predicts eight fundamentals, all active in the Raman effect, which are either totally symmetric (A_1) or doubly degenerate (E). Previous work on boron compounds has shown that B—H stretching frequencies fall in the range between 2000 and 2600 cm^{-1}. Three frequencies appear in this range in the BH_3CO spectrum. Deuterium substitution affects only two, however; and, on the basis of their polarization characteristics, the band at 2380 cm^{-1} is assigned as ν_1 and the band at 2434 cm^{-1} as ν_5. In the BD_3CO spectrum, the asymmetric frequency ν_5 occurs at 1825 cm^{-1} but the position of ν_1 cannot be determined exactly because of Fermi resonance with the overtone of the fundamental at 860 cm^{-1}. The two members of the Fermi doublet occur at 1678 and 1749 cm^{-1}. The latter is assigned as the overtone and the former to the fundamental on the basis of the B^{10} satellite appearing on the high-frequency side of 1749 at 1777 cm^{-1}. Comparison of the intensities of the two bands indicates that the coincidence between the overtone and the fundamental is very close and consequently the unperturbed value of ν_1 probably is not far from 1700 cm^{-1} on the high-frequency side. ν_1 was not observed in the infrared spectrum of the hydrogen compound[1] but its predicted value agrees with that given above. The third band in the 2000 cm^{-1} region is immediately identified as the C—O stretch, both from its nearness to the carbon monoxide frequency at 2143 cm^{-1} and from the fact that deuterium substitution does not shift its position. The assignment of the band is further confirmed by its polarization characteristics.

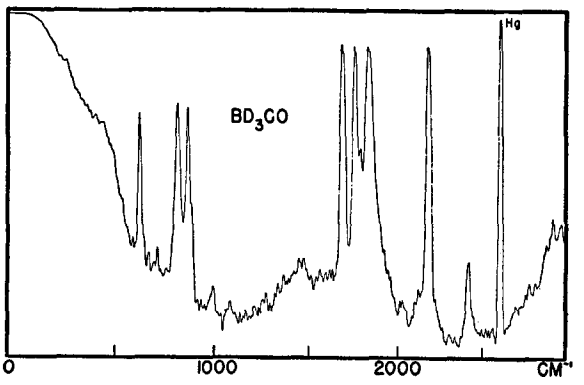

FIG. 2. The Raman spectrum of BD_3CO at −80°C.

The situation with regard to the B—H bending modes is somewhat more complicated. In the hydrogen compound, a triplet is observed in the 1100 cm^{-1} region with maxima at 1073, 1101, and 1133 cm^{-1}, the first being the most intense and probably polarized. In the BD_3CO spectrum, two bands of approximately equal intensity appear at 808 and 860 cm^{-1}, the latter having a weak satellite on its high-frequency side at 881 cm^{-1}. Since polarization measurements were not made on the deuterated spectrum, the product rule plus the results of the normal coordinate treatment were necessary to arrive at a satisfactory assignment. Fortunately, the dimensions and moments of inertia of the four possible isotopic molecules of C_{3v} symmetry, $B^{11}H_3CO$, $B^{11}D_3CO$, $B^{10}H_3CO$, $B^{10}D_3CO$, have been determined from microwave results[3] so that the theoretical product ratios can be calculated with no assumptions. The closest agreement with the theoretical values is obtained by assigning ν_3 to the 1073 cm^{-1} and ν_6 to the 1101 cm^{-1} band in the hydrogen compounds and ν_3 to the 860 cm^{-1} and ν_6 to the 808 cm^{-1} bands of the deuterium species. Confirmation for the interchange in the relative position of the two bands in the deuterium case comes from the normal coordinate calculation of the B^{10} shift. For the A_1 frequency of the deuterated molecule, the calculated shift is 22 cm^{-1}, while for the E frequency it is only 5 cm^{-1}, a separation that would not be resolved by the equipment used. The presence of a weak satellite 21 cm^{-1} higher than 860 cm^{-1} is therefore accepted as additional evidence that the higher band is the A_1 frequency, the satellite being assigned as ν_3 of the B^{10} isotopic species. In the hydrogen compound, the B^{10} isotope shifts are calculated to be +12 and +4 cm^{-1} respectively for ν_3 and ν_6. Since the observed spacings between the members of the observed triplet are 28 and 32 cm^{-1}, it appears that neither can easily be assigned to the B^{10} species. However, the combination of the two E modes at 816 and 317 cm^{-1} has a calculated value of 1133 cm^{-1} and the correct symmetry to resonate with an E fundamental and borrow sufficient intensity to appear as a weak band. The band at 1101 cm^{-1} accordingly is assigned as ν_6. Cowan, in his infrared work,[1] assigned ν_6 to a band at 1392 cm^{-1}. No band at this position was observed in the Raman spectrum, and it appears that the infrared band most likely is $\nu_3+\nu_8$ which, from the Raman data, is calculated at 1390 cm^{-1}. He assigned ν_3 to a band at 1105 cm^{-1} but comments that this band had some peculiar features which now appear explained.

The remaining fundamentals may all be classed as

[3] Gordy, Ring, and Burg, Phys. Rev. 78, 512 (1950).

skeletal modes. The only polarized, fairly intense band left occurs at 692 cm^{-1} in the BH_3CO spectrum and shifts to 619 cm^{-1} upon deuteration. This is assigned to ν_4 in agreement with the infrared results. A satellite was observed at 705 cm^{-1} in the more intense exposures on the hydrogen compound and, on the basis of a calculated shift of +16 cm^{-1} from the force constant treatment, is assigned to ν_4 of $B^{10}H_3CO$. The corresponding shift in the deuterated molecule is calculated to be only 5 cm^{-1} and accounts for the failure to observe a satellite to the 619 cm^{-1} band.

The two fundamentals ν_7 and ν_8 can be considered as bending motions of the axial chain of atoms. The second, ν_8, the B—C—O deformation, is to be expected at a rather low frequency in view of the masses of the atoms involved. It consequently is assigned to the moderately intense depolarized band at 317 cm^{-1} in the BH_3CO spectrum. This fundamental was not observed in the infrared work, but its position was predicted quite accurately. In the deuterated spectrum it appears at 264 cm^{-1}.

The last fundamental, ν_7, which is most simply described as a BH_3 rock, is assigned to 816 cm^{-1} partly by a process of elimination and partly from the infrared evidence. The corresponding band at 706 cm^{-1} in the deuterated compound is rather weak, but the correctness of the assignment is substantiated by the product rule calculations (Table V).

NORMAL COORDINATE TREATMENT

Cowan[1] carried out a normal coordinate treatment of the BH_3CO molecule based on the results of his infrared study and obtained a set of force constants which produced reasonably satisfactory agreement with his assignments. However, in view of the incorrect assignment for ν_6 and of the fact that data on the deuterated molecule were not available, it would appear that a better approximation can now be obtained. Since his equations did not include interaction force constants, the molecule was reanalyzed using the *FG* method of Wilson and the following symmetry coordinates:

A_1 species:

$$S_0=6^{-\frac{1}{2}}(\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}+\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)\equiv 0$$
$$S_1=\Delta T$$
$$S_2=\Delta R$$
$$S_3=3^{-\frac{1}{2}}(\Delta r_1+\Delta r_2+\Delta r_3)$$
$$S_4=6^{-\frac{1}{2}}(\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}-\Delta\beta_1-\Delta\beta_2-\Delta\beta_3)$$

E species:

$$S_5=2^{-\frac{1}{2}}(\Delta r_2-\Delta r_3)$$
$$S_6=2^{-\frac{1}{2}}(\Delta\beta_2-\Delta\beta_3)$$
$$S_7=2^{-\frac{1}{2}}(\Delta\alpha_{31}-\Delta\alpha_{12})$$
$$S_8=\Delta\delta_x$$

TABLE I. Observed Raman frequencies of liquid BH_3CO at −80°C.

Band position (in cm^{-1})	Intensity	Assignment
317	m	ν_8-e fundamental
632	vvw	$2\nu_8$
692	w (pol.)	ν_4-a_1 fundamental
705±2	vw	$\nu_4'-B^{10}$ isotopic species
816	w	ν_7-e fundamental
1073	s (pol.?)	ν_3-a_1 fundamental
1101	m	ν_6-e fundamental
1133	w	$\nu_7+\nu_8$
1626	vvw	$2\nu_7$
1761	vvw	$\nu_3+\nu_4$
1887	vvw	$\nu_6+\nu_7$
2129	vw	$2\nu_3$
2169	s (pol.)	ν_2-a_1 fundamental
2380	s (pol.)	ν_1-a_1 fundamental
2434	s	ν_5-e fundamental
2703	vvw	$\nu_1+\nu_8$

In terms of the molecule parameters, T refers to the C—O bond, R to the B—C bond, r_i to the ith B—H bond, α_{ij} to the H—B—H angle between r_i and r_j, β_i to the ith H—B—C angle and δ_x to the B—C—O angle. The equilibrium values for these parameters taken from the microwave work[3] are as follows: $T=1.131$ A, $R=1.540$ A, $r=1.194$ A, $\alpha=113°52'$, $\beta=104°37'$, $\delta=180°$.

The elements of the inverse kinetic energy (G) matrix were evaluated from the tables of Decius[4] and the note by Ferigle and Meister.[5] As a check on the correctness of the equations, the force constants of Cowan were substituted into the secular equation and the roots were found to agree with his calculated values. The present calculations were carried out in terms of the symmetry force constants, F_i and F_{ij}, where the single index indicates principal force constants and the double, interaction constants. It was found that the calculated frequencies were rather insensitive to most of the possible interaction force constants but were quite sensitive to two. It was not necessary to give values to any of the insensitive constants to obtain a satisfactory fit, and the potential energy, therefore, is given ade-

TABLE II. Observed Raman frequencies of liquid BD_3CO at −80°C.

Band position (in cm^{-1})	Intensity	Assignment
264	w	ν_8-e fundamental
619	m	ν_4-a_1 fundamental
706	w	ν_7-e fundamental
808	m	ν_6-e fundamental
860	m	ν_3-a_1 fundamental
881	w	$\nu_3'-B^{10}$ isotopic species
991	w	?
1678	s	ν_1-a_1 fundamental
1749	s	$2\nu_3$
1777	w	$2\nu_3'-B^{10}$ isotopic species
1825	s	ν_5-e fundamental
2169	s	ν_2-a_1 fundamental
2411	w	B—H stretch

[4] J. C. Decius, J. Chem. Phys. **16**, 1025 (1948).
[5] S. M. Ferigle and A. G. Meister, J. Chem. Phys. **19**, 982 (1951).

TABLE III. Force constants for the BH_3CO molecule.

Symmetry force constant	Value (millidynes/A)	Valence force constant	Value (millidynes/A)
F_1	17.9800	k_T	17.9800
F_2	2.7875	k_R	2.7875
F_3	3.2980	k_r	3.1607
F_4	0.7057	k_α	0.2799
F_{24}	−0.1778	k_β	0.2644
		k_δ	0.2744
F_5	3.0920	k_{rr}	0.0687
F_6	0.2203	$k_{\alpha\alpha}$	0.0365
F_7	0.2434	$k_{\beta\beta}$	0.0442
F_8	0.2744	$k_{\alpha\beta}=k_{\alpha\beta'}$	−0.1176
F_{68}	0.0793	$k_{R\alpha}=-k_{R\beta}$	−0.0726
		$k_{\beta\delta}$	0.0647

$$k_{RT}=k_{rR}=k_{r\alpha}=k_{r\alpha'}=k_{r\beta}=k_{r\beta'}=k_{\alpha\delta}=k_{r\delta}=0$$

quately by the following expression containing only ten constants:

$$2V=F_1S_1^2+F_2S_2^2+F_3S_3^2+r^2F_4S_4^2+2RF_{24}S_2S_4+F_5S_5^2 +r^2F_6S_6^2+r^2F_7S_7^2+RTF_8S_8^2+2R^2F_{68}S_6S_8.$$

This reproduces the sixteen frequencies of the $B^{11}H_3CO$ and $B^{11}D_3CO$ molecules with a standard deviation from the observed values of 0.3% which undoubtably is less than the error introduced by the harmonic approximation. Since there are four product rule relations among the sixteen fundamental frequencies, twelve independent data exist, and the problem is slightly overdetermined. By inspection of the potential function, it will be seen that the F matrices are nearly diagonal, only one off-diagonal element appearing in each symmetry block. The off-diagonal element in the A_1 block is F_{24} linking the symmetrical bending coordinate and the B—C stretching coordinate, while the off-diagonal element of the E block, F_{68}, links the BH_3 rocking coordinate with the B—C—O deformation. In both cases, the two lowest frequencies in the respective symmetry classes are involved, and considerable mixing of the two motions is indicated.

The valence force potential constants are related to the symmetry force constants through the elements of the F matrix and are obtained by solving a set of simultaneous equations. By including the redundant coordinate, S_0, in the transformation from internal to symmetry coordinates and equating the resulting elements of the F matrix to zero, sufficient relationships are obtained to enable all combinations of the valence force constants to be resolved. The values obtained in this way together with those of the symmetry force constants are listed in Table III. The calculated values of the fundamentals are compared with those observed in Table IV. Since two frequencies attributed to B^{10} molecules were observed, the calculations were extended to include both boron isotopic species. The calculated values for the B^{10} molecular frequencies are given in Table IV in the form of the shifts in frequency from the calculated values of the corresponding B^{11} frequencies. As an additional check on the calculations, the B^{11}/B^{10} product rule ratios were calculated using a set of B^{10} frequencies obtained by adding the calculated isotope shifts to the experimentally observed B^{11} frequencies. The agreement as shown by the numerical values in Table V is quite satisfactory.

Comparisons of force constants from different molecules are not always as meaningful as one would like because published values inevitably depend on such factors as the type of potential function used and the number of interaction constants retained, the closeness of fit secured, the magnitude of the anharmonicity errors, and so on. Bond stretching force constants are the least affected by such variations and when derived by the usual valency force field can be used qualitatively in the same fashion as bond energies and bond lengths to give an indication of the electron density concentrated in a given bond. In the carbon monoxide borane molecule, one of the interesting observations is the small effect which the presence of the borane group has on the C—O bond. The force constant of the C—O bond in carbon monoxide gas calculated from the observed infrared frequency of 2143 cm^{-1} is 18.5 md/A. This is decreased only to 17.98 md/A in BH_3CO, whereas in nickel carbonyl the C—O force constant is 15.9 md/A[6]

TABLE IV. Comparison of observed and calculated values of the fundamental frequencies for the various isotopic species of the BH_3CO molecule.[a]

Fundamental		$B^{11}H_3CO$ Obs	$B^{11}H_3CO$ Calc	$B^{11}H_3CO$ Diff.	$B^{11}H_3CO$ %	$B^{11}D_3CO$ Obs	$B^{11}D_3CO$ Calc	$B^{11}D_3CO$ Diff.	$B^{11}D_3CO$ %	$B^{10}H_3CO$ Calc shift	$B^{10}H_3CO$ Obs	$B^{10}D_3CO$ Calc shift	$B^{10}D_3CO$ Obs
A_1	ν_1	2380	2380	0	0	(1700)[b]	1703	···	···	+2.5	···	+4.3	···
	ν_2	2169	2169	0	0	2169	2169	0	0	0.4	···	0.4	···
	ν_3	1073	1070	−3	0.3	860	863	+3	0.3	12.1	···	22.5	21±2
	ν_4	692	691	−1	0.1	619	621	+2	0.3	16.0	13±2	4.8	···
E	ν_5	2434	2431	−3	0.1	1825	1827	+2	0.1	15.0	···	21.3	···
	ν_6	(1101)[b]	1101	···	···	808	805	−3	0.4	3.6	···	5.4	···
	ν_7	816	816	0	0	706	704	−2	0.3	6.3	···	3.2	···
	ν_8	317	315	−2	0.6	264	265	+1	0.4	0.0	···	0.1	···

[a] Stnd. deviation for 14 freqs. =0.3%.
[b] The data enclosed in parentheses are for fundamentals disturbed by Fermi resonances and are estimated values.

[6] B. L. Crawford and P. C. Cross, J. Chem. Phys. 6, 525 (1938).

and in carbon dioxide it is 15.5 md/A. This small change is consistent with the small (*ca* 0.001 A) increase in CO bond length and with the chemical instability of the molecule. However, the adjacent B—C bond is not as weak a bond as one might expect from this, its force constant of 2.79 md/A being only slightly less than the value 2.9 md/A predicted by Badger's rule. Unfortunately, there appear to be no other data available on B—C bond constants for further comparisons. However, the calculated value for BH_3CO does not seem entirely consistent with the rather large amount of no-bond character which has been proposed[3] for this bond.

The two molecules, perhaps, with which it would be of most interest to compare B—H stretching force constants are diborane and the borohydride ion. A value of 3.42 md/A has been used in a normal coordinate treatment of diborane[7]; however, this figure was transferred unaltered from an earlier treatment of borazine,[8] and it is of doubtful significance to do more than note that it is of the same magnitude as the value found in the present work. The value of 3.16 md/A found for BH_3CO, however, appears to be significantly greater than the value 2.75 md/A for the B—H stretching constant in the borohydride ion.[9] This difference can be interpreted as indicating that the electronic configuration around the boron atom is somewhere intermediate between the trigonal sp^2 hybridization expected for the hypothetical free BH_3 molecule and the tetrahedral sp^3 hybridization in the borohydride ion and as indicating that the lone pair of electrons on the carbon atom have not been utilized fully in forming the boron-carbon bond. The same conclusion, of course, can be drawn from the larger than tetrahedral angle (113°) in BH_3CO.

Finally, it may be pointed out that the experimental product rule ratios for the hydrogen-deuterium substitution listed in Table V are greater than the theoretical values, even though the differences are not large. Exact agreement, of course, is not to be expected since the observed rather than harmonic values have been used in calculating the ratios. However, the normal effect of anharmonicity is to cause the experimental ratios calculated in this way to be less than the theoretical.[10] In view of the weight of other evidence and of the fact that all experimental ratios are greater than the theoretical, it does not seem probable that there is an error in the assignments. The difference, therefore, may also reflect the specific electronic structure of the molecule or the BH_3 group and, if so, should be found in other molecules containing the borane group.

TABLE V. Comparison of product rule ratios for various isotopic combinations of the BH_3CO molecule.

Isotope held constant	Isotopes compared	Symmetry class	Frequency product ratio Theoret.[a]	Calc[b]	Dev.
B^{11}	H/D	A_1	1.931	1.953	1.1%
B^{11}	H/D	E	2.513	2.522	0.4
B^{10}	H/D	A_1	1.929	1.951	1.1
B^{10}	H/D	E	2.498	2.507	0.4
H	B^{11}/B^{10}	A_1	1.036	1.036	0.0
H	B^{11}/B^{10}	E	1.017	1.017	0.0
D	B^{11}/B^{10}	A_1	1.037	1.037	0.0
D	B^{11}/B^{10}	E	1.024	1.023	−0.1

[a] Calculated from moments of inertia of reference 3 and the masses involved.
[b] The frequencies for the B^{11} molecules were those observed; the frequencies for the B^{10} molecules were obtained by adding the shifts determined in the force constant treatment to the experimental values of the B^{11} frequencies.

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[7] R. P. Bell and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A183**, 357 (1945).
[8] B. L. Crawford and J. T. Edsall, J. Chem. Phys. **7**, 223 (1939).
[9] Unpublished datum from a complete quadratic valence force treatment based on the Raman frequencies of the borohydride and borodeuteride ions dissolved in liquid ammonia.
[10] F. Halvorsen, Revs. Modern Phys. **19**, 87 (1947).