

The out-of-plane Band Contour of Dichloroborane Molecules

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The out-of-plane bending, vibrational-rotational FT-IR spectra of dichloroborane molecule were analyzed. The band centers are 785.992, 785.723, 647.217, and 646.997 cm^{-1} and centrifugal distortion constants are 2.2×10^{-6} , 5.5×10^{-6} , 0.2×10^{-6} , and $0.7 \times 10^{-6} \text{ cm}^{-1}$ for $\text{H}^{11}\text{B}^{35}\text{Cl}_2$, $\text{H}^{11}\text{B}^{35}\text{Cl}^{37}\text{Cl}$, $\text{D}^{11}\text{B}^{35}\text{Cl}_2$, and $\text{D}^{11}\text{B}^{35}\text{Cl}^{37}\text{Cl}$, respectively. The theoretical spectrum of $\text{D}^{11}\text{B}^{35}\text{Cl}_2$ was plotted to conform the molecular constants and the rotational constants for the first excited vibrational state of this molecule were $A' = 1.165932$, $B' = 0.106166$, and $C' = 0.097229 \text{ cm}^{-1}$. The calculated spectra were in good agreement with the observed spectra.

Introduction

It is well known that tetra-atomic carbonyl, thiocarbonyl and seleno carbonyl molecules are planar in the ground electronic state but adopt non-planar geometries in the first excited singlet and triplet states.¹⁻³ A bent equilibrium structure in these excited states of such molecules leads to a double minimum potential function in the out-of-plane bending coordinate. Clouthier et al.⁴ suggested an exact formula within the rigid bender for the evaluation of the mass-weighted coordinate Q for the out-of-plane bending which is applicable to C_s or C_{2v} tetra-atomic molecules. The fundamental frequency of dichloroborane have been observed by many authors.⁵⁻⁹ Gaseous infrared spectra of HBCl_2 and DBCl_2 produced by a TEA CO_2 laser enhanced reaction have been observed by an FT-IR spectrophotometer at a resolution of 0.2 cm^{-1} .¹⁰ And all of the six fundamental bands and a ν_1 band regions were analyzed with a symmetric-top approximation.¹¹ However, the out-of-plane vibration-rotation bands of this molecule have not been reported in detail.

The purpose of the present study is to analyze the vibrational-rotational spectra of C-type band, ν_4 , out-of-plane of HBCl_2 and its isotopes. The molecular constants which were obtained from the infrared and microwave spectra in the state were conformed and compared with the calculated results.

Experimental and Calculation

The BCl_3/H_2 and BCl_3/D_2 gas mixtures were irradiated with a CO_2 laser beam in a glass reaction vessel to yield the HBCl_2 and DBCl_2 . The infrared spectra were measured with a Nicolet 7199 FT-IR spectrometer. The other details were described in previous reports.¹⁰ In order to calculate the infrared band contours of an asymmetric-top molecule, a computer program presented by Nakanaga et al.¹² was used. The program was made to print out energy levels, frequencies and intensities of transition line, and band contours. In the calculation of a band envelope, absorption coefficients of transition line were accumulated at each point with an interval of 0.01 cm^{-1} under a Lorentz type line broadening and then

Table 1. Symmetry Coordinates for HBCl_2 Molecule

Species	Band type	Symmetry Coordinates	Mode
A_1	B	$S_1 = \Delta R$	B-H str
		$S_2 = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2)$	B-Cl sym str
		$S_3 = \frac{1}{\sqrt{6}} (2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2)$	B-Cl sym defor
B_1	C	$S_4 = \Delta\gamma$	out-of-plane
B_2	A	$S_5 = \frac{1}{\sqrt{2}} (\Delta r_1 - \Delta r_2)$	B-Cl asym str
		$S_6 = \frac{1}{\sqrt{2}} (\Delta\beta_1 - \Delta\beta_2)$	B-H in-plane defor

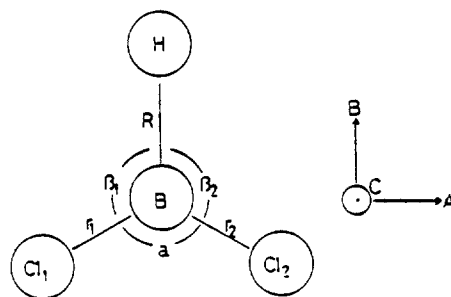


Figure 1. Cartesian coordinates system for the HBCl_2 molecule.

transformed into the percent absorbance through a 0.24 cm^{-1} slit width.

Results and Discussion

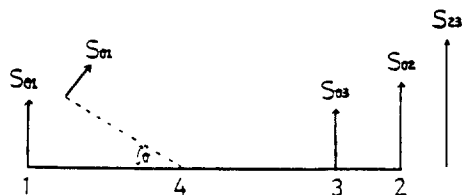
The symmetry coordinates of HBCl_2 molecule, C_{2v} planar, are given in terms of the internal coordinates in Table 1. The internal coordinates of HBCl_2 are illustrated in Figure 1 and the out-of-plane coordinate, r is the angle between the BH bond and the CIBCI plane. The rigid bender model assumes that the only molecular deformation allowed is displacement of nucleus 1 in or out-of-the plane defined by nuclei 1,2,3 and 4 in such a way that the B-H bond length, r_{41} , remains constant. The potential for such a rigid bender may be expressed using the formula of Coon et al.¹³

$$V(Q) = \frac{1}{2} \lambda Q^4 + A \exp(-a^2 Q^2) \quad (1)$$

Table 2. The Rotation vibration Constants of ν_4 Band of $\text{HBCl}_2(\text{cm}^{-1})$

K	$\text{H}^{11}\text{B}^{35}\text{Cl}_2$		$\text{H}^{11}\text{B}^{35}\text{Cl}^{37}\text{Cl}$		$\text{D}^{11}\text{B}^{35}\text{Cl}_2$		$\text{D}^{11}\text{B}^{35}\text{Cl}^{37}\text{Cl}$	
	obs	obs-calc	obs	obs-calc	obs	obs-calc	obs	obs-calc
2	793.375	0.015						
3	796.355	-0.030						
4			799.217	-0.008	654.535	-0.002	654.295	-0.005
5			802.313	0.010	656.570	-0.012	656.333	-0.006
6	805.647	0.000	805.406	-0.001	658.608	0.001	658.332	-0.025
7	808.805	0.008	808.541	0.005	660.615	0.004	660.366	0.012
8	811.990	0.009	811.689	0.001	664.558	0.002	664.297	0.011
9	815.203	0.006	814.845	-0.016	666.505	0.008	666.246	0.025
10	818.436	-0.012	818.065	0.009	668.416	-0.002	668.109	-0.026
11					674.049	-0.003		
-4	775.819				639.642	0.003	639.434	0.013
-5	772.990				637.442	0.014	637.207	0.001
-6					635.184	-0.013	634.972	0.003
-7			767.469	0.000				
-8	764.654							
ν_0	785.922(25)		785.723(71)		647.217(22)		646.997(44)	
$A'-\bar{B}'$	1.4757(28)		1.4725(52)		1.0590(12)		1.057(31)	
	0.01421(63)		0.0166(16)		-0.01031(78)		-0.0109(13)	
D_k	-0.000022(23)		0.000055(46)		0.0000016(144)		0.0000069(298)	
$A''-\bar{B}''$	1.4614		1.4553		1.0690		1.0680	
$A''-\bar{B}''^*$	1.4619		1.4592		1.0707		1.0632	

* Microwave data.

**Figure 2.** Definition of the S vectors employed in the calculation of G_0 .

where Q is a mass weighted coordinate defined by $2T = \dot{Q}^2$. The coordinate Q may be related to the geometry of the rigid bender through the Wilson G matrix element for out-of-plane bending by

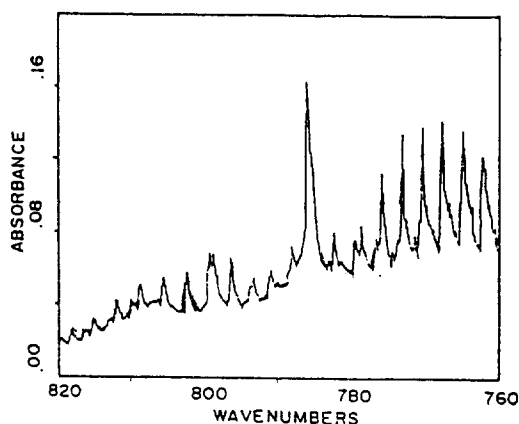
$$Q(\theta') = \int_0^\theta G_0^{-1/2} dQ \quad (2)$$

The G matrix element for the out-of-plane bending motion is given by the equation

$$G_{00} = \sum_{\alpha=1}^4 \mu_\alpha S_{0\alpha} \cdot S_{0\alpha} \quad (3)$$

where μ_α is the inverse mass of atom α and the S vectors are defined as in Ref 14. The magnitude of the last term in the summation $S_{04} = -(S_{01} + S_{02} + S_{03})$ can be found by considering Figure 2.

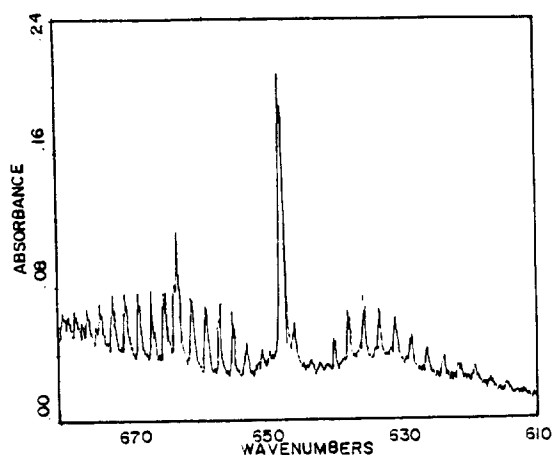
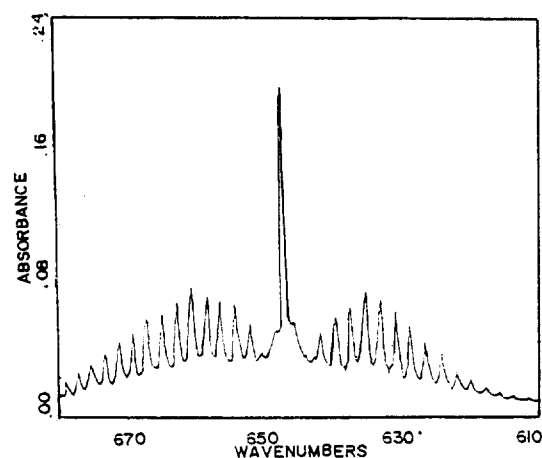
The moments of inertia I_A , of A axis through the center of mass and parallel to the $\text{Cl}_2\text{-Cl}_1$ line is small compared to the moment of inertia, I_B and I_C . Since the two moment of inertia, I_B and I_C , are approximately equal, we assumed a prolate symmetric-top approximation. The frequencies of the Q branch peaks are given by

**Figure 3.** The ν_4 spectrum of HBCl_2 .

$$\nu_0^{s'ub} = \nu_0 + (1+2K)(A' - B') + [(A' - A'') - (\bar{B}' - \bar{B}'')]K^2 \mp D_k(2K^2 \mp 2K + 1)(2K + 1) \quad (4)$$

where the single and double primes refer to the first excited and the ground vibrational states, respectively. D_k is a centrifugal distortion constant. \bar{B} is the average of B and C rotational constants.

The observed ν_4 band in the spectra which are associated with the out-of-plane mode is shown in Figure 3 and Figure 4 for HBCl_2 and DBCl_2 , respectively. The former band showed an asymmetric band contour due to interference of the B-Cl stretching band, and the latter by the B-H deformation. The least square fitting of the observed frequencies to eq(4) led to the results in Table 3. The band centers of ν_4 for $\text{H}^{11}\text{B}^{35}\text{Cl}_2$, $\text{H}^{11}\text{B}^{35}\text{Cl}^{37}\text{Cl}$, $\text{D}^{11}\text{B}^{35}\text{Cl}_2$ and $\text{D}^{11}\text{B}^{35}\text{Cl}^{37}\text{Cl}$ were 785.992,

Figure 4. The ν_4 spectrum of DBCl_2 .Figure 5. The calculated ν_4 spectrum of DBCl_2 .Table 3. Calculated Transitions for the ν_4 band of $\text{D}^{11}\text{B}^{35}\text{Cl}_2$

K	ν_0	JG	KP	KO	JV	KP	KO	Height
-11	623.992	22	9	14	21	8	14	0.182
-10	626.106	22	8	15	21	7	15	0.208
-9	628.278	33	9	25	33	8	25	0.236
-8	630.502	32	8	25	32	7	25	0.236
-7	632.896	32	7	26	32	6	26	0.294
-6	635.192	31	6	26	31	5	26	0.322
-5	637.448	32	2	30	31	1	30	0.344
-4	639.645	27	4	25	28	3	25	0.316
-3	641.825	18	3	15	18	2	17	0.179
-2	644.018	35	3	33	35	2	33	0.099
-1	646.027	24	2	23	24	1	23	0.155
	648.156	35	1	35	35	0	35	0.518
1	650.357	35	2	33	35	3	33	0.104
2	652.480	21	2	20	21	3	18	0.191
3	654.542	28	3	26	28	4	24	0.325
4	656.578	31	1	30	32	2	30	0.355
5	658.615	31	5	26	31	6	26	0.340
6	660.621	32	6	27	32	7	25	0.324
7	662.510	32	7	26	32	8	24	0.298
8	664.561	33	8	25	33	9	25	0.272
9	666.509	19	7	12	20	8	12	0.245
10	668.419	19	8	12	20	9	12	0.214
11	670.361	19	9	11	20	10	11	0.180

785.723, 647.217 and 646.997 cm^{-1} , respectively. Generally, the assignments were made so that the resulting values of the rotational constants agree well with the microwave values. The centrifugal distortion constants for the upper state were assumed equal to those for the ground state. No assignments of K values were made for the interfering peaks.

In order to conform the infrared band contour of an asymmetric top molecule, a modified computer program was used. The calculated frequencies and band contour shown in Table 3 and Figure 5, respectively. JG and JV are the J values for the ground and the first excited vibrational levels, respectively. KP and KO are the K values in the prolate and the oblate limits, respectively. A slight differences between the observed and calculated frequencies may well be due to the fact that the Coriolis constants were not included in this calculation. The rotational constants which were

determined by microwave spectroscopy were used for ground state, that is, $A'' = 1.172583$, $B'' = 0.106274$, and $C'' = 0.097342 \text{ cm}^{-1}$ respectively. Since the band center area is very sensitive to B'' and C'' rotational constants, a simulation method was adopted to decide rotational constants for the first excited vibrational state. The correction of the rotational constants was refined by using a standard least squares of Jacobian. The results for the first excited vibrational state were $A' = 1.169532$, $B' = 0.106166$, and $C' = 0.097229 \text{ cm}^{-1}$, respectively. The centrifugal effect shifts the peaks in the P and R branches by 0.7 cm^{-1} or less toward the band origin.

The calculated band envelopes are in agreement with the observed spectra not only in the positions the band center of the P- and R-branch lines but also in their shapes which are characteristic of a C-type band.

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