The Absorption Spectrum of Diborane

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The absorption spectrum of diborane has been investigated in the infra-red from 1–25μ and in the vacuum ultraviolet down to 1000A. The rotational structure obtained for certain of the infra-red bands rules out the ethane-type structure but agrees very well with the interpretation of the electron diffraction results in terms of a bridge model. The ultraviolet spectrum indicates a simple electronic structure and a first ionization potential about 11–12 volts.

INTRODUCTION

IN a recent review of the evidence bearing on the problem of the structure of diborane Professor R. S. Mulliken[1] stressed the fact that while there was a growing weight of experimental data favoring the bridge model as against the ethane-type structure, it was desirable that some unambiguous direct evidence should be forthcoming so that a clear-cut decision could be made between the two. This has now been obtained in the present work as a result of the examination of the infra-red spectrum of diborane under greater resolving power than had hitherto been used. The rotational structures of some of the perpendicular bands have been resolved, and these have been found to show the alternation of intensity to be expected from a bridge model but which cannot possibly be associated with a structure of the ethane type in either the eclipsed or staggered form. A very close analogy of the band structures and envelopes observed in diborane with those of certain ethylene bands is evident. In particular, those bands of ethylene and diborane (bridge model) in which the CH_2 and the terminal BH_2 groups undergo the same bending and stretching moments exhibit a striking similarity in their band envelopes. This indicates that the degree of departure from a symmetrical top is much the same for both molecules. The assignments seem to fit in well with a normal coordinate treatment of the bridge model due to Bell and Longuet-Higgins,[2] though there are some minor discrepancies.

[1] R. S. Mulliken, Chem. Rev. 41, 207 (1947).
[2] R. P. Bell and H. C. Longuet-Higgins, Proc. Roy. Soc. 183, 357 (1945).

EXPERIMENTAL

A specimen of diborane of high purity prepared by Dr. G. W. Schaeffer of the chemistry department was used. It was fractionally distilled from liquid air in the usual gas-handling apparatus into the absorption cell which was of glass with windows of rock salt or potassium bromide. The cell length was 10 cm and runs were made at pressures varying from a few tenths of a mm up to 70 cm. The instrument employed was a Perkin-Elmer recording spectrometer fitted with lithium fluoride, sodium chloride, and potassium bromide prisms. Its performance can be judged by the fact that it was capable of resolving the rotational structure of the 4.2μ band of carbon dioxide without difficulty.

RESULTS

Apart from the greater detail observed in the bands as a result of the higher resolving power, the general features of the spectrum obtained were essentially similar to those reported by Stitt.[3] There are some minor differences in the wave-lengths of the weaker bands but the most important discrepancy is our failure to reproduce the band structure reported by Stitt in the 25μ region although our prisms and aperture were several times greater than his.

The general view of the spectrum is given in Fig. 1. Higher resolution pictures of the bands around 2600, 1175, and 974 wave numbers are shown in Figs. 2a and 2b. Table I gives the frequencies of the band centers and their assignments. Table II contains the Raman data of Anderson and Burg[4] with the assignments of

[3] F. Stitt, J. Chem. Phys. 9, 780 (1941).
[4] T. F. Anderson and A. B. Burg, J. Chem. Phys. 6, 586 (1938).
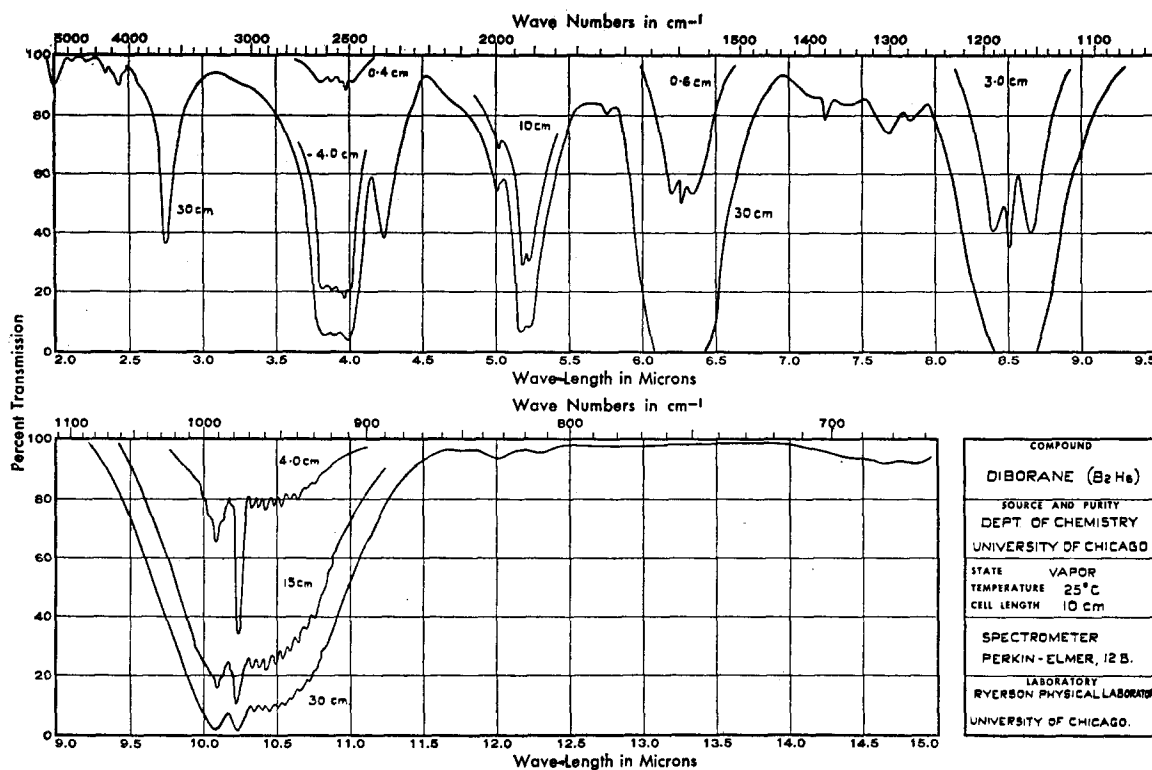
FIG. 1. The spectrum of diborane from 1.5 to 15μ.

Bell and Longuet-Higgins.[2] In our preliminary note[5] the axes of reference in the molecule were taken the same as those used by Herzberg for ethylene[6] (Ox axis of smallest moment of inertia, Oz axis of largest moment of inertia). However in order to preserve continuity with the treatment of Bell and Longuet-Higgins their axes have been retained—Ox axis of smallest moment of inertia, Oy axis of largest moment of inertia. While a change to the more conventional axes only affects the symmetry species by interchanging B_1 and B_2, it would involve the renumbering of nine of the fundamental frequencies.

DISCUSSION

The interpretation of the electron diffraction results in terms of a bridge model[7,8] is given in Fig. 3 while Fig. 4 gives the normal vibrations of the bridge model according to Bell and Longuet-

[5] W. C. Price, J. Chem. Phys. 15, 614 (1947).
[6] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 107.
[7] S. H. Bauer, Chem. Rev. 31, 43 (1942).
[8] R. P. Bell, private communication.

Higgins.[2] The factors which eliminate the ethane-type model will be discussed in greater detail as we come to them, but for the sake of convenience they are enumerated here. (1) the alternation of intensity of the rotational structure; (2) the asymmetric top character of the band envelopes; (3) the incompatibility of the magnitude of the rotational separations with the interpretation of the electron diffraction results in terms of an ethane-structure; (4) the comparative success of the normal coordinate treatment of a bridge model in explaining the Raman and infra-red spectra of the molecule.

The rotational structures of the perpendicular bands: The most striking features of the spectrum are exhibited by the perpendicular bands illustrated in Figs. 2a and 2b. The alternation of intensity indicates that the molecule belongs to the symmetry group D_{2h} like ethylene. The alternation to be expected in the perpendicular bands due to the spins of the three pairs of hydrogen nuclei is 9:7.[9] It is, of course, super-

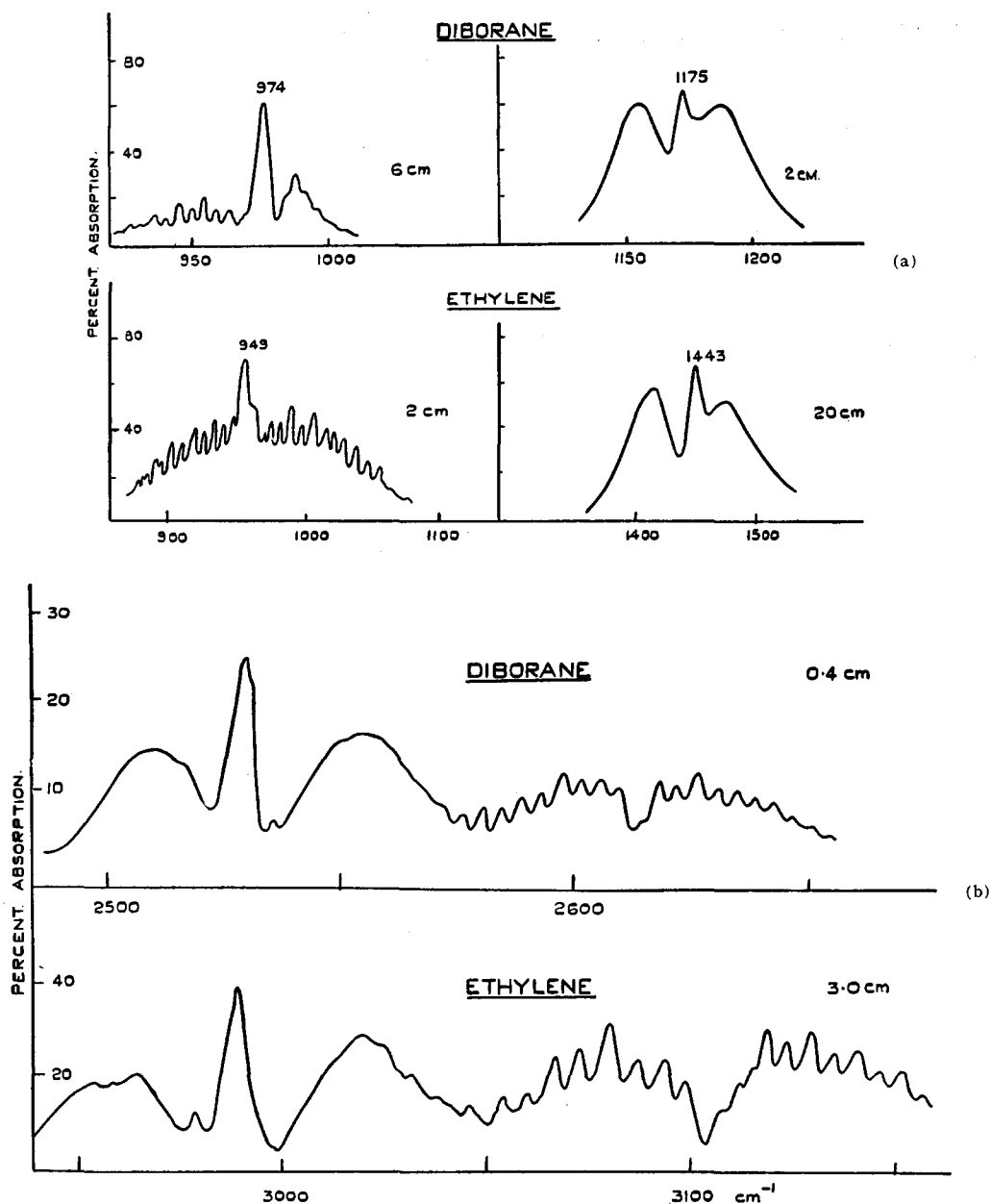[9] G. Herzberg and E. Teller, private communication.

FIG. 2. Corresponding bands in diborane and ethylene in which the terminal XY_2 groups undergo the same bending and stretching motions. The pressure of the gas is given in each case in cm of Hg.

imposed upon a Boltzmann distribution due to the temperature, and is also affected by the finer rotational structures within the Q sub-branches. It is further influenced by the existence of the two isotopes B^{10} and B^{11}, their abundance being such that the relative numbers of $B^{11}-B^{11}$, $B^{11}-B^{10}$, and $B^{10}-B^{10}$ molecules are roughly $2:1:0.125$; however, as the vibrations involved are largely in the $B-H$ bands and the borons move but little, the isotope effects are small. In addition, the intensity alternation in polyatomic molecules cannot be expected to be as regular as in diatomic molecules, since the various sub-bands overlap and true integrated intensities cannot be measured. This overlapping, as well as slight differences in the structures of the dif-

ferent sub-bands, may affect the observed intensities of the various Q branches, thus producing apparent anomalies in the intensities of the observed maxima. The intensity alternation is best brought out with only moderate resolution—sufficient to resolve the Q branches of the various sub-bands from each other, but low enough to integrate the intensity of each Q branch—and with the lowest feasible total absorption. (With higher pressures or longer paths, much of the sharp structure may be giving 100 percent absorption even though the apparent absorption with moderate resolution may be much less than this.)

The alternation of intensity shows up clearly in the ^PQ branch of the 974-cm^{-1} diborane band, though slightly inadequate resolving power prevents its being observed distinctly in the ^RQ branch. It is also quite clear in both branches of the 2614-cm^{-1} band. In both bands the alternation is nearly, though not quite, as pronounced as it is in the corresponding bands of ethylene, for which the spin factor is 10:6.[10]

The analysis for the two perpendicular bands in terms of a symmetric top rotator, to which the molecule closely approximates, is given in Table III. In the case of the 2614-cm^{-1} band, the numbering of the Q branches was determined by the fact that the band should be approximately symmetrical about its origin, with the $^PQ_1$ and $^RQ_0$ maxima weak or absent as a result of energy level shifts caused by the slight asymmetry of the molecule. This numbering associates odd values of K'' with the strong Q maxima and even values of K'' with the weak maxima, in agreement with theoretical predictions. The numbering in the case of the 974-cm^{-1} band is less unambiguous, but the most reasonable choice (the four central Q maxima missing) also associates odd values of K'' with the strong maxima. (In the case of ethylene, the situation is reversed because of the presence of only two pairs of hy-

[10] The intensity alternation in the 949-cm^{-1}-ethylene band is shown in American Petroleum Institute spectrograms, and is shown in both the 3105 and 949-cm^{-1} bands in records made by the present author (Fig. 2). It is not shown in the record of the 949-cm^{-1} band given by Gallaway and Barker [J. Chem. Phys. 10, 88 (1942)], but this may be ascribed to the high resolution and high pressure used. For a theoretical discussion of alternating intensities in the ethylene bands, see G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 480 and elsewhere.

TABLE I. Table of frequencies of centers of diborane bands and their assignments.

Frequency (Stitt)	Intensity	Frequency (Price)	Intensity	Assignment
393⎫ 412⎬ 431⎭	strong	ca. 430	medium	$n \times \nu_{10}$
673⎫ 685⎭	weak	not found	(impurity?)	
—		811	v. weak	
831	weak	831	v. weak	
—		849	v. weak	
981	strong	974 (ps. Q)	strong	ν_{14} (⊥ type C)
1154⎫ 1178⎬ 1197⎭	very strong	1175 (ps. Q)	v. strong	ν_{18} (∥ type A)
1274		1267	fairly weak⎫	ν_9 (1283)
1311	medium	1302	fairly weak⎭	⊥ type B?
1377	medium	1377	fairly weak	
1405	medium	ca. 1405	v. weak	
1587⎫ 1608⎬ 1626⎭	very strong	1604 (ps. Q)	v. strong	ν_{17} (∥ type A)
1722	weak	?		
1852⎫ 1874⎭	strong	1850⎫* −1870⎭	strong	
1993	medium	1984*	weak	ν_{13} (⊥ type C)
2134	very weak	2088⎫ 2124⎬ 2143⎭	v. weak	
2217	very weak	2200⎫ 2215⎬ 2230⎭	v. weak	
2353	strong	2345*	medium	$\nu_3 + \nu_{18}$ (∥ type A)
2558	strong	2522 (ps. Q)	strong	ν_{16} (∥ type A)
2625	strong	2614 ($^RQ(0)$)	strong	ν_8 (⊥ type B)
3135	very weak	3135	v. weak	
3670	strong	3600–3700	strong	$\nu_1 + \nu_{18}, \nu_{11} + \nu_{18}, \nu_3 + \nu_{16}, \nu_3 + \nu_8$
4040	weak	4035	v. weak	
4250	weak	4155	weak	$\nu_1 + \nu_{17}$
—		4350	weak	$\nu_1 + \nu_{13}, \nu_2 + \nu_3 + \nu_{18}$
4550	weak	4473	v. weak	
—		4815	v. weak	
5150	weak	5022	weak	(∥ type A) $\nu_1 + \nu_{16}$
—		5140	v. weak	
—		5210	v. weak	
—		5400	v. weak	
5800	weak	5760	weak	$\nu_1 + \nu_2 + \nu_{18}, \nu_2 + \nu_{11} + \nu_{18}, \nu_2 + \nu_3 + \nu_{16}, \nu_2 + \nu_3 + \nu_8$

* These bands have been examined in greater detail by Dr. R. D. Cowan and will be reported by him in a subsequent article.

drogen nuclei instead of three, even values of K'' being associated with the strong Q branches.[10])
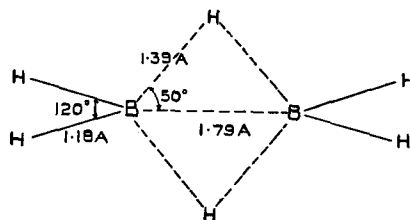

FIG. 3. Structure of diborane molecule according to the interpretation of the electron diffraction results in terms of a bridge model.
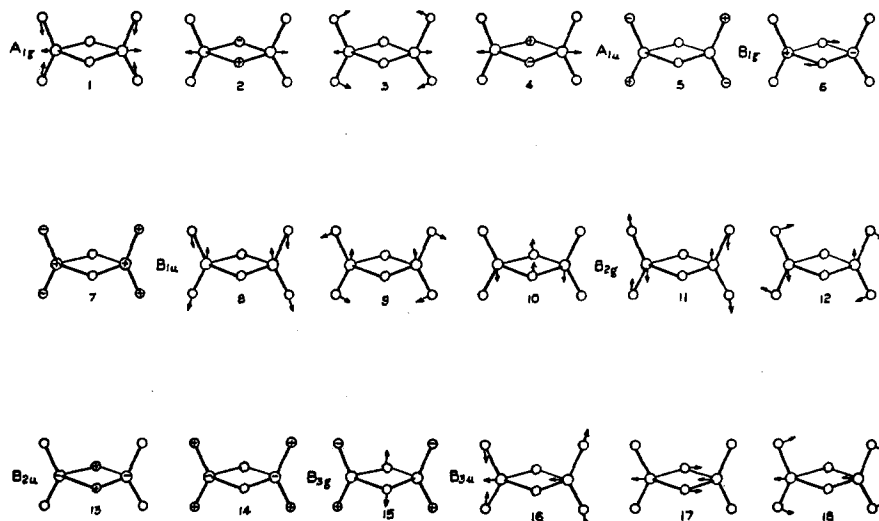
FIG. 4. The character of the normal vibrations of "bridge" diborane.
(After Bell and Longuet-Higgins.[2])

The accuracy of the measurements is not much better than 0.5 cm^{-1} and in fact the absolute values in the 2614 band may be out by as much as two wave numbers because of the lack of good wave-length standards in the immediate vicinity of the bands. The convergence of the bands is so small that no separate values of $C-D$ could be derived for the upper and lower states. The value of $C-D$ for the 2614 band is 2.07 cm^{-1}. That for the 974 band is 2.05 cm^{-1}. The expected values for C and D calculated from data based on the bridge model interpretation are $C=2.63$ cm^{-1} and $D=0.58$ cm^{-1} or 0.55 cm^{-1}, according to which of the two larger moments of inertia is taken. This is as good agreement as can be expected, while on the other hand the values calculated using the data obtained by interpreting the electron diffraction results in terms of the ethane-

TABLE II. The Raman data of Anderson and Burg* with the assignments of Bell and Longuet-Higgins.**

ν in cm^{-1}	Intensity	Assignment
793	5	$\nu_4(B^{11}-B^{11})$
806	4	$\nu_4(B^{11}-B^{10})$
821	3 (broad)	$\nu_4(B^{10}-B^{10})$, ν_{12}
1008	diffuse	ν_7
1180	2	ν_3
2102	10	ν_2
2489	3	ν_{11}
2523	10	ν_1

* See reference 4.
** See reference 2.

type structure[11] give $C=1.94$ and $D=0.65$ cm^{-1}, i.e., a spacing of consecutive rotational lines by 2.6 cm^{-1}, which is quite incompatible with the value of *ca.* 4.1 cm^{-1} observed. Moreover for an ethane-type molecule it is to be expected that as a result of the influence of nuclear spin every third line should be accentuated as for example in the 12μ band of ethane.[12] In many bands of ethane the rotational structure is quite complicated owing to effects such as Coriolis interaction. It is clear that at least for the bands so far discussed such effects are not operative.

Another perpendicular band at 1980 cm^{-1} has been resolved by Dr. R. D. Cowan[13] who will be discussing it in a later report. It has a rotational structure very similar to the band at 974 cm^{-1} (Fig. 2a). Spectroscopic values for the geometrical parameters of the diborane molecule cannot be calculated until data on the rotational structure of the parallel bands and also on the isotope substituted molecules become available.

The nature of the band envelope of an infrared absorption band depends upon the symmetry of the vibration and the magnitudes of the principal moments of inertia of the molecule. For molecules like ethylene and diborane (bridge model) the deviations from the symmetrical top

[11] S. H. Bauer, J. Am. Chem. Soc. 59, 1096 (1937).
[12] R. G. Owens and E. F. Barker, J. Chem. Phys. 10, 146 (1942).
[13] R. D. Cowan, to be published shortly in J. Chem. Phys.

envelope are large for low values of the rotational quantum number (i.e., close to the band center) but rapidly disappear for the higher values. Thus the shape of the center of a band is a very good indication of the degree of asymmetry. It is clear from Figs. 2a and 2b that the asymmetry of ethylene and diborane must not be very different. The ratios of their principal moments of inertia are for ethylene $1:0.825:0.0172$ and for diborane $1:0.94:0.022$—that is, diborane according to the bridge model interpretation of the electron diffraction data is a somewhat closer approximation to a symmetrical top than ethylene. Slight adjustments such as small increases in the terminal BH_2 angle and diminutions in the internal BH_2 angle would bring the ratios closer. Figure 2 shows the great similarity which also exists in the band envelopes of the corresponding parallel bands of ethylene and diborane. These bands correspond to the vibrations in which the CH_2 and the terminal BH_2 groups undergo the same bending and stretching motions. No similarity of this sort could be established with any bands of ethane.

ASSIGNMENT OF THE BANDS

Apart from minor differences (particularly ν_9 and ν_{13}) and the extension to the overtones, our assignments given in Table I agree with those of Bell and Longuet-Higgins.[2] The more important bands will now be discussed individually and features which support the assignments will be elaborated.

400 cm^{-1}: Definite confirmation of the bands 412 and 393 reported by Stitt[3] has not been obtained in spite of the fact that larger prisms and greater apertures were used in this work. Stitt remarks in his paper that the shape on the long wave-length side of the 412-cm^{-1} band is rather uncertain due to the high percentage of stray radiation and the consequent low sensitivity in this extreme range of the KBr prism. At high pressures (ca. 40 cm) we find relatively continuous absorption below 450 cm^{-1} and there appears to be the possibility of a weak diffuse maximum around 430, but the peaks reported at 412 and 391 occur in our background. The absorption is probably not to be associated with a fundamental vibration. It could be the differ-

TABLE III. The line positions in the perpendicular-type bands of diborane.

| K″ | 2614-cm^{-1} band | | K″ | 974-cm^{-1} band | |
	P_Q	R_Q		P_Q	R_Q
0		2614.0	0	—	—
1	—	2619.0	1	—	—
2	2608.5	2624.5	2	—	983.9
3	2604.5	2627.8	3	962.7	986.9
4	2599.5	2632.0	4	958.1	990.7
5	2594.5	2635.5	5	954.1	994.5
6	2590.5	2639.5	6	950.0	999.0
7	2587.5	2642.3	7	946.0	1003.4
8	2581.5	2647.5	8	942.0	
9	2577.0		9	937.9	
10	2573.0		10	933.0	
11	2567.0				

ence band $\nu_{17} - \nu_3$ $(1604 - 1180 = 424)$. Bell[2, 14] has assigned it to the $2 \rightarrow 3$ transition of the rocking vibration ν_{10}. This is a special type of vibration which might be expected to have a low frequency and for which the intensities of the overtones $1 \rightarrow 2$, $2 \rightarrow 3$ are comparable with the fundamental. It has been shown by Bell[2] that in this type of ring bending the potential energy is proportional to the fourth power of the displacement and as such it is not subject to the same symmetry restrictions as the other bands. The magnitude of ν_{10}, judging from normal coordinate analysis and specific heat data, appears to be about 266 cm^{-1}.

974 cm^{-1}: This is a strong perpendicular band of type C (ν_{14}). Data on its rotational structure has already been given. While the P branch is well resolved and shows clearly the alternation of intensity, the R branch owing to its slight convergence is not so well separated. The isotopic $B^{11}B^{10}Q$ branch is not quite resolved from the main $B^{11}B^{11}Q$ branch and this has the effect of making this branch appear shaded slightly towards shorter wave-lengths. The isotopic separation between these two branches cannot be greater than about 3 wave numbers. Its strength relative to the 949 band in ethylene is approximately $1:3$.

1175 cm^{-1}: A very strong parallel band type A (ν_{18}), i.e. BH_2 deformation. The similarity of the band envelope with the corresponding band of ethylene at 1443 is quite striking. The ratio of their strengths is about $10:1$, which is much the same as that of the bands of the BH_2 and CH_2 stretching vibrations, the greater intensities

[14] R. P. Bell, Proc. Roy. Soc. A183, 328 (1944).

in diborane resulting from the larger polarities that can be produced in the BH_2 groups. The isotopic separation between the two Q branches which are not resolved cannot be greater than two or three wave numbers. Its closeness to the Raman frequency ν_3 (1180) indicates the almost complete absence of coupling via the BH_2B bridge for this type of vibration. This important point will be referred to again in connection with the 2522-cm^{-1} band.

1267, 1306-cm^{-1} peaks; 1283-cm^{-1} trough: This is tentatively assigned to ν_9 and should be perpendicular type B. Bell and Longuet-Higgins[2] have identified ν_9 with the 1405 frequency given by Stitt.[3] This is a very weak absorption barely perceptible amongst a great deal of water vapor structure and is most likely the R branch of a weak band whose Q branch is at 1375 (see next paragraph). Various factors, the main one of which is inadequate resolution in this region, prevent the observation of the rotational structure of the 1267 and 1306 peaks, though there are some indications that they are resolvable. The weakness of this band is in agreement with its interpretation as a rocking vibration as such distortion does not create appreciable polarity. In fact the analogous band in ethylene at 995 cm^{-1} is also very weak and its strength relative to the 949 ethylene bending vibration is about the same as this diborane band to the corresponding diborane bending mode at 974 cm^{-1}.

1340, 1374, 1405 cm^{-1}: A very weak band with 1374 as the pseudo Q branch. It is not easy to assign any plausible combination to this weak band.

1604 cm^{-1}: This is a very strong parallel band type A, presumably ν_{17} with R and P maxima at 1620 and 1580 cm^{-1}. It is the strongest band in the whole spectrum, being about 3 times as strong as the next strong band (1175). The assignment indicates that it involves a vibration of the bridge hydrogens along the 'protonated' double bond. It is suggested that the great strength of the band is associated with the tendency toward the formation of $BH_2^+BH_4^-$ and $BH_4^-BH_2^+$ at the turning points of the vibration. These structures which are the combination of a linear BH_2^+ and a tetrahedral BH_4^- can no doubt make a considerable contribution to the state of a suitably distorted molecule.

The protonated double-bond conception of the bridge would also require the band to be very strong since as the main electron deficiency resides in the bridge any distortion within it will produce large charges. The greater part of this band lies within the water vapor transmission maximum at 6.3μ and an examination of its structure by a grating would seem feasible and worth while.

1850 and 1880 cm^{-1}: This is a very difficult region to work in because of the atmospheric water vapor lines. It has been examined with the lithium fluoride prism by Dr. R. D. Cowan who will be reporting on it in a subsequent article. It appears that the bands present have structures part of which are perpendicular in type and part of which are parallel. Such complications may arise from resonance or Coriolis interactions. If the band is to be ν_{13}, as suggested by Bell and Longuet-Higgins,[2] then it should be a perpendicular type C band similar to that at 974 cm^{-1}. It must be admitted that it has not yet been possible to obtain a satisfactory explanation of this strong absorption. Possibilities such as a combination of the twisting vibrations ν_5 and ν_{15} with intensity borrowed from ν_{17} by Fermi resonance must await a more complete knowledge of the rotational structure. Work at higher dispersion preferably in vacuum will be needed to clear up this region. It is felt unlikely that the assignments of the other bands will require radical alteration to meet the interpretive requirements of this absorption.

1990 cm^{-1}: This has been shown by Dr. Cowan[13] to be a typical type C band and has been assigned by him to ν_{13}. Neither of the combinations suggested by Bell and Longuet-Higgins give the right band type. The isotope separation of the pseudo Q branch is about $+4$ cm^{-1}.

2345 cm^{-1}: Medium parallel band, type A probably $\nu_3+\nu_{18}$ ($1180+1175 = 2355$), isotope shift of Q branch, $ca.$ $+3$ cm^{-1}.

2522 cm^{-1}: Strong parallel band type A (ν_{16}) obviously analogous to the corresponding band in ethylene at 2989.5 cm^{-1} (see Fig. 2b). The absolute intensities of both this and the 2614 band in diborane are greater than the corresponding bands in ethylene by a factor of seven, which is presumably connected with greater

polarity in the BH bond. The isotope effect of the $B^{11}B^{10}Q$ branch is $+2.4$ cm^{-1}. The closeness of the frequency of this band to the Raman frequency ν_1 (2523 cm^{-1}) is very interesting since it indicates the great weakness of the coupling of the terminal BH$_2$ groups. The frequencies ν_1 and ν_{16} can be regarded as the "in phase" and "out of phase" combinations of the symmetrical valence BH frequency of the terminal BH$_2$ groups. Thus in diborane the coupling between the two groups is so weak that the two combinations do not have appreciably different frequencies. Exactly the same phenomenon is exhibited by the corresponding combinations of the deformation vibration of the BH$_2$ groups which results in the close agreement of the Raman frequency ν_3 at 1180 cm^{-1} with the infra-red fundamental ν_{18} at 1175 cm^{-1}. In the case of ethylene the coupling is fairly strong, as can be judged by the differences between the corresponding infra-red and Raman frequencies which are 2989.5 and 3019.3 (CH stretching) and 1443.5 and 1342.4 (CH deformation), respectively.

2614 cm^{-1}: Strong perpendicular band type B (ν_8). The rotational structure of this band has already been described. Although its structure is well resolved it does not show any appreciable vibrational isotope effect which must certainly be less than 1 cm^{-1}. It would not be expected to show any rotational isotope effect. The relative intensities and locations of the 2522 and the 2614-cm^{-1} bands of diborane with respect to one another are very similar to those of the corresponding bands in ethylene, a fact which must be regarded as strong evidence of the analogy drawn between them. This frequency (ν_8) can be regarded as the in-phase combination of the antisymmetrical valence frequency of the BH$_2$ groups, the out-of phase combination being the Raman frequency (ν_{11}) 2489. The fairly large difference between the two results from the relatively large displacements which the boron atoms undergo in the antisymmetrical valence BH$_2$ vibration as compared with the symmetrical valence and deformation frequencies of this group. This leads to considerably greater coupling between the two groups for these vibrations. The analogous frequencies in ethylene, *viz.* 3272 and 3105 cm^{-1} show a still larger difference. The apparent absence of vibrational isotope effect in
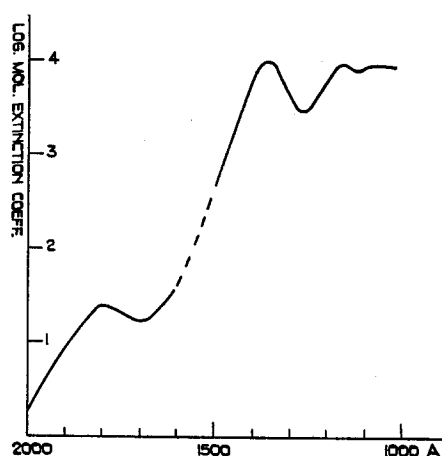

FIG. 5. The absorption of diborane in the region 2000–1000A.

the band may be due to the isotopic shift coinciding with the rotational spacing.

COMBINATION BANDS

The assignments of the combination bands of diborane are governed by the selection rule that since the molecule has a center of symmetry, no combination of two infra-red active frequencies can be infra-red active. This can be broken down if the vibrations are strongly anharmonic or if the molecule loses its center of symmetry by the presence of the two different isotopes in the molecule. However it does not appear likely that combination bands of any appreciable strength could result from either of these causes. The tentative assignments in Table I have therefore been made in conformity with the rule, with the exception of the very weak band at 3135. The only ones which call for comment are the following:

3135 cm^{-1}: This is a very weak band, parallel type A, which it is difficult to interpret.

3660 cm^{-1}, (3600 $-$ 3700): This is quite a strong band, probably parallel type A, though its structure is difficult to determine because of interference from atmospheric absorption. The strength of the absorption is probably due to overlapping due to the many combinations which are possible in this range, *viz.*:

$$\nu_{11}+\nu_{18} \quad (2489+1175=3664),$$
$$\nu_1 \ +\nu_{18} \quad (2523+1175=3698),$$
$$\nu_3 \ +\nu_{16} \quad (1180+2522=3702),$$
$$\nu_3 \ +\nu_8 \quad (1180+2614=3794).$$

5022 cm^{-1}: An attempt was made to resolve this band on the high dispersion grating spectrograph at Northwestern University through the courtesy of Professor W. S. Huxford. While this failed as a result of a variety of causes it was adequate to show that the band was parallel type A and that the isotope shift of the $B^{10}B^{11}$ molecule was about 4 cm^{-1} relative to that of the $B^{11}B^{11}$. The assignment $\nu_1+\nu_{16}$ (2523+2522 = 5045), which gives the right band type, seems most probable.

5760 cm^{-1}: This band, which is a well marked band, is of interest since it must correspond to at least three vibrational quanta. It seems likely that it is linked to the strong absorption around 3660 cm^{-1} by the addition of a quantum of the ν_2 (2102) vibration. It can thus correspond to $\nu_2+\nu_{11}+\nu_{18}$ (2102+2489+1175 = 5766) or $\nu_2+\nu_3+\nu_{16}$ (2102+1180+2522 = 5804) or both. Its breadth indicates that both combinations are probably present.

ULTRAVIOLET ABSORPTION

The ultraviolet absorption spectrum of diborane has been examined at low pressures down to 1000A using a 1 meter normal incidence grating vacuum spectrograph with the Lyman continuum. The first strong absorption is a broad diffuse band appearing in the region of 1350A at an equivalent thickness of 0.004 mm of the gas at N.T.P. It is followed by further diffuse absorption of similar strength below 1200A. This is compatible with an ionization potential between 11 and 12 electron volts and shows that all the electrons are fairly tightly bound. At higher pressures the bands spread out to longer wave-lengths and presumably merge into the relatively weak band reported by Blum and Herzberg.[15] Figure 5 is a plot of the absorption in which the actual values of absorption have been roughly estimated.

[15] E. Blum and G. Herzberg, J. Phys. Chem. 41, 91 (1937).