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## Infrared Spectrum of $\nu_2$ of Dichloroborane and Dichloroborane-d

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The  $\nu_2$  fundamental of HBCl<sub>2</sub> and DBCl<sub>2</sub> has been observed under high resolution. A series of evenly spaced lines occurs, which has the appearance of a  $\perp$  band of a symmetric top molecule. Analysis of the spectra gives an approximate value for the smallest moment of inertia, from which the following molecular dimensions are calculated: B-H bond length= $1.13\pm0.2$  Å and Cl-B-Cl bond angle= $119.7\pm3^{\circ}$ . The position of the band center, 2616.9 cm<sup>-1</sup>, for HBCl<sub>2</sub>, has also been determined.

#### INTRODUCTION

THE synthesis, some chemical reactions, and qualitative infrared spectra of dichloroborane, HBCl<sub>2</sub>, have been reported previously.1-3 A complete investigation of the infrared spectrum has been undertaken to determine the potential constants of this unusual molecule. However, the unavoidable presence of BCla due to disproportionation<sup>4</sup> is a serious hindrance to the location and assignment of all the normal modes of HBCl<sub>2</sub>.<sup>5</sup>

The vibrational spectrum of HBCl<sub>2</sub> consists of six fundamentals, which are all infrared and Raman active for both a planar  $(C_{2v})$  and nonplanar  $(C_s)$ model. Although there is no evidence to eliminate the latter, we make the reasonable assumption that the molecule is planar.<sup>6</sup> This form allows the maximum opportunity for  $\pi$ -orbital interactions, which act to stabilize the planar structure of  $BX_3$  molecules, when X contains lone pair electrons. The bands of HBCl<sub>2</sub> which have thus far been observed cannot be assigned with certainty. However, the highest frequency band, 2617 cm<sup>-1</sup> must be associated with  $\nu_2$ , the B-H stretching motion. Previously, this band had been reported as a singlet<sup>1-3</sup>; however, under medium dispersion, it appears as a doublet. Close examination of the band reveals the presence of an evenly spaced series of lines, separation  $\approx 3$  cm<sup>-1</sup>, on either side of the central minimum. The deuterated compound has been prepared, and the fine structure of the B-D band has also been resolved. Analysis of the spectra yields a value for the smallest moment of inertia. Results for both HBCl<sub>2</sub> and DBCl<sub>2</sub> provide sufficient information to determine the bond angle, Cl-B-Cl, and the bond length,  $r_{\rm BH}$ .

#### **EXPERIMENTAL**

The presence of  $B_2H_6$  due to the disproportionation reaction introduces BH<sub>2</sub> stretching motions (2500-2600 cm<sup>-1</sup>) which must be avoided. Mixtures of BCl<sub>3</sub> and HBCl<sub>2</sub> (20-50 mole %) are stable and suppress the formation of B<sub>2</sub>H<sub>6</sub>. Mixtures were prepared by reducing BCl<sub>3</sub> (or <sup>11</sup>BCl<sub>3</sub>) with hydrogen or deuterium in the presence of magnesium maintained at 350°C in a stainless-steel tube. The stainless-steel reactor was sealed into a vacuum system having a facility for lowtemperature separations and storage. Pure hydrogen and deuterium were generated, respectively, from uranium hydride and deuteride by heating. Enriched boron was obtained from Oak Ridge National Laboratory, and mass analysis indicated 98.6% 11B. The enriched <sup>11</sup>BCl<sub>3</sub> was prepared by direct combination of elements followed by distillation and purification procedures.

A Perkin-Elmer Model 421 Spectrophotometer with the dual grating interchange provided adequate resolution. Calibration against HCl and CO<sub>2</sub> provided an accuracy estimated to be  $\pm 0.5$  cm<sup>-1.7</sup> Spectral slitwidths were programmed for 0.43 cm<sup>-1</sup> and 0.22 cm<sup>-1</sup> for 2617 and 1970 cm<sup>-1</sup> regions, respectively. A 10-cm cell was used for gas samples.

The B–D band  $(\nu_2)$  suffered strong interference from the first overtones,  $2\nu_3^{10}$  (1991 cm<sup>-1</sup>) and  $2\nu_3^{11}$  (1911 cm<sup>-1</sup>) of BCl<sub>3</sub>.<sup>8</sup> This was eliminated by placing an equivalent pressure (10-cm cell) of pure BCl<sub>3</sub> in the reference beam. It was possible to resolve the highfrequency side and locate the central minimum but resolution of the low-frequency side was not successful due to loss of sensitivity even with automatic gain control.

<sup>&</sup>lt;sup>1</sup> L. Lynds and D. R. Stern, J. Am. Chem. Soc. **81**, 5006 (1959). <sup>2</sup> H. G. Nadeau and D. M. Oaks, Jr., Anal. Chem. **32**, 1481 (1960)

<sup>&</sup>lt;sup>3</sup> H. W. Mayers and R. F. Putnam, J. Inorg. Chem. 2, 655 (1963)

<sup>&</sup>lt;sup>4</sup> 6HBCl<sub>2</sub> $\rightleftharpoons$ 4BCl<sub>3</sub>+B<sub>2</sub>H<sub>6</sub>.

<sup>&</sup>lt;sup>5</sup> Preliminary studies of a mixed crystal, BCl<sub>2</sub>-HBCl<sub>2</sub> at 77°K, and BCl3-HBCl2 isolated in an Ar matrix at 4°K, indicate a band of  $HBCl_2$  in the region covered by the intense vibration-rotation envelope of  $\nu_2$  of BCl<sub>3</sub>. Work is currently in progress to determine the complete potential function of HBCl<sub>2</sub> and will be reported at a later date. <sup>6</sup> H. A. Levy and L. O. Broackway, J. Am. Chem. Soc. **59**, 2085

<sup>(1937).</sup> 

<sup>&</sup>lt;sup>7</sup> E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, J. Res. Natl. Bur. Std. A. Phys. and Chem., **64**, No. 1 (1960). <sup>8</sup> The overtone bands were reported by Scruby *et al.* [R. E. Scruby, J. R. Lacher, and J. D. Park, J. Chem. Phys. **19**, 386 (1951)] at 1916 and 1948 cm<sup>-1</sup>. Under higher dispersion, these bands appeared as doublets with their centers located very near to the calculated values, 1910 and 1990 cm<sup>-1</sup>.

#### RESULTS

The spectra are shown in Fig. 1. Spectra of H<sup>11</sup>BCl<sub>2</sub> appeared unchanged and signified rotational envelopes rather than isotopic splitting. The most striking feature is the symmetrical appearance of the rotational fine structure. A  $C_{2v}$  molecule, in general, has three different moments of inertia  $I_A < I_B < I_C$ . The rotational fine structure is extremely irregular and difficult to analyze. It may happen, however, that two of the moments of inertia are approximately equal, and the molecule becomes an accidental symmetric top. For HBCl<sub>2</sub>, the moment of inertia about the axis A, through the center of mass and parallel to the Cl-Cl line (Fig. 2), is small, and  $I_B \approx I_C(I_A + I_B = I_C)$ . The vibrationrotation band associated with the B-H stretching motion will then be a type B band (dipole moment change along B) which will approach in structure a  $\perp$  band (dipole moment change  $\perp$  to the top axis) of a symmetric top as  $\rho = I_A/I_B$  becomes small.<sup>9</sup>



FIG. 1. Fine structure of the fundamental  $\nu_2(a)$  of HBCl<sub>2</sub> and (b) DBCl<sub>2</sub>.

We shall consider the symmetric top approximation to determine the molecular constants. The rotational energy levels are given by

$$F_{(v)}(J,K) = B_{(v)}J(J+1) + (A_{(v)} - B_{(v)})K^{2},^{10}$$
(1)

neglecting the effect of centrifugal distortion. For an accidental symmetric top, B is an average of the two small rotational constants:  $\tilde{B} = (B+C)/2$ .

The selection rules for a  $\perp$  band

$$\Delta K = \pm 1; \qquad \Delta J = 0, \pm 1,$$

give rise to a band which consists of a number of subbands. The Q branches  $(\Delta J=0)$  of the subbands, according to (1), are located at

$$\nu_0^{\text{sub}} = \nu_0 + (A' - \tilde{B}') \pm 2(A' - \tilde{B}')K + [(A' - \tilde{B}') - (A'' - \tilde{B}'')]K^2. \quad (2)$$

<sup>9</sup> H. H. Nielsen, Phys. Rev. 38, 1432 (1931).

<sup>10</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), p. 400 ff.



FIG. 2. HBCl<sub>2</sub> model, showing axis of smallest moment of inertia A and  $\phi$ , one-half the apex angle. The  $B(C_2)$  axis coincides with the boron-hydrogen bond line; the C axis is  $\perp$  to the plane.

The single prime refers to the upper state, double prime to the lower state; the + sign applies to  $\Delta K = +1$ ,  $K=0, 1, 2, \dots$ , and the - sign applies to  $\Delta K = -1$ ,  $K=1, 2, \dots$ .

Although the molecular constants may be calculated from (2), they may be more accurately determined from combination differences,<sup>11</sup>

$$F''(J, K+1) - F''(J, K-1) = R(Q)_{K-1}$$
$$- P(Q)_{K+1} = 4(A'' - \tilde{B}'')K, \quad (3)$$

and

$$F'(J, K+1) - F'(J, K-1) = R(Q)_{K}$$
$$-P(Q)_{K} = 4(A' - \tilde{B}')K, \quad (4)$$

which are obtained from (1) or (2).

If the rotational constants in the upper and lower states are the same, the lines in each Q branch fall at

TABLE I. Rotational fine structure of  $\nu_2$  of HBCl<sub>2</sub>.

K	$R(Q)_{\kappa}$ (obs)	$R(Q)_{\mathbf{K}}$ (calc)	$P(Q)_{\mathbf{K}}$ (obs)	$P(Q)_{\mathbf{K}}$ (calc)					
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17	2624.2 2627.1 2629.7 2632.5 2635.4 2638.3 2641.2 2644.7 2647.4 2650.0 2652.4 2655.0 2658.5 2660.8 2663.4 2666.0	$\begin{array}{c} 2624.1\\ 2627.0\\ 2629.8\\ 2632.7\\ 2635.6\\ 2638.4\\ 2641.3\\ 2644.1\\ 2646.9\\ 2649.8\\ 2652.6\\ 2655.4\\ 2655.4\\ 2658.2\\ 2661.0\\ 2663.7\\ 2666.5\\ 0 = 2616.9 \ cm\\ \phi \ \widetilde{p}'' = 1 \ 457 \ \delta = 1 \$	2603.6 2600.6 2597.5 2594.9 2592.0 2589.1 2586.3 2583.1 2579.9 2576.7 2573.7	2603.7 2600.7 2597.8 2594.8 2591.8 2588.9 2585.9 2585.9 2582.9 2579.9 2576.9 2576.9 2573.9					
$A' - \tilde{B}' = 1.450 \text{ cm}^{-1}$									

<sup>11</sup>  $R(Q)_K$  and  $P(Q)_K$  refer to the Q branches of a subband with  $\Delta K = +1$  and  $\Delta K = -1$ , respectively. The subscript refers to the K value of the lower state.

TABLE II. Rotational fine structure of  $\nu_2$  of DBCl<sub>2</sub>.

$R(Q)_{\mathcal{K}}(\text{Expt. I})$	$R(Q)_{\mathcal{K}}(\text{Expt. II})$	
2029.4	2029.7	
2027.0	2027.2	
2024.3	2024.4	
2021.9	2021.9	
2019.5	2019.8	
	2018.1	
2017.0	2016.8	
2014.7	2014.9	
2012.9	2012.6	
2011.2	2010.9	
2009.0	2009.2	
$2(A - \tilde{B}) = 2$	$2.16 \pm 0.3 \text{ cm}^{-1}$	

 $\nu_0^{\text{sub}}$  and form, according to (2), a series of equidistant lines, separated by  $2(A-\tilde{B})$ . The *P* and *R* branches generally form an unresolved background, and the series of *Q* lines is particularly prominent when  $A \gg B$ . The energy level diagram, the first few subbands and the complete  $\perp$  band of a symmetric top molecule are shown on p. 425, Fig. 128, of Herzberg.<sup>10</sup>

The average separation of the lines for HBCl<sub>2</sub> is 2.97 cm<sup>-1</sup>. Using this as a first approximation for  $2(A-\tilde{B})$ , it is possible to assign several different K values to the first lines observed on either side of the central minimum.  $A''-\tilde{B}''$  and  $A'-\tilde{B}'$  were determined from (3) and (4) for a number of assignments, and the band center  $\nu_0$  was calculated from the average values of the rotational constants. With these values for the constants, the spectrum was calculated for each assignment. The calculations were programmed for the IBM 7090. The assignment and constants which best reproduce the observed spectrum are shown in Table I. It is seen that the positions of the lines may be fit quite well to the symmetric top expression.

The rotational fine structure of the B-D stretching band is not quite as symmetrical in appearance. Two factors contribute to the deterioration of its appearance relative to HBCl<sub>2</sub>: (1)  $I_A$  is slightly larger, and the deviation from a symmetric top is greater, and (2) there are overtones of BCl<sub>3</sub>( $2\nu_3^{10}$ ,  $2\nu_3^{11}$ ) which reduce the sensitivity of the instrument on the low-frequency side of the band center. The observed frequencies are listed in Table II. The separation of the lines is  $2.16\pm0.3$  cm<sup>-1</sup>, and this will be used as the value for  $2(A-\tilde{B})$ .

The moment of inertia about A is

$$I_{A} = \frac{h}{8\pi^{2}cA} = \frac{2M_{C1}(M_{H} + M_{B})}{M_{T}} r_{B-C1}^{2} \cos^{2}\varphi + \frac{4M_{H}M_{C1}}{M_{T}} r_{B-C1}r_{B-H} \cos\varphi + \frac{M_{H}(M_{T} - M_{H})}{M_{T}} r_{B-H}^{2}$$
(5)

$$B = -(A - \tilde{B}) + (A^{2} + \tilde{B}^{2})^{\frac{1}{2}}$$
(6)

$$C = (A + \tilde{B}) - (A^2 + \tilde{B}^2)^{\frac{1}{2}}.$$
 (7)

The results appear in Table III.

An estimation of the isotopic shift was obtained with the Teller-Redlich product rule.<sup>13</sup> The  $\nu_2$  mode belongs to the symmetry type  $A_1$ , and the product rule involves the frequencies of all modes belonging to  $A_1$ . Neglecting anharmonic effects and assuming the other type  $A_1$  modes ( $\nu_1$  and  $\nu_3$ ) experience a small shift, the product rule simplifies to

$$\frac{\nu_2^{\text{BH}}}{\nu_2^{\text{BD}}} \approx \left[ \left( \frac{M_{\text{D}}}{M_{\text{H}}} \right) \left( \frac{M_{\text{HBCl}_2}}{M_{\text{DBCl}_2}} \right) \right]^{\frac{1}{2}} = 1.40.$$
(8)

The central minimum for the BH stretching mode was located at 2617 cm<sup>-1</sup>. The calculated frequency for BD was 1870 cm<sup>-1</sup>, and the observed frequency was 1969 cm<sup>-1</sup>. The frequency ratio  $\nu_2^{\rm BH}/\nu_2^{\rm BD}$  is 1.33 and is in excellent agreement with ratios reported for other BH–BD compounds.<sup>14–16</sup>

#### DISCUSSION

Nielsen<sup>9</sup> calculated the spectra of Type *B* vibration-rotation bands for a planar molecule having various  $\rho = I_A/I_B$ , and the data conforms to the structures predicted from  $\rho$  given in Table III. This can be cited in support of the band assignment ( $\nu_2$ ) and presence of a monomeric specie. The BH stretching

TABLE III. Results.

	A (cm <sup>-1</sup> )	<i>B</i> (cm <sup>-1</sup> )	$C (cm^{-1})$	ρ	∠ClBCl	<i>т</i> <sub>В-Н</sub>
HBCl <sub>2</sub>	1.556	0.103	0.097	0.066	119.7 ±3°	1.13 ±0.2Å
DBCl <sub>2</sub>	1.179	0.103	0.095	0.088		

<sup>12</sup> M. Atoji and W. N. Lipscomb, J. Chem. Phys. **27**, 195 (1957). <sup>13</sup> G. Herzherg, *Infrared and Raman Spectra* (D. Van Nostrand

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 <sup>1605 (1958).
&</sup>lt;sup>15</sup> W. J. Lehmann, H. G. Weiss, and I. Shapiro, J. Chem. Phys.
30, 1222 (1959).

<sup>&</sup>lt;sup>16</sup> W. J. Lehmann, T. Onak, and I. Shapiro, J. Chem. Phys. **30**, 1215 (1959).

frequency (2617 cm<sup>-1</sup>) is the highest reported and appears to be consistent with our model having a BH distance slightly shorter than any boron-hydrogen compound previously reported. This may result from an increased ionic contribution of the BH bond to the over-all structure due to the strongly electrophylic nature of the BCl<sub>2</sub> group. Rapid addition of HBCl<sub>2</sub> to olefinic and acetylenic centers<sup>1</sup> may also be considered as evidence for partial ionic behavior of the BH bond.

The uncertainty in the value of  $r_{B-H}$  is quite large,  $\pm 0.2$  cm<sup>-1</sup>, and is due mainly to the uncertainty in the measurement of DBCl<sub>2</sub>. Also, the value  $r_{B-Cl} = 1.75$  Å was taken from other molecules, but it appears to be fairly constant in several types of B-Cl compounds.<sup>17-19</sup> In order to obtain more accurate results, it will be necessary to measure B, which was obtained indirectly from these experiments.

Finally, it should be mentioned that the results obtained are from effective values of the rotational constants, in the ground vibrational state, and are not equilibrium values. We conclude, therefore, that for HBCl<sub>2</sub> the bond angle Cl-B-Cl is near 120°, and the B-H bond distance is near 1.13 Å.

<sup>17</sup> A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, Trans. Faraday Soc. **33**, 852 (1937). <sup>18</sup> M. Atoji and W. N. Lipscomb, Acta Cryst. **6**, 547 (1953). <sup>19</sup> M. Atoji, P. J. Wheatley, and W. N. Lipscomb, J. Chem. Phys. **27**, 196 (1957).

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# Orbital Following in the Methyl Radical\*

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Incomplete orbital following of the molecular vibrations in the methyl radical is examined through its relationship to the hyperfine splittings observed in the ESR spectrum. A semiempirical nonionic valencebond theory with different degrees of carbon sigma-orbital following is used to estimate the proton and C<sup>13</sup> splitting constants as a function of the nuclear positions that correspond to the out-of-plane bending mode. It is found that a considerable "lag" in the orbital motion with respect to that of the nuclei is required to achieve a consistent interpretation of the hyperfine spectrum in the methyl radical and its isotopic analogs. A variety of additional factors (i.e., integral parameter variation, breakdown of Born-Oppenheimer approximation, ionic contributions, other vibrations) are also investigated to determine their effects on the hyperfine splittings. Although some of the factors are found to be significant (particularly the choice of integral parameters), it appears that they cannot serve to explain the hyperfine data in the presence of complete following. Comparisons of the present conclusions with other studies of hyperfine splittings and related investigations of orbital following are presented.

### I. INTRODUCTION

THE vibrations of the nuclei in a molecule give rise L to a number of problems concerning the effects of this motion on the electron distribution. Much attention has been focused recently on the consequences of electronic degeneracies and the resultant possibility of a breakdown of the Born-Oppenheimer separation of nuclear and electronic motion.<sup>1</sup> In the absence of degeneracy, the electronic wavefunction can be obtained, in principle, by solving the static problem corresponding to each of the nuclear positions involved in the molecular vibrations. For systems whose charge distribution can be interpreted in terms of localized bonds, it is of interest to determine whether the bonding electrons "rigidly" follow the motion of the nuclei. A lag of the bonding electron density with respect to the internuclear axis may occur if the valence-state energy or electron repulsions are decreased by the presence of "bent bonds."2

For bending vibrations, the possibility of incomplete orbital following has been examined in a number of investigations. Linnett and Wheatley<sup>3</sup> considered the vibrational frequencies of the deuteromethanes and found that the interpretation of the measured values could be improved by use of a valence force field which included bond bending; that is, to the usual potential function, which is the sum of terms associated with

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<sup>&</sup>lt;sup>1</sup> For a recent review, see H. C. Longuet-Higgins, Advan. Spectry. II, 429 (1961).

<sup>&</sup>lt;sup>2</sup> See, for example, F. O. Ellison, J. Chem. Phys. 36, 3107, 3112

<sup>(1962).</sup> <sup>3</sup> J. W. Linnett and P. J. Wheatley, Trans. Faraday Soc. 45, 33, 39 (1949).