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The absorption spectra of aluminum, lithium, and sodium borohydride have been obtained in the region from 1–25μ. The aluminum borohydride was investigated as gas and an analysis of the infra-red and Raman bands fits a bridge-type structure of symmetry D_3 (probably D_{3h}). The spectra of lithium and sodium borohydrides were obtained from finely ground slurries of these materials. Their spectra indicate how the bridge structure of the H_2BH_2 metal groups passes over to the tetrahedral structure in a completely ionic lattic.

Using certain bond-distance force-constant relationships in conjunction with data from the diatomic hydrides and accepting electron and x-ray diffraction data for bond distances between the heavier atoms, values for the geometrical parameters are calculated for beryllium, aluminum, and sodium borohydride. These seem more plausible than any so far suggested. Observations on the electronic spectrum of aluminum borohydride have also been

made down to 1000A. The diffuseness of the absorption obtained at short wave-lengths prevented any detailed interpretation.

The spectrum of a compound formed between beryllium borohydride and sodium chloride has also been obtained and a consideration of its absorption bands has given information concerning the nature of this material. A spectrum of a slurry of the methyl derivative of lithium borohydride (LiBH$_3$CH$_3$) indicates considerable change in the structure relative to that of lithium borohydride.

A table of frequencies of related bands in the metal and other borohydrides is given which illustrates the changes referred to above. It includes a number of boron-nitrogen hydrides and shows that the BH frequency, when it is associated with analogous electronic groups, behaves in much the same way as that of CH when it is attached to saturated, olefinic or aromatic groups.

INTRODUCTION

DEFINITE information about the geometrical structure of the metal borohydrides is clearly the preliminary step to the formulation of a satisfactory theory of the nature of their chemical binding. While electron and x-ray diffraction experiments can determine the positions of the heavier atoms in these molecules in a satisfactory manner, the positions of the hydrogen atoms cannot be established with certainty by these methods alone. Now a vibrational analysis of the infra-red and Raman spectra of the molecules, particularly of the bands associated with motion of the hydrogen atoms, might be expected to give a great deal of information about the molecular symmetry and nature of the BH bonds present thus, making it possible to decide between different structures. In this way spectral data can greatly enhance the value of electron diffraction results since, once the form of the molecule is fixed, the scattering curve can then usually be fitted fairly well by a suitable choice of the BH bond distances and angles. Thus information can be obtained which cannot be directly deduced from the spectra. It is also possible, when the vibration bands of a molecule have been satisfactorily assigned, to calculate approximate values for some of the bond distances by using certain force-constant bond-distance relationships. In this way it is possible to check electron-diffraction values for the geometrical parameters in a molecule.

The present work forms part of a program of spectroscopic research being carried out at the University of Chicago on compounds of boron prepared by Professor

H. I. Schlesinger's group. The Raman spectrum of aluminum borohydride was obtained by Professor T. F. Young and Dr. B. Rice of the Chemistry Department, and the infra-red results reported here will be described in terms of a normal coordinate analysis which they have made for a model of D_{3h} symmetry with which the experimental evidence is in closest agreement.

EXPERIMENTAL

The aluminum borohydride was a pure sample prepared by Dr. A. Finholt. Owing to its explosive nature care had to be taken to make all gas cells completely leakproof and to cover them with protective wire screen. The cell windows, which were of sodium chloride or potassium bromide, were only lightly attacked by the gas. The hard black wax used for sealing on the windows and the apiezon "L" grease used to grease ground joints were likewise not appreciably affected. An attempt to obtain the spectrum of beryllium borohydride was frustrated by its attack on the rocksalt windows. The spectrum of the fine powder formed on the windows was however recorded and found to give interesting information about its structure. The spectra of lithium and sodium borohydride were obtained by grinding the powders into a fine slurry with liquid paraffin and squeezing this between two rocksalt plates. This procedure had to be carried out immediately on the removal of these substances from the dry box in order to prevent attack by atmospheric moisture.

RESULTS

The spectrum of aluminum borohydride is given in Fig. 1. It shows many features which are clearly analogous to similar ones in diborane.[1] This is because

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[1] W. C. Price, J. Chem. Phys. **16**, 894 (1947): We wish to call attention to a slight error in Fig. 1 in this article. The band at 1860 cm^{-1} has been plotted 50 cm^{-1} too high due to a misreading of the scale.

most of the bands of frequencies greater than 700 cm^{-1} correspond to vibrations in which the motion is mainly that of the boron and the hydrogen atoms. This general similarlity is considerable evidence for the presence of hydrogen bridges (protonated double bonds) corresponding to those whose existence has been established in diborane. The two bands at 2559 and 2493 cm^{-1} clearly correspond to the infra-red active vibration of terminal BH$_2$ groupings (2614 and 2522 cm^{-1}) in diborane. This is evidence against the girdle structure originally suggested by Bauer and co-workers.[2,3] In this model, which can be represented by the formula

$$\left[\begin{array}{c} \text{H} \qquad\;\; \text{H} \\ \diagdown\;\; \diagup \\ \text{H---B---} \\ | \\ \text{H} \end{array}\right]_3 \text{Al,}$$
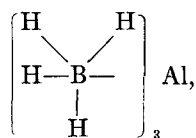
three hydrogen atoms are located between each boron and the aluminum atom, forming a "girdle" round the B—Al bond and there is a single terminal BH which is co-linear with this bond. Such a terminal group would be expected to give rise to only a single band at this frequency, as for example in the spectrum of acetylene. Professor Bauer has kindly informed the author in correspondence that recent calculations involving

quite highly unsymmetrical bridge structures now permit of a satisfactory fit with a bridge model. It should also be mentioned that chemical evidence favors a bridge structure as against a girdle structure for diborane.

The bands at 2031 and 1500 cm^{-1} are clearly analogous to the characteristic BH$_2$B bridge vibrations in diborane (1860 and 1604 cm^{-1}). The shift of one to shorter and the other to longer wave-lengths is to be related to the fact that, as the binding of the boron to the metal becomes more ionic, the higher frequency vibration becomes a stretching vibration of the $(BH_4)^-$ group while the lower one becomes a BH deformation vibration of the same group. This is to be expected from the nature of the vibration assigned to these bridge bands in diborane. The bands at 1114 and 978 cm^{-1} are by analogy associated with in-plane and out-of-plane vibrations of the terminal BH$_2$ group respectively. The band at 604 cm^{-1} is interpreted naturally as a stretching vibration of the AlB$_3$ skeleton.

Table I gives the frequencies and assignments of the fundamental bands and includes the Raman frequencies observed by Young and Rice,[4] with whom close cooperation has been maintained. Their assignments have been adopted here. For the detailed normal coordinate treatment and the nature of the normal modes
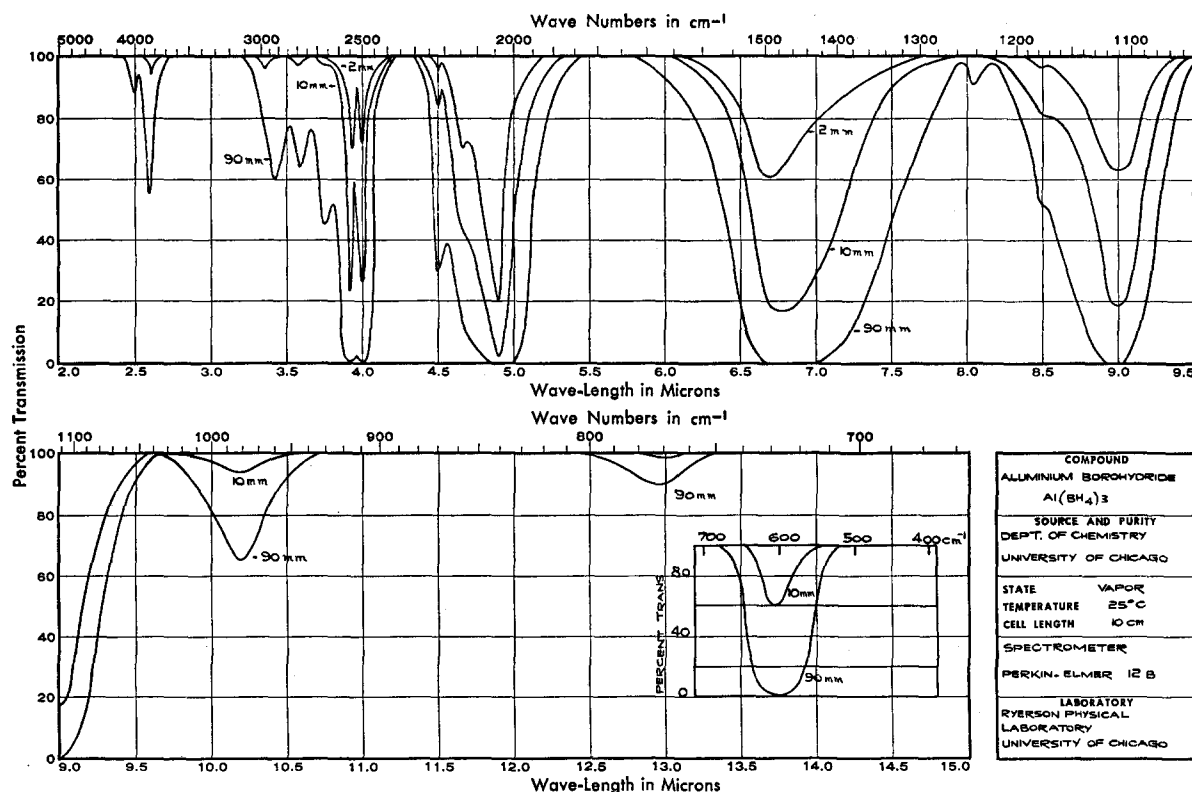

FIG. 1. The infra-red absorption spectrum of aluminum borohydride.

[2] J. Y. Beach and S. H. Bauer, J. Am. Chem. Soc. **62**, 3440 (1940).
[3] G. Silbiger and S. H. Bauer, J. Am. Chem. Soc. **68**, 312 (1946).
[4] T. F. Young and B. Rice, J. Chem. Phys. (in press).

reference should be made to their article. The assignments have been made with respect to a prismatic model of symmetry D_{3h}. This model and the octahedral model (symmetry D_3) have been discussed by Longuet-Higgins.[5] They are illustrated diagrammatically in Figs. 2(a) and 2(b). (To prevent confusion the terminal hydrogens have not been drawn in; but by analogy with diborane each terminal pair would be expected to lie on a line perpendicular to the line joining the pair of bridge hydrogens in the same H_2BH_2Al arm.) The following argument shows that it is difficult to reconcile the most plausible values for bond angles and distances with a regular octahedral model. If the bridge hydrogens are assumed to be equidistant between the boron and the aluminum atom then in a regular octahedral arrangement the angles AlBH and BAlH would have to be 45° and the H—H distance would have to equal the AlB distance. There is no *a priori* reason why this should actually be the case. It is to be expected that the H—H distance will only be slightly larger than its value in diborane (2.13A)[6,†] whereas the AlB distance is 2.19A.[2] These happen to be roughly equal but if, as seems likely, the bridge hydrogens are closer to the boron than to the aluminum, then for the bridge hydrogens to lie at the vertices of a regular octahedron there must be a considerable increase in the HH distance. For example if BAlH = 45°, AlBH = 50° (as in diborane bridge) and AlB = 2.19A, then HH = 2.39A; if AlBH = 55°, then HH = 2.58A. The most plausible value for the AlBH angle is probably in the neighborhood of 50°, the value of the BBH angle in diborane. Using this value for the angle AlBH, the value 2.19A for the AlB distance as determined by electron diffraction and a BAlH angle of 45°, the BH bridge bond length works out at 1.56A as compared with 1.39A in diborane. For a 55° AlBH angle the BH bond length works out as 1.69A. These values for HH and BH are not considered plausible; but in order to maintain AlBH at about 50° and HH at about 2.13A the octahedral bonds would have to be considerably distorted (see later), and this would require considerable energy. The octahedral arrangement of the hydrogen atoms

about the Al atom thus seems to lose much of its attractiveness. On the other hand, Longuet-Higgins[5] has shown that a prismatic arrangment is compatible with a "protonated" double bond structure in which three 120° coplanar "π" bonds radiate from the Al atom. The "s," "p" and "d" atomic Al orbitals can combine linearly to form such bonds.

The bearing of the present work on this problem of the structure of aluminum borohydride may be summarized as follows. The vibrational analysis appears to be in good agreement with a molecular symmetry D_{3h}, i.e., the prismatic structure. The normal coordinate analysis of an unsymmetrical octahedral arrangement has not yet been carried out, but this structure is considered improbable on other grounds. The girdle structure is considered to be eliminated by the general resemblace of the spectrum to that of diborane, in particular the existence of two bands corresponding to terminal BH vibrations. Also, as will be shown later, it is difficult to reconcile the frequencies of the observed BH stretching vibrations with the rather large BH distances predicted by the interpretation of the electron diffraction results in terms of a girdle structure.

DISCUSSION OF INDIVIDUAL BANDS

Terminal BH_2 Vibrations

As with diborane it is convenient to discuss the vibrations involving motion of the terminal BH_2 groups in terms of the normal vibrations of this triatomic group and then to consider how the various group vibrations are coupled together. In diborane the symmetrical valence vibrations of the BH_2 group are not much affected by coupling in-phase (2523 cm) or out-of-phase (2522 cm). The same is true of aluminum borohydride where the corresponding frequencies are 2480 and 2493 cm^{-1}. The antisymmetrical valence vibrations are affected more strongly in diborane, being 2614 for the in-phase and 2591†† for the out-of-phase. Assuming the whole of the splitting in diborane is caused by this coupling, then the uncoupled antisymmetrical valence vibration of this group should have a frequency equal the mean of these $(2614+2591)/2 = 2603$, i.e., 80 cm^{-1} greater than the symmetrical BH_2 valence frequency. In aluminum borohydride ν_{15} (2556) is the only active normal mode involving the antisymmetric BH_2 valence frequency. This resembles fairly closely, though not exactly, the in-phase combination ν_8 (2614) in diborane and as such should be higher than the antisymmetric BH_2 group valence vibration. A reasonable guess can be made for this difference. In diborane ν_8 is higher than the value deduced for the isolated antisymmetric valence vibration of the BH_2 group by 11 cm^{-1} (2614–2603). Since the coupling is probably not as strong in aluminum borohydride, being exerted across two bonds
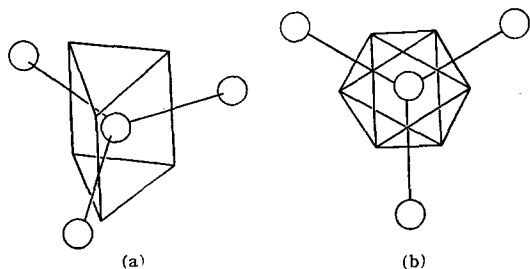
FIG. 2. (a) Prismatic model for aluminum borohydride (symmetry D_{3h})—terminal hydrogens omitted. (b) Octahedral model for aluminum borohydride (symmetry D_3)—terminal hydrogens omitted.

[5] H. C. Longuet-Higgins, J. Chem. Soc. 14, 139 (1946).
[6] S. H. Bauer, Chem. Rev. 31, 43 (1942).
† It will be shown later that it is probably appreciably smaller.

†† We are indebted to Professor K. S. Pitzer for the information that the Raman line previously reported at 2489 cm^{-1} is spurious and that it should be replaced by a line at 2591 cm^{-1}.

instead of one, it might be expected that in this compound the difference would be considerably lower, say *ca.* 3 cm⁻¹. This gives $2556-3=2553$ cm⁻¹ for the antisymmetric BH₂ valence vibration which is thus higher than the symmetrical valence vibration of the group (taken as $(2480+2493)/2=2487$) by 66 cm⁻¹. This compares favorably with the value of 80 cm⁻¹ (2603–2523) obtained for diborane and indicates that the terminal groups in the two compounds are essentially the same except that the valence frequencies of the BH₂ group in aluminum borohydride are *ca.* 40 cm⁻¹ less than they are in diborane, this being probably accompanied by a corresponding increase in BH distance.‡ The deformation vibrations of the terminal BH₂ groups are also consistently reduced in aluminum borohydride in comparison with those in diborane. The symmetrical in-phase vibration in diborane is 1180 cm⁻¹ as compared with 1156 in aluminum borohydride. The corresponding out-of-phase vibrations are 1175 and 1118 respectively. The out-of-phase rocking vibration is hardly changed—974 to 978, i.e., a slight increase in aluminum borohydride.

Bridge Vibrations

A consideration of the data vailable on the infra-red spectra of molecules in general makes it clear that for a molecule such as aluminum borohydride, bands occurring in the region 2100–1400 cm⁻¹ can only be due to the stretching of bonds to hydrogen atoms probably tied into some sort of a ring. It will be shown that as the bridge structure gives place to a more ionic structure

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‡ In the light of the new data on the Raman spectrum of diborane it is worth while comparing the values for the stretching frequencies of the CH₂ group in ethylene with those of the BH₂ group in diborane. The values of the uncoupled group frequencies are taken as the mean of the molecular frequencies corresponding to coupling of the group frequencies in-phase and out-of-phase. They are set out in Table A.

TABLE A. Calculation and comparison of XH₂ valence vibrations in ethylene and diborane (frequencies in cm⁻¹).

Ethylene CH₂ antis. vib.	CH₂ sym. vib.
3105.5 out-of-phase 3272.3 in-phase	2989.5 out-of-phase 3019.3 in-phase
3188.9 mean (uncoupled) ±83.4 due to coupling	3004.4 mean (uncoupled) ±14.9 due to coupling
Difference (antis. −sym.) = 184.5	

Diborane BH₂ antis. vib.	BH₂ sym. vib.
2614 out-of-phase 2591 in-phase	2523 out-of-phase 2522 in-phase
2602.5 mean (uncoupled) ∓11.5 due to coupling	2522.5 mean (uncoupled) ∓0.5
Difference (antis. −sym.) = 80.0	

The two sets of data for ethylene and diborane seem to be reasonably consistent in view of the weaker coupling and valence forces in diborane. However, the coupling terms have opposite signs. The explanation of this is thought to be along the following lines. A compression along the C=C bond arising from the motion of one carbon atom in ethylene is reflected from the other carbon atom as a compression, but in diborane the compression from a boron atom through a BH bond is reflected as a rarefaction because of the lightness of the hydrogen atom. It is thought that this change in phase will account for the change in sign of the coupling term.

TABLE I.† Frequencies and assignments of the fundamental infra-red vibration bands of aluminum borohydride including also the Raman data and assignments of Young and Rice (symmetry D₃ₕ).

Character	A₁'(R)*	A₂''(IR)**	R & E'(IR)	E''(R)	Assignment
B-H sym. stretching	ν₁				R. 2480
B-H sym. stretching (out-of-phase)		ν₁₆			IR. 2493
B-H antisym. stretching			ν₁₅		R. 2553, IR. 2550
Bridge expansion	ν₂				R. 2082
Bridge expansion (out-of-phase)		ν₁₇			IR. 2031
Bridge stretching (⊥)			ν₁₁		IR. 2154
Bridge stretching (‖)		ν₃			R. 1502
Bridge stretching (‖) antisym.			ν₁₈		IR. 1500 (Broad)
BH₂ deformation	ν₄				R. 1156
BH₂ deformation (out-of-phase)			ν₁₉		R. 1122, IR. 1114
BH₂ rocking (in-plane)			ν₂₀		R. 1407 (?)
BH₂ rocking (out-of-plane)		ν₁₃			IR. 978
BH₂ rocking (out-of-plane) (out-of-phase)				ν₂₄	R. 977
Bridge shearing		ν₁₂			
Bridge shearing (antisym.)				ν₂₅	R. 1407 (?)
BH₂ twisting				ν₂₆	R. 600 (?)
Al-B stretching	ν₅				R. 518
Al-B stretching (antisym.)			ν₂₁		R. 600, IR. 603

† R = Raman, IR. = infra-red. Frequencies in cm⁻¹.

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involving (BH₄)⁻ the bands gradually move out of this region. Some go up to higher frequencies and become free stretching vibrations and the others go to lower frequencies and become deformation vibrations of the (BH₄)⁻ ion. This process has clearly started in aluminum borohydride where the bands in the 2050 region correspond to the diborane bands around 1870 cm⁻¹, and the broad band around 1500 cm⁻¹ corresponds to the diborane band at 1600 cm⁻¹. As with diborane these bands are the strongest in the spectrum and this is to be associated with the fact that the bridges are the seat of the electron deficiency and displacements of the atoms in this part of the molecule are liable to produce large local dipoles.‡‡ Aluminum borohydride has of course three times as many bridges per molecule as diborane and one and a half times as many terminal BH₂ groups. However, even allowing for this numerical increase, the intensity of the bridge and BH₂ bands (per group) is in general greater than that in diborane. This probably results from the general increase in the ionic character of the molecule.

It was pointed out in the article on diborane that there is still some doubt about the exact nature of the mode of vibration of the bands in the 1870 cm⁻¹ region of this molecule as the rotational structure did not agree

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‡‡ Electron deficiency in the bridges makes itself apparent in the large values obtained for the bridge BH distances when the electron diffraction data are interpreted in terms of a bridge model.

TABLE II. Table giving the frequencies and assignments of the overtone and combination bands of aluminum borohydride.

Frequency	I	Assignment
3995	w	$\nu_2 + \nu_{17} = 2031 + 2082 = 4113$
3924	m to w	$2 \times \nu_2 = 2 \times 2031 = 4062$
2938	m to w	$\nu_3 + \nu_{18}$ or $2\nu_{18-}$ ca. 3000
2790	w	
2695	w	
2222	w	$\nu_4 + \nu_{19} = 1156 + 1118 = 2274$ Or $2\nu_{19} = 2236$
1246	w	
770	w	
ca. 400	s	Possibly analogous to diborane band at same frequency

with the vibrational assignment (unless a weaker band at 1993 cm^{-1} was taken as ν_{13}). The exact interpretation of the aluminum borohydride bands around 2000 cm^{-1} must therefore wait until this matter is cleared up.

AlB$_3$ Vibrations

There is a broad strong band at 603 cm^{-1} which fits in naturally as a vibration of the AlB$_3$ group. Its strength indicates that there is some ionic character in the AlB bonds as is to be expected.

OVERTONE AND COMBINATION BANDS

Table II gives the frequencies of overtone and combination bands. It is not easy to assign these because of the large number of possibilities. However, the assignments given appear to be the most plausible ones.

ELECTRONIC SPECTRUM

Aluminum borohydride is transparent in the visible and near ultraviolet. An examination of its spectrum in the region 2000–1000A showed diffuse absorption rather similar to that of diborane. The first strong absorption is a broad diffuse band appearing around 1340A at very low pressure equivalent to a thickness of 0.005 cm gas to N.T.P. This is followed by further diffuse absorption of similar strength below 1200A. At higher pressures the absorption spreads to long wavelengths quickly reaching 1500A with a weaker step-out covering the region out to 2000A. The spectrum would be consistent with a first ionization potential of the molecule of about 11 volts but its lack of discrete bands prevents any deductions being made concerning the nature and origin of the electron removed.

THE SPECTRA OF LITHIUM AND SODIUM BOROHYDRIDE

The spectra of these materials obtained as finely ground slurries in liquid paraffin are shown in Fig. 3. The bands of the liquid paraffin used to make the slurries occur mainly in the regions ca. 2950, 1450 and 1365 cm^{-1}. As far as could be judged no bands of the borohydrides were overlapped by the paraffin absorption. The bands corresponding to the BH valence vibrations are quite obviously those occurring around 2300 cm^{-1} (slightly higher for the lithium than the sodium compound). Sodium borohydride is considered to be completely ionic both from its ordinary physical proper-
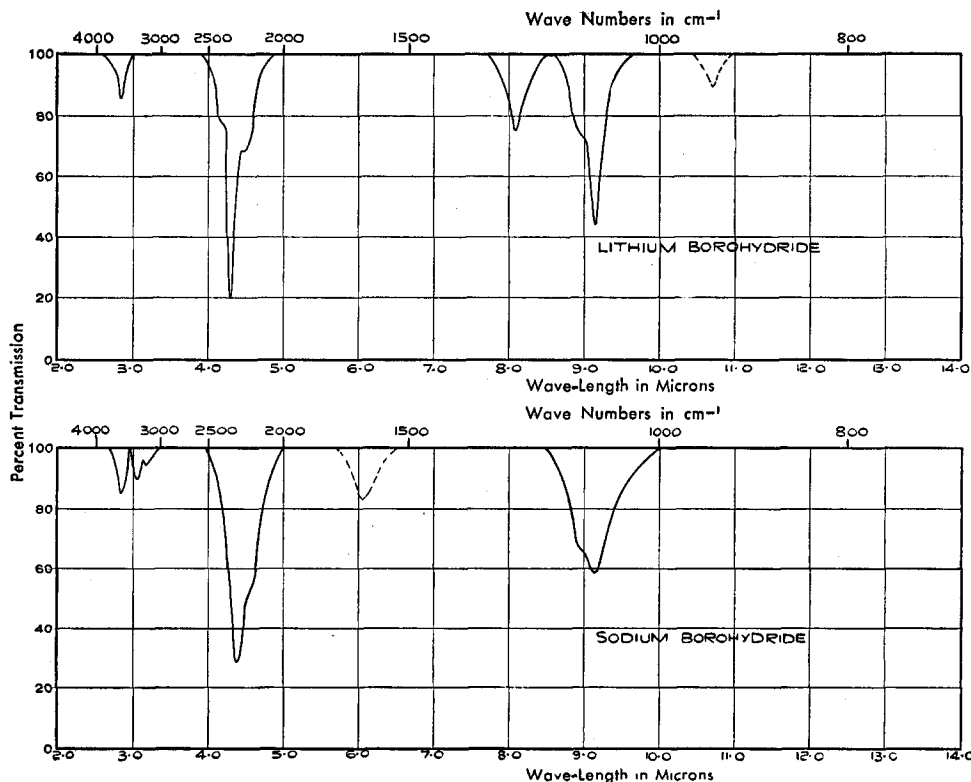

FIG. 3. The infra-red spectra of lithium and sodium borohydride as slurries in liquid paraffin (paraffin bands not shown).
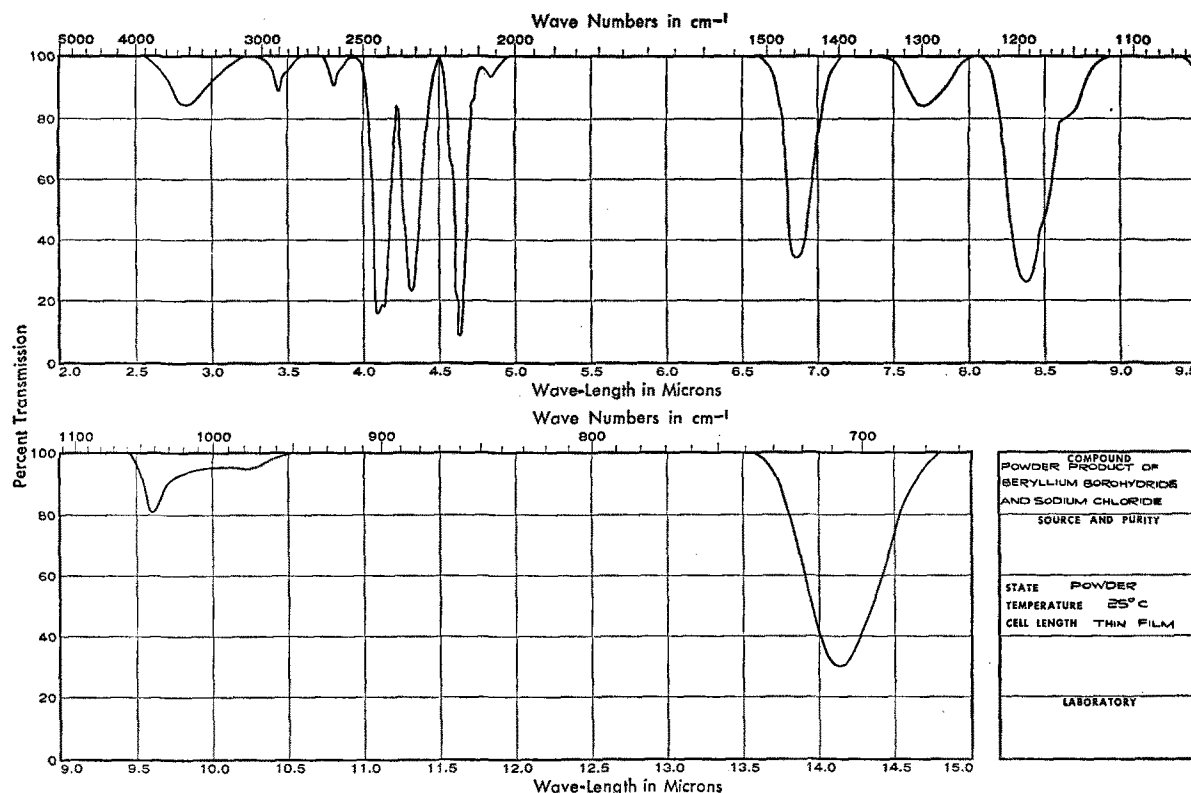
FIG. 4. The infra-red spectrum of a powder product of beryllium borohydride and sodium chloride.

ties and from the x-ray crystal analysis of Soldate.[7] The bands are thus to be associated with the $(BH_4)^-$ ion. Bands at *ca.* 1100 cm^{-1} found for these materials presumably correspond to a deformation vibration of this ion. The binding in lithium borohydride is probably mainly ionic,[7a] but less completely so than that of sodium borohydride in view of the slightly higher BH stretching frequency. It is interesting to note that the spectrum of a slurry of the methyl derivative of lithium borohydride (LiBH$_3$CH$_3$) showed the BH valence frequency considerably reduced—bands being obtained at 2190 and 2130 cm^{-1}. This may result from a large polarizability effect by the methyl group or possibly from a major rearrangement such as might occur if the methyl group took up a position along the LiB axis. The $(BH_4)^-$ group in the ordinary lithium borohydride may only differ from that of a bridge structure by a slight alteration in the angles of the BH bonds. The configuration of the methyl derivative may be one in which the lithium, boron and carbon atoms are colinear and the three BH bonds may be arranged in a trigonal formation around the B—Li bond forming a "girdle" around it.

Both the lithium and sodium borohydride have a strong combination band in the region 3250–3400 cm^{-1}. This appears to be a combination of BH valence and deformation frequencies and is probably analogous to

the corresponding combination band in diborane at slightly higher frequency (3600–3700).

Attempts to obtain the spectra of the LiAlH$_4$ and NaAlH$_4$ have so far been unsuccessful, though some indication that the AlH valence frequency is *ca.* 1700 cm^{-1} has been obtained.

THE SPECTRUM OF A POWDER PRODUCT OF BOROHYDRIDE AND SODIUM CHLORIDE

In an unsuccessful attempt to obtain the spectrum of beryllium borohydride, it was found that this material attacked the sodium chloride windows of the cell, giving a white powder and liberating some diborane. The spectrum of this powder is shown in Fig. 4. It

TABLE III. Table of frequencies of related bands in the metal and other borohydrides.

Substance	Terminal valence BH cm^{-1}		Bridge		Deformation	
			Class (a)	Class (b)	in-plane	out-of-plane
B$_2$H$_6$	2614	2522	1990–1850	1600	1175	974
Be(BH$_4$)$_2$	2630	2515	2165–1985	1530		
Al(BH$_4$)$_3$	2559	2493	2220–2000	1480	1114	978
LiBH$_4$	2320	(2404–2245)	No strong band		1096	—
NaBH$_4$	2270	(2380–2150)	No strong band		1080	
B$_2$H$_2$(CH$_3$)$_4$			2000–1850	1600	—	—
B$_3$N$_3$H$_6$	2535				ca. 1100	920
B$_3$N$_3$H$_3$(CH$_3$)$_3$	2495				1050–1100	900
H$_2$BN(CH$_3$)$_2$	2447 and 2369		No strong band		1156–48	964
H$_3$BN(CH$_3$)$_3$	2384	2281	No strong band		1175	
BH	2366					

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[7] A. M. Soldate, J. Am. Chem. Soc. **69**, 987 (1947).
[7a] P. M. Harris and E. P. Meeholm, J. Am. Chem. Soc., **69**, 1231 (1947).

has interesting features which throw considerable light on the nature of the material. Bands occurring in the 2450 cm^{-1} region (2465 and 2440 cm^{-1}) are clear evidence of terminal BH_2 groups. The strong band at 2180 cm^{-1} and another at 1450 cm^{-1} are the bands of a BH_2Be bridge which is probably slightly ionic. That at 1196 cm^{-1} corresponds to BH_2 deformation. The new band at 708 probably corresponds to a beryllium-chlorine link, as it did not appear when potassium bromide windows were used. (Admission of air to the cell immediately destroyed the material, the reaction being
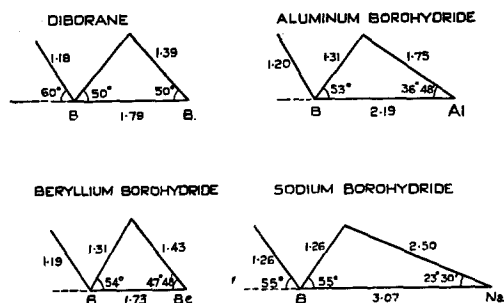

FIG. 5. Structures of metal borohydrides as calculated using electron (or x-ray) diffraction data for bonds between the heavy atoms and assuming certain force constant/bond distance relationships. Diborane data is according to electron diffraction. Terminal BH bonds are shown rotated through 90.

accompanied by the usual green flash.) It is thus clear that the infra-red method can be usefully employed to give information on this peculiar class of compounds which would be very difficult to obtain in any other way.

Frequencies of Related Bands in the Metal and Other Borohydrides

The frequencies of a number of related bands in the metal borohydrides are given in Table III. This shows how the terminal BH_2 frequencies are reduced as the material becomes ionic. The groups of frequencies associated with the hydrogen bridges fall into two classes— (a) a high frequency class occurring at frequencies greater than 1700 cm^{-1} and (b) a low frequency class occurring below this frequency. A correlation of the spectra with the expected ionic character of the molecule indicates that as the bonding to the metal becomes more ionic, the higher bridge frequencies increase and become valence frequencies of the $(BH_4)^-$ ion at *ca.* 2300 cm^{-1}. Those of the lower frequency class are decreased and tend to become deformation frequencies of this ion at *ca.* 1100 cm^{-1}. This is presumably accompanied by a gradual change of the BH bond angles to the tetrahedral value.

The table also contains data on a number of boron-nitrogen hydrides. When these are compared with the corresponding hydrocarbon analogues the interesting point emerges that the BH valence frequency, when it is associated with analogous electronic groups, behaves

in much the same way as that of CH. It is well established for instance that the infra-red bands corresponding to the stretching of an aromatic C—H bond lie in the range from 3110 to 3010 cm^{-1}, those of olefinic CH from 3080 to 2980 cm^{-1} and those of saturated CH from 2980 to 2830 cm^{-1},[8,9] i.e., saturated molecules have lower CH frequencies than olefinic or aromatic ones. Similar behavior occurs for the infra-red bands of the BH valence vibration. For borazole the frequency is 2535 cm^{-1} (for N. trimethyl borazole—2495 cm^{-1}), for H_2B $=N(CH_3)_2$ bands at 2447 and 2369 cm^{-1} were obtained, while for $H_3BN(CH_3)_3$ the frequency of the BH valence band is 2384. It should, however, be mentioned that the polarity differences which occur in these compounds but not in the analogous hydrocarbons, are likely to be at least as important a cause of the frequency differences as the differences in hybridization.

Bond Distances and Angles in the Borohydrides

While data by which all the geometrical parameters of the borohydrides can be calculated directly are not available and, with perhaps the exception of beryllium borohydride, may not be available for some time, it seems worth while inquiring whether indirect methods can give any information about them. There is in fact sufficient direct data known which in combination with semi-empirical relationships between force constant and bond distance, etc., can establish beyond reasonable doubt the values of these parameters to a first degree of approximation. The accuracy of the results obtained is adequate for understanding many points in the structure of these molecules. Clearly the policy to be followed in making such calculations is to use as far as possible data which can be reliably determined directly, such as electron diffraction values for BB, BBe, BAl, and BNa (x-ray) distances, also the spectroscopically determined frequencies and distances of the associated diatomic hydrides. The minimum use should be made of empirical relationships or plausible assumptions.

Consider first diborane. The fact that the geometrical parameters obtained by interpreting the electron diffraction data in terms of a bridge model give values of the small moment of inertia which are in agreement with the rotational structure of the perpendicular bands of this molecule is strong, though not absolute, confirmation of the reliability of the electron diffraction results. The BB distance found can certainly be accepted. A value for the terminal BH distance can be calculated from a force-constant bond-distance relationship. We use the Birge-Mecks relationship[10] $-\omega_e r_e^2 =$ constant in the form $k_e r_e^4 =$ constant in preference to the other

[8] Barnes, Gore, Stafford, and Williams, Analytical Chem. **20**, 402 (1948).

[9] H. W. Thompson, J. Chem. Soc. 328, 1948.

[10] R. T. Birge and R. Mecks, Zeits. f. Physik **32**, 823 (1925).

empirical relationships¶ because it appears to be particularly good for hydrides. Now it has been shown in an earlier paragraph that the terminal BH_2 group in diborane behaves as though it had an antisymmetrical valence "group" vibration of 2602 cm^{-1} and a symmetrical one of 2522 cm^{-1}. Assuming the HBH angle of 120°, this gives a force constant for the BH bond which in a diatomic BH molecule would correspond to a frequency of 2550 cm^{-1}. The possible error in this value does not appear to be more than 10 cm^{-1}. Taking the values $\omega_e = 2366$, and $r_e = 1.2326$ for diatomic BH in its ground state[11] and using the $\omega_e r^2 =$ constant relationship we get 1.19A for the terminal BH distance compared with 1.18A by electron diffraction. The same procedure applied to ethylene gives 1.08A for the CH distance as compared with 1.071A obtained spectroscopically.[12] Thus the electron diffraction value for the BH distance is confirmed. A BH distance of 1.27A as is obtained by the interpretation of the electron diffraction results in terms of an ethane-type structure would correspond to BH valence frequencies of about 2200 cm^{-1}. This is a further argument against this model. It can be shown to a fair approximation that for the bridge model the angle between the BB bond and the bridge BH is $= \nu_{13}/\nu_{17}$ which agrees with a value of *ca.* 50° for the bridge. The valence force constants for the bridge BH bonds has also been calculated approximately and shown to be consistent with BH distances of about 1.39A.* As these calculations cannot be made without neglecting certain factors, it is not worth while reproducing them here.

It has already been pointed out that along the series from B_2H_6 to $LiBH_4$ some of the frequencies characteristic of the bridge increase towards the value of the valence frequencies of the $(BH_4)^-$ ion. This process must clearly be accompanied by a decrease in the bridge BH distances. At the same time there is a decrease in the terminal BH_2 valence frequencies and a corresponding increase in their distances as their values approach that of the ion. The next step is thus to calculate a value for the BH distance in the $(BH_4)^-$ ion from the frequencies reported here for sodium borohydride. The magnitude of this distance turns out to be 1.26A (i.e., roughly $(2336/2280)^{\frac{1}{2}} \times 1.233$); the method gives for the CH distance in methane, 1.085A as against the spectroscopic value 1.0936A.[13]

For the calculation of the bond distances in beryllium and aluminum borohydride, the bridge angles have been assigned the values BeBH = 54° and AlBH = 53°. These are unlikely to be more than a degree or so in error since they must be between 50 and 55°. The boron-metal distances are known from electron diffraction[2,3] and the position of the bridge hydrogens appears to be best fixed by placing them so that, for example, in beryllium borohydride the ratio of the BeH and BH distances is equal to the ratio of the internuclear distances in the corresponding diatomic hydrides. This assumption is supported by the fact that the BH bridge distances then appear to be consistent with the values observed for the BH bridge frequencies. Appreciably different values of distance and angles would lead to unacceptable values of the bridge frequencies. The bond distances in the bridges are slightly less than those which might be expected for single electron bonds from hydrogen to the metals, as judged by data available on the spectra of the diatomic hydrides and their ions. The terminal BH distances in beryllium borohydride have been assigned values on the basis of its infra-red spectrum alone.[14] As no Raman data are available, the values for this molecule must be regarded as least certain. The terminal BH_2 angle for the borohydrides cannot be determined with sufficient precision by, for example, a valence force field treatment of the uncoupled BH_2 groups. Such calculations give angles of about 100°.

The dimensions of the bridge structures in beryllium, aluminum, and sodium borohydrides, as calculated according to the above postulates, are shown in Fig. 5. It is believed that they will form a useful guide to further speculation on the structures of these and similar boron compounds. In the case of aluminum borohydride, they indicate that the octahedral structure is improbable, the BAlH angle expected being only 37° as against that of *ca.* 45° which would be necessary to make an octahedral structure stable.

It is stated by Soldate[7] in his paper on the crystal structure of sodium borohydride that "With the assumption of a covalent boronhydrogen bond distance of 1.16A, a van der Waals' radius of 1.00A for hydrogen, and a crystal radius of 0.95A for sodium, it can be seen that the boron-sodium distance of 3.07A and the boron-boron distance of 4.35A are large enough to cause very little steric hindrance to rotational displacements of the BH_4^- tetrahedra." However, it is clear that with the BH distance of 1.26A calculated here, the amount of steric hindrance to be expected in the crystal is considerably increased. Certainly the infra-red spectrum showed no evidence of rotational structure although the resolution employed was more than adequate for its detection.

¶ For a review of the various force-constant bond-distance relationships see G.B.B.M. Sutherland, Ann. Report Chem. Soc. **33**, 53 (1936); Ann. Report Chem. Soc. **35**, 37 (1938).

[11] G. W. King, J. Chem. Phys. **6**, 378 (1936).

[12] W. S. Galloway and E. F. Barker, J. Chem. Phys. **10**, 88 (1942).

* Valence force constants have also been calculated for the bridge model of diborane by Bell and Longuet-Higgins in their original paper (Proc. Roy. Soc. **183**, 357 (1945)) which showed the compatibility of such a model with the observed spectra. The extension here is that values are found for the bond distances by using the force constant bond distance relationship and the diatomic BH distance, which are in agreement with those obtained from the electron diffraction results.

[13] G. Herzberg, *Infra-red and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 439.

[14] Price, Longuet-Higgins, Young, and Rice, J. Chem. Phys. **17**, 217 (1949).

In conclusion, the author wishes to acknowledge the valuable collaboration he has had with Professor T. F. Young and Dr. B. Rice in the work on aluminum borohydride. He is also greatly indebted to Drs. R. D. Cowan and H. C. Longuet-Higgins for much helpful criticism and for permission to quote unpublished data, to members of Professor H. I. Schlesinger's group for providing the materials, and to Professor R. S. Mulliken for his active interest in the spectra of boron compounds,

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Note added in proof.—It should not be inferred from the comparison of the spectra of *gaseous* beryllium and aluminum borohydride with those of *crystalline* lithium and sodium borohydride that, if the binding in the former were completely ionic, their BH frequencies should approximate those of the latter. The terminal and internal BH frequencies should still fall into two fairly distinct groups in "ionic" beryllium and aluminum borohydrides in the gas phase. These two groups are of course equivalent in sodium borohydride where the $(BH_4)^-$ is surrounded by Na^+ ions.

Internal Motion and Molecular Structure Studies by Electron Diffraction*

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A procedure has been developed for the determination of molecular structure by electron diffraction which yields accurate intensity data and obviates the necessity for visual examination of the diffraction photographs. The theory for computing radial distribution curves has been extended to permit accurate curves to be obtained from scattering data covering only a restricted range of angle. From this method, it is possible to obtain not only equilibrium distances but also the probability distributions for the vibrational motion between pairs of atoms in a molecule. The procedure has been applied to CCl_4 and CO_2 and when comparisons may be made with spectroscopic results, satisfactory agreement is obtained.

THE study of molecular structures using electron diffraction by gases has usually involved the visual examination of the diffraction pattern[1] which consists of small oscillations about a steeply falling background. The positions of the apparent maxima and minima are measured, their relative intensities are estimated visually, and some estimate is made of the shape of those features which appear to be neither maxima nor minima. The observed curve is used as the basis for evaluating the equilibrium distances in the molecule being studied. This is accomplished by calculating a radial distribution curve which is used as a guide for selecting various models to represent the structure of the molecule. From these models intensity curves are computed and compared to the visually observed curve. The model chosen to represent the structure of the molecule depends upon the agreement between the computed and observed curves. Some differences are found in the form of the functions used by various investigators to compute the radial distribution and intensity curves.

The uncertainties in the visual examination of the diffraction patterns and in the mathematical analysis, make it very desirable to establish a quantitative procedure which uses an unambiguous theory and eliminates the visual study of the photographs. A procedure to eliminate this visual study has been developed by the Norwegian school and they have used it to study

the structures of a large number of molecules.[2] Their procedure involves the use of a rotating sector[3] in order to accentuate the oscillating features of the pattern and the photographs are scanned with a microphotometer. The main difference between their procedure and the one to be outlined concerns the method of analyzing the scattering data. By our method accurate values of the equilibrium distances can be expected and, in addition, it is possible to evaluate the magnitude of the vibrational motion between pairs of atoms in a molecule.

THEORY

When free molecules are struck by a beam of fast electrons, part of the scattering of the primary beam arises from the spacings between the atoms in individual molecules and can be represented by the formula

$$I_m(s) = \sum_{i=1}^{n} \sum_{j=1}^{n} c_{ij} A_{ij}. \quad (i \neq j) \qquad (1)$$

The rest of the scattering does not depend upon the molecular structure and forms a steeply falling background upon which the molecular scattering, Eq. (1), is superimposed. The upper limit n in the summation is

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[1] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).

[2] (a) Chr. Finbak, Avhandl. Norske Vid.-Akad. Oslo, I Mat.-Naturv. Kl., No. 7 (1941). (b) Chr. Finbak and O. Hassel, Archiv. f. Mat. o. Naturvid. **B45**, No. 3 (1941). (c) H. Viervoll, Acta Chem. Scand. **1**, 120 (1947). (d) O. Hassel and H. Viervoll, Acta Chem. Scand. **1**, 149 (1947).

[3] (a) C. Finbak, Avhandl. Norske Vid.-Akad. Oslo, Mat.-Naturv. Kl., No. 13 (1937). (b) P. P. Debye, Physik. Zeits. **40**, 66, 404 (1939).