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Infrared Spectrum of ν_2 of Dibromoborane and Dibromoborane-*d*

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The fundamental associated with the B–H and B–D stretching motions in $HBBr_2$ and $DBBr_2$ have been observed under high resolution. A series of evenly spaced lines occurs which has the appearance of a ⊥ band of a symmetric-top molecule. Analysis of the spectra gives an approximate value for the smallest moment of inertia from which the apex angle Br–B–Br was calculated to be 119.3±2°. It was possible to assign K values to the individual lines and to determine the position of the band centers for both $HBBr_2$ (2622.4 cm^{-1}) and $DBBr_2$ (1960.1 cm^{-1}).

INTRODUCTION

THE inertial constants and molecular geometry of dichloroborane, $HBCl_2$, have been determined from an analysis of the vibrational–rotational structure of the band associated with the B–H and B–D stretching motions.[1] Dibromoborane ($HBBr_2$) and dibromoborane-*d* ($DBBr_2$) have now been prepared, and a similar analysis has been undertaken. A vibrational analysis of the dihaloboranes utilizing the Green's function approach[2–4] has led to a complete assignment of the normal modes and a unique determination of the potential constants.[5]

As a class of compounds the dihaloboranes (assuming a planar C_{2v} model) are accidental symmetric-top rotators. Since the B–H stretching motion is perpendicular to the accidental top (unique) axis and is contained in the axis of intermediate moment of inertia, a typical Type B band[6,7] is observed. Under high dispersion the band reveals the presence of an evenly spaced series of lines on either side of a central minimum. The relatively small moment of inertia associated with the top axis results in a spacing which is easily resolvable with most commercially available infrared spectrophotometers. Data can be treated with relatively simple symmetric-top formulas from which the rotational constant A can be derived. With the aid of a computer the rotational levels can be assigned and the band centers can be located. Results for $HBBr_2$ and $DBBr_2$ provide sufficient information to determine the bond angle Br–B–Br.

EXPERIMENTAL

A mixture of diborane (0.60 mM) and BBr_3 (2.4 mM) was placed in a clean Pyrex 1-liter bulb with a long condensing tip. Periodic examination of the mixture during the course of several days indicated the formation of only small quantities of HBr. Several turns of copper wire were wrapped around the bottom of the condensing tip and the mixture was frozen into the area with liquid nitrogen. A continuous 20-kV discharge was then applied externally through the coil into the solid. The solid was allowed to evaporate under discharge and was then refrozen into the same area. This procedure was repeated half a dozen times. Spectral examination of the mixture indicated a reaction had taken place in good yield. The mixture was then partially separated into its constituents by slowly pumping through a series of traps maintained at −45°, −55°, and −196°C. The −55°C trap contained predominantly $HBBr_2$ which appeared to slowly disproportionate into BBr_3 and B_2H_6 upon standing, although the stoichiometry of this reaction has not yet been established. The −45°C trap contained a mixture of BBr_3 and $HBBr_2$ which appeared to be quite stable with respect to disproportionation. The more volatile fraction in the −196°C trap contained unreacted diborane and a substituted diborane (possibly B_2H_5Br). Small quantities of BBr_3, $HBBr_2$, and HBr were also identified in this fraction. As before, the presence of B_2H_6 due to the disproportionation reaction introduces BH_2 stretching motions (2500–2600 cm^{-1}) which must be avoided. It was most convenient to work with mixtures of BBr_3 and $HBBr_2$ (20–50 mole %) which are quite stable and suppress the formation of B_2H_6. $DBBr_2$ was prepared quite simply by exchanging the above mixtures directly with D_2 at room temperature. Mixtures remaining in contact 48 h were approximately 50% exchanged. Pure deuterium was generated from uranium deuteride by heating. BBr_3 was obtained from the Eagle–Picher Company and was claimed to be 99.99% pure.

A Perkin–Elmer Model 421 spectrophotometer with a dual grating interchange provided adequate resolution. Calibration against HBr[8] and H_2O[9] provided an accuracy estimated to be ±0.5 cm^{-1}. Spectral slit-

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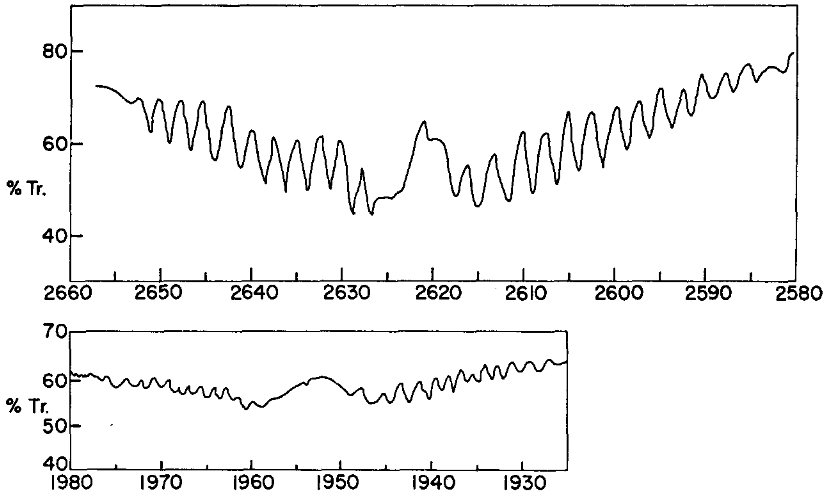

FIG. 1. Fine structure of the fundamental ν_2 of $HBBr_2$ (upper) and $DBBr_2$ (lower). Frequency in cm^{-1}.

widths were programmed for 0.29 cm^{-1} and 0.95 cm^{-1} for the 2620- and 1960-cm^{-1} regions, respectively. A 10-cm cell was used for gas samples. In the case of $HBBr_2$ and $DBBr_2$ there were no problems with interfering bands from BBr_3.

RESULTS

The spectra are shown in Fig. 1. The most dominant feature is the symmetrical and well defined appearance of the rotational fine structure of the BH band. The B–D band is not as well defined and is somewhat irregular. A planar model for $HBBr_2$ is presented in Fig. 2. The moment of inertia (I_A), about Axis A through the center of mass and parallel to the Br–Br line, is small compared to I_B and I_C. In this case the inertial relationship $I_A+I_B=I_C$ for a planar system shows $I_B\approx I_C$. Actually, this relationship holds only for equilibrium moments of inertia but is a good approximation for the ground state values (I_A^0, I_B^0, I_C^0) which are derived from our experimental measurements. The vibration–rotation band associated with the B–H stretching motion will then be a Type B band which will approach in structure a $\perp$ band (dipole moment change $\perp$ to the top axis) as the ratio $\rho=I_A/I_B$ becomes small.[10] This ratio is smaller for $HBBr_2$ than for $HBCl_2$ and the symmetric-top relationships should be even closer approximations.

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

$$F_{(v)}(J,K)=B_{(v)}J(J+1)+(A_{(v)}-\tilde{B}_{(v)})K^2,\text{[11]} \qquad (1)$$

neglecting the effects of centrifugal distortion, Coriolis interaction, and vibrational anharmonicity. For an accidental symmetric top, $\tilde{B}$ 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

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

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

Although the molecular constants may be calculated from (2), they may be more accurately determined

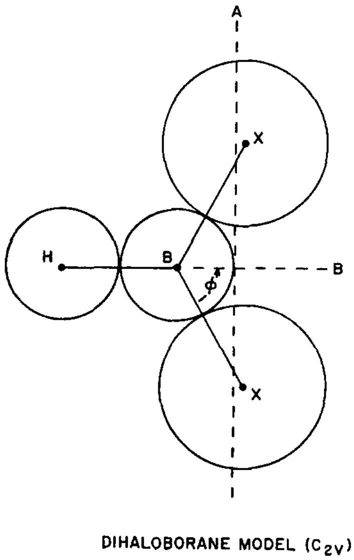

FIG. 2. $HBBr_2$ model, showing axis of smallest moment of inertia A and ϕ, one-half the apex angle. The $B(C_2)$ axis coincides with the boron–hydrogen bond line; the C axis is $\perp$ to the plane.

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[11] Reference 6, pp. 400 ff.

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from combination differences[12]

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

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 ν_0^{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 average separation of the lines for $HBBr_2$ is 2.45 and 1.57 cm^{-1} for $DBBr_2$ cm^{-1}. 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 ν_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 Tables I and II. It is seen that the positions of the lines may be fit quite well to the symmetric-top expression.

TABLE I. Rotational fine structure of ν_2 of $HBBr_2$.

K	$R(Q)_k$ (obs.)	$R(Q)_k$ (calc.)	$P(Q)_k$ (obs.)	$P(Q)_k$ (calc.)
1	2626.4	2626.0		
2	2628.5	2628.5		
3	2630.9	2630.9	2617.5	2616.3
4	2633.5	2633.4	2615.0	2613.9
5	2635.9	2635.8	2611.7	2611.5
6	2638.3	2638.3	2608.9	2609.0
7	2640.9	2640.7	2606.5	2606.6
8	2643.8	2643.2	2603.8	2604.2
9	2646.5	2645.7	2601.2	2601.8
10	2648.8	2648.1	2598.5	2599.4
11	2651.1	2650.6	2596.1	2597.0
12	2653.1	2653.1	2593.7	2594.6
13			2591.7	2592.2
14			2589.2	2589.8
15			2586.8	2587.4

$\nu_0=2622.4$ cm^{-1}, $A''-\tilde{B}''=1.216$, $A'-\tilde{B}'=1.218$

TABLE II. Rotational fine structure of ν_2 of $DBBr_2$.

K	$R(Q)_k$ (obs.)	$R(Q)_k$ (calc.)	$P(Q)_k$ (obs.)	$P(Q)_k$ (calc.)
3	1965.3	1965.5		
4	1967.8	1967.1		
5	1969.3	1968.7	1953.6	1953.1
6	1970.8	1970.2	1951.3	1951.5
7	1972.3	1971.8	1949.7	1949.9
8	1973.3	1973.4	1947.8	1948.3
9	1974.8	1974.9	1946.4	1946.8
10	1975.9	1976.5	1945.2	1945.2
11	1977.3	1978.0	1943.8	1943.6
12	1979.2	1979.6	1942.5	1942.1
13	1980.9	1981.1	1940.8	1940.5
14	1982.3	1982.7	1939.3	1938.9
15			1937.8	1937.4
16			1935.7	1935.8

$\nu_0=1960.1$ cm^{-1}, $A''-\tilde{B}''=0.782$, $A'-\tilde{B}'=0.782$

The moments of inertia about the principal axes were obtained from the relationship[13,14]:

$$I_AI_BI_C=\begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix}. \quad (5)$$

Elements of the matrix, I_{xx}, I_{xy}, I_{xz}, etc., are the moments and products of inertia with respect to an arbitrary Cartesian coordinate system (x', y', z'). By orienting the coordinate system so that the x' axis coincides with the twofold axis, the off-diagonal elements (products of inertia) vanish and the eigenvalues become I_{xx}, I_{yy}, and I_{zz} which are expressed as follows:

$$I_{xx}=\sum_i M_i(y_i'^2+z_i'^2)-(M_T)^{-1}(\sum_i M_iy_i')^2-(M_T)^{-1}(\sum_i M_iz_i')^2, \quad (6)$$

$$I_{yy}=\sum_i M_i(x_i'^2+z_i'^2)-(M_T)^{-1}(\sum_i M_ix_i')^2-(M_T)^{-1}(\sum_i M_iz_i')^2, \quad (7)$$

$$I_{zz}=\sum_i M_i(x_i'^2+y_i'^2)-(M_T)^{-1}(\sum_i M_ix_i')^2-(M_T)^{-1}(\sum_i M_iy_i')^2. \quad (8)$$

When the origin is fixed at the boron atom, coordinates of the atoms (x_i', y_i', z_i') having mass M_i can be expressed in terms of bond distances and the apex angle,

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[12] $R(Q)_K$ 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.

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TABLE III. Results.

	A (cm^{-1})	B (cm^{-1})	C (cm^{-1})	ρ	$\angle$BrBBr
$HBBr_2$	1.256	0.041	0.039+	0.033	119.3°±2°
$DBBr_2$	0.822	0.041	0.039−	0.050	

and Eqs. (6), (7), and (8) become:

$$I_{xx}=I_B=h/8\pi^2cB=2M_x r_{BX}^2\sin^2\phi, \qquad (9)$$

$$I_{yy}=I_A=\frac{h}{8\pi^2cA}=\frac{2M_x(M_H+M_B)}{M_T}r_{BX}^2\cos^2\phi+\frac{4M_HM_X}{M_T}r_{BX}r_{BH}\cos\phi+\frac{M_H(M_T-M_H)}{M_T}r_{BH}^2, \qquad (10)$$

$$I_{zz}=I_C=\frac{h}{8\pi^2cC}=2M_x r_{BX}^2\sin^2\phi+\frac{2M_x(M_H+M_B)}{M_T}r_{BX}^2\cos^2\phi+\frac{4M_HM_X}{M_T}r_{BX}r_{BH}\cos\phi+\frac{M_H(M_T-M_H)}{M_T}r_{BH}^2. \qquad (11)$$

The moment of inertia about A for both $HBBr_2$ and $DBBr_2$ can be computed from Eq. (10).

M_T is the molecular weight, ϕ is one-half the bond angle Br–B–Br (Fig. 2), and $r_{BX}=r_{B-Br}$ was assumed to be 1.87 Å.[15] Using the computed values for I_A, shown in Tables I and II, Eq. (10) is presented graphically in Fig. 3 with the bond angle (2ϕ) as a function of the B–H distance (ρ_{BH}). The equations were solved for various values of $\tilde{B}$ until consistent values for the molecular dimensions were obtained. B and C were obtained from the relations

$$B=-(A-\tilde{B})+[A^2+\tilde{B}^2]^{\frac{1}{2}} \qquad (12)$$

$$C=(A+\tilde{B})-[A^2+\tilde{B}^2]^{\frac{1}{2}}. \qquad (13)$$

It is seen from Fig. 3 that a unique solution (intersection) does not occur for a reasonable value of ρ_{BH}. Previous work has indicated that $\rho_{BH}=1.13\pm0.2$ Å for $HBCl_2$ calculated by the same procedure. This is certainly consistent with reported values for ρ_{BH} in other boranes determined by more accurate techniques. Therefore, if we assume that $\rho_{BH}=1.20$ Å holds for the dihaloboranes, the apex angle in $HBBr_2$ is 119.3°±2°. However, the bond angle in $DBBr_2$ is somewhat smaller. Results are summarized in Table III.

Since all the frequencies for modes belonging to Symmetry Type A_1 have now been observed or calculated, the Teller–Redlich[16] product rule may be tested. The exact expression, utilizing zero-order frequencies, becomes

$$\frac{\omega_1^H\omega_2^H\omega_3^H}{\omega_1^D\omega_2^D\omega_3^D}=\left[\left(\frac{M_D}{M_H}\right)\left(\frac{M_{HBBr_2}}{M_{DBBr_2}}\right)\right]^{\frac{1}{2}}=1.410, \qquad (14)$$

and should at least be a good approximation for the observed or calculated fundamentals. Frequencies substituted into the left side of Eq. (14) were: $\nu_1^H=612$ cm^{-1}, $\nu_2^H=2622.4$ cm^{-1}, $\nu_3^H=179$ cm^{-1} (calculated), $\nu_1^D=585$ cm^{-1}, $\nu_2^D=1960.1$ cm^{-1}, and $\nu_3^D=179$ cm^{-1} (calculated). The product ratio is then 1.408 and compares closely to the right side of (14).

DISCUSSION

Nielson[10] calculated the spectra of Type B vibration–rotation bands for planar molecules with variable $\rho=I_A/I_B$, and the data conforms to the structures predicted from ρ given in Table III. Lack of an intensity alternation in the fine structure is consistent with the twofold axis being coincident with the axis of intermediate moment of inertia. This, in addition to the observed spacings, may be cited in support of the model chosen for the analysis and the presence of a monomeric species. Fine structure of ν_2 in $HBBr_2$ ($\rho=0.033$) was sharper and better defined than corresponding bands of $HBCl_2$ ($\rho=0.066$) in predictable fashion. However, bands in $DBBr_2$ having an intermediate ρ ($\rho=0.050$), were not as well defined or regular. This may be due in part to incomplete resolution of the closely spaced lines.

The calculated molecular parameters are strongly dependent on $(A'-\tilde{B}')$ derived from the combination

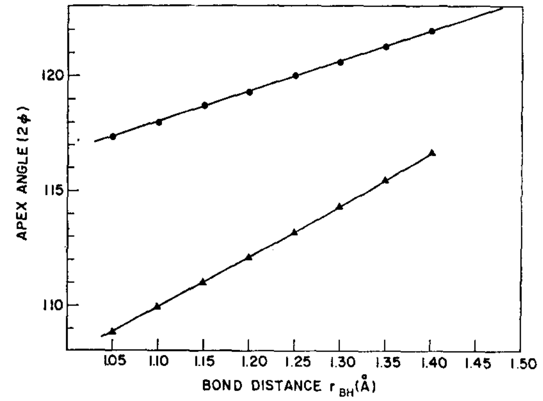

FIG. 3. Apex angle (2ϕ) plotted as function of the BH and BD bond lengths. $HBBr_2$ (circles), $DBBr_2$ (triangles).

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[16] Reference 6, pp. 227 ff.

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differences of the observed frequencies according to Eq. (4). Spacings in $HBBr_2$ were reproducible within an estimated ± 0.05 cm^{-1} from which the accuracy in measuring the apex angle was estimated to be $\pm 2°$. Since the spacing in $DBBr_2$ was smaller and less regular, it was reasonable to suspect the calculations to be less reliable. Examination of Fig. 3 illustrates that this procedure is not a sensitive measure of the BH bond distance since the mass of H or D contributes little to the observed moment of inertia. Also, the B–Br bond distance was transferred from BBr_3. In order to obtain more accurate results, it will be necessary to independently measure B or C which was obtained indirectly from these experiments.

Finally, it should be mentioned that the results obtained are from the effective values of the rotational constants, in the ground vibrational state, and are not equilibrium values.

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Studies on the Hydrogen Evolution Reaction Down to −150°C and the Role of Proton Tunneling

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(Received 29 June 1964)

An investigation of the hydrogen evolution reaction (h.e.r.) at low temperatures down to −150°C is reported for two metals, Hg and Pt. The purpose of the investigation was to examine the kinetic behavior for evidence of proton tunneling. The H/D isotope effect at mercury at low temperatures and the heat of activation behavior do not support any significant contribution from proton tunneling in the reaction. The situation is not as clear, however, for the case of smooth platinum. On the basis of the observation of a linear Arrhenius relation for the heat of activation down to −150°C, it is concluded that a proton tunneling mechanism cannot be appreciable for the h.e.r. on smooth platinum in ethanolic solutions.

I. INTRODUCTION

IN a number of recent papers,[1–3] the question of the role of proton tunneling in the electrochemical hydrogen evolution reaction (h.e.r.) has been considered theoretically in relation to Tafel slopes,[2] potential dependence of H/D separation factors,[2] and the values of separation factors themselves.[3,4] Proton tunneling in the ion-discharge step of the h.e.r. was first discussed by Bawn and Ogden and Appelby and Ogden,[5] following the work of Bell,[6] but in the early work,[4] too wide a potential barrier was considered, and the effect of varying electrode potential was not examined. The high values of separation factor S obtained by Appelby and Ogden[5] and claimed to support a proton transfer by tunneling have never been confirmed. It was suggested by Conway[2] (cf. Ref. 7) that a more definitive indication of the role of proton tunneling, if any, in the h.e.r. could be made by low-temperature electrode kinetic measurements and examination of Tafel slopes[2] for H and D discharge. It is the aim of the present paper to report and discuss such experiments carried out at mercury and platinum in cooled and supercooled alcoholic solutions down to −150°C. In aqueous solutions, low temperatures can only be attained in strong salt or acid solutions from which specific anion adsorption may arise and complicate the kinetic behavior. The electrochemical proton-transfer case is of particular interest with regard to the problem of participation of appreciable tunneling since special criteria are available[2] for evaluating the role of tunneling, which do not arise in the case of ordinary homogeneous proton-transfer reactions. In other respects, however, the process of electrochemical proton transfer is analogous to that in homogeneous prototropic acid–base reactions[2] and, in fact, a cathode for the hydrogen evolution reaction may be regarded, in the general sense, as a

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