Spectroscopic Properties of Methylberyllium Borohydride

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Abstract: Under the conditions of these experiments the vapor of methylberyllium borohydride consists of a mixture of monomer and dimer. Sufficient data are available for the monomer to conclude that its structure has a linear carbon–beryllium–boron skeleton, with the carbon bound to beryllium *via* a normal σ bond and the boron bound to the beryllium *via* a double hydrogen bridge. The dimer has a linear boron–beryllium–beryllium–boron skeleton. Each boron is bound to the adjacent beryllium atom *via* a double hydrogen bridge and the two beryllium atoms are bound *via* a double methyl bridge. BH_2 terminal groups were found in both monomer and dimer. Nuclear magnetic resonance data confirm the structure of the dimer in solution.

In 1940 Burg and Schlesinger allowed dimethylberyllium to react with diborane to give first a methyl-rich, nonvolatile, mobile liquid, then to form a compound having the stoichiometry CH_3BeBH_4, and finally with excess diborane to yield beryllium borohydride.[1] Spectroscopic studies of methylberyllium borohydride were initiated to assist in the elucidation of the spectra of beryllium borohydride[2] and to define the nature of the compound itself.

Experimental Section

Diborane, $^{n}B_2H_6$ (natural abundance boron), was produced by adding an ether solution of lithium aluminum hydride to boron trifluoride.[3] For diborane-d_6, lithium aluminum deuteride was substituted for lithium aluminum hydride. The resulting diborane was collected and purified on a vacuum line. ^{10}B diborane (96% ^{10}B, 4% ^{11}B) was prepared in a similar manner except that the ^{10}B boron trifluoride etherate was prepared (rather than purchased).[4] Calcium fluoride boron-10 trifluoride complex was heated slowly to 300° in a stream of dry nitrogen and the boron-10 trifluoride–nitrogen mixture was bubbled through ether at −80°, thus forming the boron-10 trifluoride etherate. For the boron-10, diborane-d_6 reaction, 15 g of the calcium fluoride boron-10 trifluoride complex and 3.0 g of lithium aluminum deuteride were used. A yield (based on ^{10}B content) of 76% (940 ml) was obtained. Dimethylberyllium was prepared by the reaction of dimethylmercury with beryllium metal in a sealed tube.[1]

Methylberyllium borohydride was synthesized by placing approximately 0.2 g of dimethylberyllium in a 56-ml reaction vessel. Enough diborane was added (knowing the pressure and volume of the vacuum manifold) to have 0.3 atm of diborane. The mixture was then heated to 95° for 1 hr, at which time the walls of the reaction chamber became "wet" in appearance. The entire contents of the vessel were frozen with liquid N_2, then warmed to −80°. The resulting trimethylboron (shown by gas-phase infrared) and remaining diborane were pumped away. The entire process was repeated five times and no liquid remained within the reaction vessel. The material within the tube was a white volatile material having the properties of methylberyllium borohydride (CH_3BeBH_4) as described by Burg and Schlesinger.[1] No elemental analysis was obtained, but the nmr spectrum showed a methyl:borohydride ratio of 1:1. Methylberyllium borohydride is most easily purified by passing it *slowly*, with continuous pumping, through a −45° trap (chlorobenzene slush) and trapping it at −80°. It was found to slowly decompose at room temperature and was stored at −80°.

Lithium aluminum hydride and deuteride were purchased from Alpha Inorganics and Dia Prep Inc., respectively, and used without further purification. Boron trifluoride etherate was purchased from Eastman Organic Chemicals and vapor transferred off calcium hydride. $CaF_2 \cdot {}^{10}BF_3$ was obtained from Oak Ridge (Union Carbide Corp.) and dried *in vacuo* at 110°. Beryllium metal and dimethylmercury were obtained from Alpha Inorganics.

Molecular weights were obtained using a manually stirred freezing point depression apparatus equipped with a 0–6° Brooklyn thermometer (1/100°). The apparatus was calibrated with dry benzene and a compound of known molecular weight.

The gas infrared cell was constructed from a 10-cm length of thick-walled Pyrex tubing, and windows were attached in the manner previously described.[5] For example, windows were attached for room-temperature work, by applying Apiezon W-100 wax to the hot ground surfaces of the cell body. The tube was allowed to cool and the windows, polyethylene-coated KBr or BaF_2, were positioned on the ground surfaces. The windows were held in place with a spring-loaded press and the entire apparatus was slowly heated to 95° for 30 min. Upon cooling, the press was removed and the wax seal inspected by looking through the windows.

The KBr windows were conveniently coated with a thin film of polyethylene by affixing with Fisher Sealit the 2-mil polyethylene film onto a washer-shaped piece of cardboard whose inside hole was about 1 cm larger than the diameter of the window to be covered. This polyethylene-covered washer was then placed on the KBr plate and the entire assembly heated in a vacuum oven to 135° for 30 min.

All infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer.

Magnetic resonance spectra of degassed, sealed samples were recorded on a Varian Associates HA-100 nuclear magnetic resonance spectrometer. Proton chemical shifts were recorded relative to the solvent signal and converted to τ units.

All operations were carried out in a vacuum line or in an inert atmosphere enclosure, owing to the pyrophoric nature of these compounds.

Results and Discussion

Properties in Solution. A molecular weight determination (freezing point depression) shows that methylberyllium borohydride is dimeric in benzene. A 0.0611-g sample of methylberyllium borohydride (boron-10) dissolved in 21.5395 g of benzene lowers the freezing point by 0.190 ± 0.013°. By using the freezing point depression constant for benzene, a molecular weight of 76.4 ± 5 g/mol is calculated for methylberyllium borohydride. A dilution study confirmed that the benzene solution was unsaturated and the results are valid. The theoretical molecular weight for dimeric methylberyllium borohydride (boron-10) is 76.0 g/mol.

The proton magnetic resonance spectrum of methylberyllium borohydride in 20% benzene–80% toluene-d_8 consists of a singlet and a quartet.

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(1) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **62**, 3425 (1940).

(2) T. H. Cook and G. L. Morgan, *ibid.*, **92**, 6493 (1970).

(3) I. Shapiro, H. G. Weiss, M. Schmich, S. S. Kolnik, and G. B. L. Smith, *ibid.*, **74**, 901 (1952).

(4) F. J. Norton, *ibid.*, **71**, 3488 (1949).

(5) R. A. Kovar, Ph.D. Thesis, University of Wyoming, 1969.

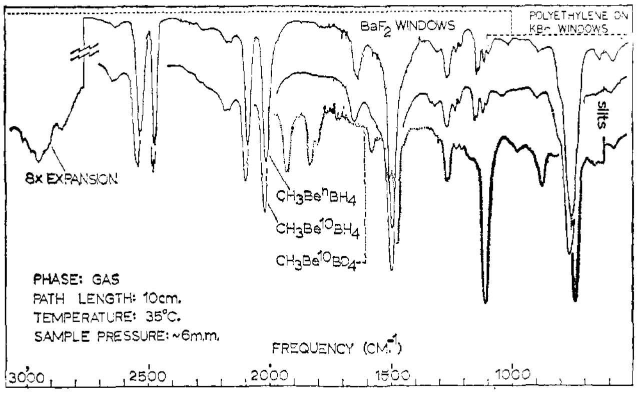

Figure 1. Infrared spectra of methylberyllium borohydride.

The experimentally measured areas of the methyl hydrogens (sharp singlet at τ 10.11) and borohydride hydrogens (four equally spaced broad peaks of equal intensity centered at τ 9.20) are in a ratio of 0.725/1.00, respectively. Within experimental error this ratio agrees well with the theoretical ratio of 0.750/1.00 (methyl hydrogens to borohydride hydrogens) for the empirical formula CH_3BeBH_4.

The four equally intense, equally spaced broad peaks centered at τ 9.20 represent equivalent, rapidly exchanging bridge and terminal borohydride hydrogens, which are split by ^{11}B (I = $^3/_2$). Because the chemical shift of τ 9.20 and the $J_{^{11}B-H}$ of 86.0 Hz of the borohydride hydrogens in methylberyllium borohydride are similar to the corresponding τ 9.31 and 86.5 Hz values for the hydrogens in beryllium borohydride, the borohydride hydrogens of the two compounds are in a similar chemical environment.

The sharp singlet at τ 10.11 results from the nonsplit methyl hydrogens of methylberyllium borohydride. This τ 10.11 chemical shift value indicates that the methyl groups are in a bridging position between beryllium atoms as it is close to the τ 10.31–10.41 values, which have been assigned to methyl bridges between beryllium atoms.[6] Terminal methyl groups attached to beryllium have a chemical shift range of about τ 10.7–11.5[6] and terminal methyl groups attached to boron are expected to have a chemical shift value of about τ 8.5–9.0.[7]

As there was a slight temperature dependence of the methyl hydrogen chemical shift in this mixed solvent and in benzene (of −0.2 Hz/°C) the spectrum was recorded in a "noninteracting"[8] solvent, cyclopentane. The chemical shifts in cyclopentane solution of τ 9.32 for borohydride hydrogens and τ 9.59 for methyl hydrogens likely represent the "true" hydrogen environments in methylberyllium borohydride. The peak at τ 9.59 has no temperature dependence and represents the lowest field resonance of any methylberyllium compound studied to date.

The solution studies therefore indicate that methylberyllium borohydride is dimeric and most likely possesses methyl bridges.

Gas-Phase Infrared Spectral Studies. Since both methylberyllium borohydride and beryllium borohydride[2] react with KBr and silicone materials (as well as with less "inert" substances) special cells had to be constructed (see Experimental Section).

The unsaturated gas-phase infrared spectra of the three isotopically different methylberyllium borohydride

Table I. Infrared Assignments of Methylberyllium Borohydride by Analogy

$CH_3Be^nBH_4$, cm^{-1}	$Be(CH_3)_2$,[a] cm^{-1}	$Al(BH_4)_3$,[b] cm^{-1}	Assignment
2170		2154	MH_2B br exp
1223	1225		CH_3, sym def (term)
1108	1081		Be–C asym str
$(CH_3Be^nBH_4)_2$	$(Be(CH_3)_2)_x$[c]		
3018 (w)			Methane
2947 (m)	2912 (s)		C–H asym str (br)
2856 (w)	2885 (m)		C–H sym str
2532 (s)		2559 (s)	B–H asym str
2469 (s)		2493 (s)	B–H sym str
2087 (s)		2154 (s)[d]	MH_2B br exp
2010 (s)		2031 (s)[d]	MH_2B asym br str
1494 (vs)		1500 (vs)	MH_2B sym br str
1315 (w)			Methane
1265 (m)	1243 (vs) 1255 (vs)		CH_3 sym def (br)
1138 (m)		1114 (s)	BH_2 def
1020 (w)		603 (w)	M–B asym str
898 (w)		978 (m)	BH_2 rock
754 (vs)	835 (vs)		CH_3 rock (br)
587 (w)	565 (m) 534 (m)		BeC_2Be asym br str

[a] Values from R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, **8**, 1099 (1969). [b] Values from W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949). [c] Values from J. Goubeau and K. Walter, *Z. Anorg. Allg. Chem.*, **322**, 58 (1963). [d] This assignment is the reverse of that of ref *b*. All data for gaseous compounds except $(Be(CH_3)_2)_x$.

Table II. Infrared Assignments of Methylberyllium Borohydride Using Deuterium and Boron-10 Shifts

$CH_3Be^nBH_4$, cm^{-1}	$CH_3Be^{10}BH_4$, cm^{-1}	$CH_3Be^{10}BD_4$, cm^{-1}	Assignment
2170 (w)	2172 (w)	1642 (w)	BeH_2B br exp
1223 (m)	1224 (m)	1225 (m)	CH_3 sym def (term)
1108 (m)	1108 (m)	Obscured	Be–C asym str
$(CH_3Be^nBH_4)_2$	$(CH_3Be^{10}BH_4)_2$	$(CH_3Be^{10}BD_4)_2$	
3948 (w)	3959 (w)		
3018 (w)	3018 (w)	3018 (w)	Methane
2947 (m)	2947 (m)	2947 (m)	C–H asym str
2856 (w)	2858 (w)	2855 (w)	C–H sym str
2629 (w)	2641 (w)		
		2515 (w)	
		2054 (w)	
2532 (s)	2543 (s)	1926 (s)	BH asym str
2469 (s)	2476 (s)	1831 (s)	BH sym str
		1803 (m)	
2087 (s)	2095 (s)	1582 (s)	BeH_2B br exp
		1508 (m)	
2010 (s)	2018 (s)	1478 (s)	BeH_2B asym str
1768 (w)	1782 (w)		
1637 (m)	1648 (m)	Obscured	
1494 (vs)	1498 (vs)	1111 (vs)	BeH_2B sym str
1315 (w)	1315 (w)	1315 (w)	Methane
1265 (m)	1265 (m)	1265 (m)	CH_3 sym def (br)
1138 (m)	1146 (m)	880 (m)	BH_2 def
1020 (w)	1035 (w)	997 (w)	Be–B asym str
898 (w)	898 (w)	667 (w)	BH_2 def
810 (sh)	810 (sh)	823 (w)	
754 (vs)	763 (vs)	742 (vs)	CH_3 rock (br)
587 (w)	593 (w)	584 (w)	BeC_2Be asym str

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(6) R. A. Kovar and G. L. Morgan, *J. Amer. Chem. Soc.*, **91**, 7269 (1969).
(7) H. H. Lindner and T. Onak, *ibid.*, 88, 1890 (1966).
(8) T. L. Brown and K. Stark, *J. Phys. Chem.*, **69**, 2679 (1965).

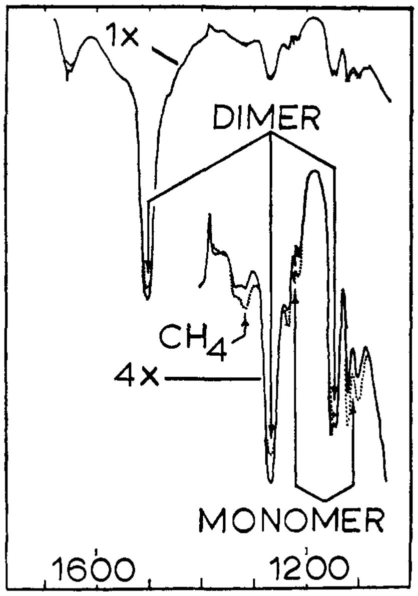

Figure 2. Infrared peak height changes in methylberyllium borohydride showing the presence of both monomers and dimers [(—) initial and (· · ·) 30 min later; after 1 hr all bands except that at 1315 cm^{-1} decrease].

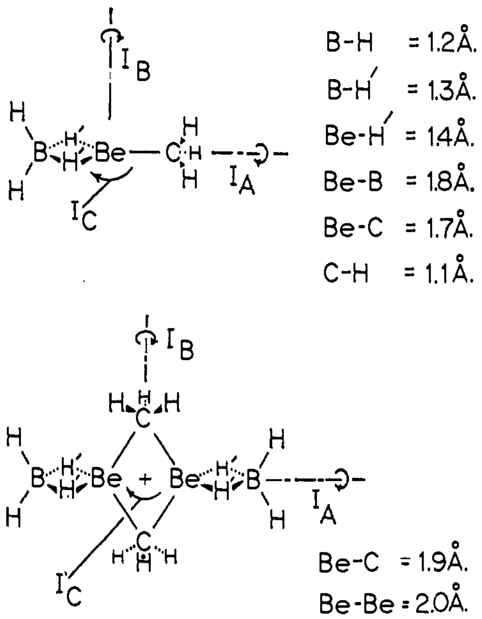

Figure 3. Proposed structures of monomeric and dimeric methylberyllium borohydride species.

compounds ($CH_3Be^nBH_4$, $CH_3Be^{10}BH_4$, and $CH_3Be^{10}BD_4$) are presented in Figure 1, and individual band assignments appear in Tables I and II. The most striking feature of the spectra is the sharpness of most of the bands. The width of these bands is determined by the rotational energy changes which occur during a vibration. Because the energy separations of rotational transitions are inversely related to the moment of inertia ($E' - E'' = \hbar^2/I[J'(J' + 1) - J''(J'' + 1)]$), a molecule with only small moments of inertia displays large rotational spacings and consequently a large P–R maxima separation, whereas a molecule with one (or more) large moment(s) of inertia displays a small rotational P–R maxima separation. In other words, the separation of the P and R rotational maxima is determined primarily by the largest moment of inertia (I_C) of the molecule and the greater the value of I_C, the more closely spaced are the P–R rotational maxima.[9]

Because the bands at 2170, 1223, and 1108 cm^{-1} are about double the width of the sharp bands, a study was undertaken to determine if methylberyllium borohydride exists in *two* forms in the gas phase. A limited amount of methylberyllium borohydride was allowed to expand into an evacuated gas-phase infrared cell and the peak height changes as a function of time were spectrally recorded as shown in Figure 2. The broad peak at 1108 cm^{-1} initially increases and then very slowly decreases, whereas the sharp peak at 1498 cm^{-1} initially decreases rapidly and then slowly decreases.

In a separate experiment, at very low sample pressure, the 1223- and 1108-cm^{-1} peaks are present, while the sharp 1265-cm^{-1} peak was entirely absent. From the rotational PR envelope discussion and from the experiments, one may reason that the broad bands at 2170, 1223, and 1108 cm^{-1} arise from a molecular form of methylberyllium borohydride (monomer), which has a small I_C value, whereas the sharp peaks arise from a different molecular form (dimer), which has at least one large moment of inertia (I_C).

Figure 3 presents the chemically most likely structures for monomeric and dimeric methylberyllium borohydride. The proposed monomeric structure of methylberyllium borohydride is analogous to the published structure of monomeric dimethylberyllium,[10,11] and the double methyl bridge of the proposed dimeric methylberyllium borohydride structure is analogous to double methyl bridge of hexamethyldialuminum.[12]

Bond distances for the $BeBH_4$ group were assumed to be the same as our previous estimates.[13] Beryllium–carbon terminal[11] and bridged[14] bond distances have been reported as well as the bridging Be–C–Be angle of 66° (70° is used in the model).

In order to test the validity of the proposed models a comparison is made between calculated and experimental P–R rotational maxima separations. The calculation is made by the method of Gerhard and Dennison[9] using the equation: $\Delta\nu = S[(kT/I_C)^{1/2}/\pi]$. Parameters of the equation are (a) $\Delta\nu$ = P–R maxima separation in cm^{-1}; (b) S = a function of the moments of inertia (S is near 1 for prolate tops and near 1.5 for oblate tops); (c) k = Boltzmann's constant; (d) T = absolute temperature.

Table III summarizes these calculations and compares calculated and experimental rotational P–R maxima separations for four species of interest. (β is a function of the moments of inertia and is used to calculate S.[9]) The calculated and experimental results are in good agreement and support the proposed structures.

In order to treat methylberyllium borohydride as a symmetric top molecule, the approximation that I_B =

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[9] S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, 43, 197 (1933).

[10] R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, 8, 1099 (1969).

[11] A. Almenningen, A. Haaland, and G. L. Morgan, *Acta. Chem. Scand.*, 23, 2921 (1969).

[12] A. P. Gray, *Can. J. Chem.*, 41, 1511 (1963).

[13] T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, 91, 774 (1969).

[14] A. Snow and R. Rundle, *Acta Crystallogr.*, 4, 348 (1951).

Table III. Calculated and Experimental P–R Maxima Separations for Dimethylberyllium and Methylberyllium Borohydride Species

	From models							P–R maxima separation ($\Delta\nu$), cm^{-1}	
Compound	I_A, 10^{-40} g cm^2	I_B, 10^{-40} g cm^2	I_C, 10^{-40} g cm^2	$I_{B,C,av}$, 10^{-40} g cm^2	β	S	ν_0, cm^{-1}	Calcd	Exptl
CH_3BeCH_3	9.96	158	158	158	14.9	1.06	1225	22.4 ± 0.5	20.7 ± 1
$CH_3Be^{10}BH_4$	12.0	157	161	159	12.2	1.07	1224	18.5 ± 0.5	19.27 ± 0.5
$(CH_3Be^{10}BH_4)_2$	158	443	579	511	2.23	1.234	2469	11.93 ± 0.05	11.92 ± 0.03
$(CH_3Be^{11}BH_4)_2$	158	471	607	539	2.41	1.226	2476	11.54 ± 0.05	11.58 ± 0.03

I_c had to be used. Hollas[15] has shown that a molecule with a moderate degree of asymmetry will behave more like a symmetric top molecule if it has large moments of inertia. Because methylberyllium borohydride dimer has large moments of inertia and because of the symmetric appearance of the 2469-cm^{-1} band, the assumption that $I_B = I_C$ is justified.

Individual infrared absorption band assignments for methylberyllium borohydride monomer and dimer are now considered. Three criteria used for the assignments are (a) comparison of band positions of compounds which have similar structural groups, (b) comparison of observed rotational contours and theoretical rotational contours which are predicted on the basis of symmetry, and (c) correlation of deuterium (deuteration of the borohydride group *only*) and boron-10 isotopic shifts. Table I presents band assignments by analogy with known compounds and Table II presents deuterium and boron-10 shift data.

In this work only three infrared absorption bands for methylberyllium borohydride monomer could be observed, because the nearly coincident strong dimer bands obscured the remaining monomer bands. The three observed bands, which arise from monomer, are at 2170 cm^{-1} (PR rotational contour), 1223 cm^{-1} (PQR rotational contour), and 1108 cm^{-1} (PR rotational contour).

The 2170-cm^{-1} band is assigned to the BeH_2B bridge expansion mode because of the rotational contour of the band. The position of this band is clearly indicative of either the asymmetric BeH_2B bridge stretch or the BeH_2B bridge expansion mode. The assignments of 2154 cm^{-1} for the asymmetric AlH_2B bridge stretch and 2031 cm^{-1} for the AlH_2B bridge expansion mode cannot be used as a guide, because Price[16] admitted that an unambiguous assignment could not be made. In diborane, because the bridge hydrogens are in a plane perpendicular to the plane containing the terminal hydrogens, the asymmetric bridge stretch (1882 cm^{-1}) shows a C-type contour (strong central Q branch), whereas the bridge expansion mode (1860 cm^{-1}) shows a B-type contour (a P–R maximum and no central Q branch).[17] Because the bridge hydrogens in methylberyllium borohydride monomer likely lie in a plane perpendicular to the plane containing the terminal hydrogens, identical symmetry rules will apply to methylberyllium borohydride monomer and diborane. Thus, because the observed band at 2170 cm^{-1} in methylberyllium borohydride monomer exhibits a P–R rotational contour (type B contours), the assignment of bridge expansion for this band is made.

Reliable deuterium shift data could not be obtained because of the strong absorptions in the 1500–1600-cm^{-1} region in the spectrum of the deuterated compound. The boron-10 shift of +2 cm^{-1} of the 2170-cm^{-1} band is consistent with the assignment of a bridging vibration in which the hydrogens are expected to have large movements and the boron is expected to have small movement. The two hydrogens comprise only about $^1/_{10}$th of the mass of the BeH_2B group and the Be movement is not being accounted for in the ^{10}B shift.

Because the 1223-cm^{-1} band of methylberyllium borohydride monomer has an almost identical position and shape to the symmetric methyl deformation (1225 cm^{-1}) of monomeric dimethylberyllium, the 1223-cm^{-1} band is clearly the symmetric methyl deformation.[10] The P–R maxima separation of this symmetric mode is 19.27 cm^{-1} and is close to the observed 20.7-cm^{-1} P–R maxima separation of dimethylberyllium. The Q branch intensity relative to the combined PQR intensity of this symmetric mode is small and consistent with a linear "metal" skeleton for both dimethylberyllium and methylberyllium borohydride monomer.[9,10] In other words, the condition of a linear polyatomic structure (all atoms along a line) is being approached and the Q branch intensity of this symmetric mode is approaching zero.

The observed deuterium and boron-10 shifts (deuteration only of the borohydride hydrogens) are entirely consistent with the assignment of symmetric methyl deformation for the 1223-cm^{-1} band. The (ν_H/ν_D) ratio and boron-10 shifts of 0.99 and +1 cm^{-1}, respectively, show that this band arises from a vibration in the molecule which is remote from the deuterated borohydride group and the borons. Only a vibration involving the methyl group, which was not deuterated, would show such low isotopic shifts.

Because the 1108-cm^{-1} band of methylberyllium borohydride monomer has a similar position and very similar shape to the beryllium–carbon stretch of monomeric dimethylberyllium (1081 cm^{-1}),[10] the 1108-cm^{-1} band is assigned to the beryllium–carbon terminal stretch. The P–R rotational contour of this parallel band also closely resembles the P–R contour of the asymmetric Hg–C stretch of dimethylmercury (at 550 cm^{-1} due to the greater mass of the mercury).[18] This P–R contour indicates that these molecules closely approximate a linear polyatomic molecule.

Because the beryllium–carbon asymmetric stretch in methylberyllium borohydride monomer occurs at higher energy (1108 cm^{-1}) than the corresponding vibration in dimethylberyllium (1081 cm^{-1}) one might conclude that the beryllium–carbon bond is stronger

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(15) J. M. Hollas, *Spectrochim. Acta*, **22**, 81 (1966).
(16) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).
(17) R. C. Lord and E. Nielsen, *ibid.*, **19**, 1 (1951).
(18) H. S. Gutowsky, *ibid.*, **17**, 128 (1949).

in the monomeric methylberyllium borohydride than in dimethylberyllium. Observed band positions may not accurately represent bond strengths because they may be influenced by vibronic interactions, resonance effects, and coupling.[19] The relative coupling of the borohydride and methyl groups are not easily predicted because of the different bonding systems, and thus a direct comparison of band positions in these compounds is not made at this time.

The boron-10 shift of 0 cm^{-1} is consistent with the assignment of 1108 cm^{-1} for the beryllium–carbon asymmetric stretch, because this mode involves atoms which are relatively remote from the boron. The vibration is obscured in the methylberyllium borodeuteride monomer spectrum because of the intense band at 1111 cm^{-1} which is a bridging mode of the dimeric species.

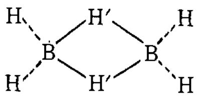
Individual infrared absorption assignments for methylberyllium borohydride dimer are now considered. In order to simplify the discussion the modes due to the methyl hydrogens are considered separately. In this way the remainder of the molecule has D_{2h} symmetry (Figure 3). The carbon–hydrogen modes at 2947, 2856, and 1265 cm^{-1} correspond to the 2912-, 2885-, and (1255- and 1243-) cm^{-1} bands of solid dimethylberyllium[20] and are assigned to the carbon–hydrogen asymmetric stretch, the carbon–hydrogen symmetric stretch, and the bridging symmetric methyl deformation, respectively. These three bands (2947, 2856, and 1265 cm^{-1}) show, within experimental measurement, no shift upon deuteration of the borohydride group and no boron-10 shift. Because these bands do not shift, the modes arise from vibrations of atoms which are remote from the borons and the borohydride hydrogens. These shift data are therefore consistent with the assignment of carbon–hydrogen vibrations.

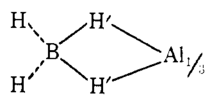
The BH_2 terminal group frequencies of methylberyllium borohydride dimer are directly compared with the BH_2 group frequencies of aluminum borohydride. Thus the 2532- (asymmetric B–H stretch), 2469- (symmetric B–H stretch), 1138- (in-plane deformation), and 898-cm^{-1} (out-of-plane deformation) bands are analogous to the 2559-, 2493-, 1114-, and 978-cm^{-1} bands of aluminum borohydride.[4] The analogous bands in diborane occur at 2625, 2558, 1178, and 981 cm^{-1}, respectively.[21] The presence of these bands in methylberyllium borohydride dimer clearly demonstrates the presence of BH_2 terminal groups. The BH_2 terminal group always exhibits two (asymmetric and symmetric) stretches, whereas the B–H terminal group exhibits only a single (asymmetric) B–H stretch.[22] All boron hydrides containing the BH_2 terminal group show deformation modes in the ranges 1205–1140 and 975–945 cm^{-1}, whereas the B–H terminal group shows a deformation mode in the 890–910-cm^{-1} region.[22] The BH_2 deformation ranges must be extended for metal borohydrides, because aluminum borohydride, which is known to contain a BH_2 terminal group, has a BH_2 deformation band at 1114 cm^{-1}. The 1138- and 898-cm^{-1} bands of methylberyllium borohydride are at slightly lower frequencies than the proposed range of BH_2 terminal deformations in the boron hydrides because of the increased ionic character of the borohydride group as compared with the boron hydrides.[16]

The rotational contours of the 2532- (P–R) and 2469-cm^{-1} (PQR) bands correspond to analogous contours of the 2625- (P–R) and 2558-cm^{-1} (PQR) bands of diborane,[21] and further support the presence of BH_2 terminal groups.

These four bands, which are characteristic of BH_2 terminal groups, exhibit a deuterium shift ratio of 1.29–1.35 and show a boron-10 shift range of 0–11 cm^{-1}. These ranges are characteristic of large hydrogen movement and small-to-moderate boron movement during the vibration. These observed isotopic shifts clearly demonstrate that these bands originate at the isotopically substituted borohydride site.

The BeH_2B bridging group frequencies are correlated with the AlH_2B bridging group frequencies. From the infrared spectrum of aluminum borohydride, Price was able to show the presence of the AlH_2B bridging group,[16] because this group exhibits absorption bands which are analogous to specific absorptions of the BH_2B group of diborane. He recognized that the BH_2B bridge of diborane is symmetric because the electronegativities of the two borons are equal and all B–H′ (bridge) distances are equal. In the AlH_2B bridge, because the electronegativity of aluminum is smaller than that of boron, the Al–H′ distance is longer (than a "normal" Al–H bridge bond) and the B–H′ distance correspondingly shorter than the B–H′ distances of diborane. Diagramatically the distances are represented (dashed line is out of the plane)





Because the B–H′ distance is shorter in aluminum borohydride than in diborane the borons are more "satisfied" and allow their terminal hydrogens to be at a greater distance. The overall effect is to increase the ionic character of the borohydride group. In other words, in aluminum borohydride the borohydride group is tending toward the borohydride *ion*. In the words of Price, "The bands at 2031 cm^{-1} and 1500 cm^{-1} (in aluminum borohydride) are clearly analogous to the characteristic BH_2B bridge vibrations in diborane (1860 cm^{-1} and 1604 cm^{-1}). The shift of one to shorter and the other to longer wavelengths 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."[16]

Thus as the binding of the metal to the boron becomes more ionic (resulting from an increase in the in the electronegativity *difference* between the metal and boron) a borohydride compound is expected to contain a borohydride group which tends toward a discrete borohydride ion and all BH vibrations tend to degenerate into vibrations of a borohydride *ion*. The terminal B–H stretch and B–H′ asymmetric bridge stretch shift toward the single B–H stretch (2300 cm^{-1}) of the discrete borohydride ion, while the terminal

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B–H deformations and B–H′ symmetric stretch shift toward the single deformation (1090 cm^{-1}) of the borohydride ion.[16]

The very strong 1498-cm^{-1} band of methylberyllium borohydride dimer is clearly analogous to the very strong 1500-cm^{-1} band of aluminum borohydride and is definitely assigned to the BeH_2B symmetric stretch. The 2087- and 2010-cm^{-1} bands of methylberyllium borohydride dimer correspond to the 2154 and 2031-cm^{-1} bands of aluminum borohydride. Price's original assignment has been reversed because the rotational contour of the 2170-cm^{-1} band is of B type, which is characteristic of the bridge expanison mode of methylberyllium borohydride *monomer* (*vide supra*). The absorption at higher energy, as shown for beryllium borohydride,[2] shows B-type contours (P–R maxima), and the assignment of BeH_2B bridge expansion to this frequency appears correct (2087-cm^{-1} band). The remaining band at 2010 cm^{-1} is assigned to the asymmetric BeH_2B bridge stretch. This band is predicted to exhibit C-type (strong central Q branch) contours and again in beryllium borohydride this assignment is indicated.[2] Unfortunately, these bands do not show rotational contours in the spectrum of methylberyllium borohydride dimer. These three bands exhibit deuterium shift ratios of 1.32–1.36 and a boron-10 shift range of 4–8 cm^{-1}, which indicate large hydrogen and small boron movement in the BeH_2B group. Coupling of the hydrogen and boron motions are expected to be small because the mass of the hydrogens is only about $^1/_{10}$th the mass of the BeH_2B group.

The 1020-cm^{-1} band of methylberyllium borohydride dimer is assigned to the beryllium–boron asymmetric stretch. The aluminum–boron asymmetic stretch in aluminum borohydride is observed at 600 cm^{-1},[16] and on the basis of the much smaller mass of beryllium the beryllium–boron asymmetric stretch should occur at a significantly higher frequency than 600 cm^{-1}. Because the mass of beryllium is comparable to that of the borohydride group and small when compared with that of aluminum, a reduced mass calculation cannot be used to predict the position of the Be–B asymmetric stretch.

The 1020-cm^{-1} band can be assigned to the beryllium–boron asymmetric stretch on the basis of the observed boron-10 shift of +15 cm^{-1} and the observed deuterium shift ratio of 1.05. A reduced mass calculation in which the beryllium is one mass and the borohydride group, as a unit, is the second mass, leads to the prediction of a boron-10 shift of +12 cm^{-1} and a deuterium shift ratio of 1.04. The assignment is made primarily on the basis of the shift data.

In methylberyllium borohydride dimer the very strong band at 754 cm^{-1} and the 587-cm^{-1} band correspond to the very strong band at 835 and the 534–565-cm^{-1} bands of *solid* dimethylberyllium and are thus assigned to the perpendicular methyl *bridge* rocking mode and the BeC_2Be asymmetric bridge stretch, respectively.[20] Hoffmann has assigned the very strong 700-cm^{-1} band to the perpendicular methyl *bridge* rocking mode of hexamethyldialuminum,[23] whereas Gray has assigned the 572-cm^{-1} band to the same mode.[12]

An error in the assignments of the 798- and 585-cm^{-1} bands of dimethylberyllium *dimer* has likely been made,[10] because the assignments are based on the Gray assignment[12] and are made with no consideration of solid dimethylberyllium bands.[20] These bands were assigned to the *terminal* methyl rocking mode (798 cm^{-1}) and the *bridge* methyl rocking mode (585 cm^{-1}) (of the dimer).[10] It is far more likely that the 798-cm^{-1} band is due to the *bridge* methyl rocking mode and that the *terminal* methyl rocking mode of the dimeric dimethylberyllium is situated at essentially the same frequency as the *terminal* methyl rocking mode of the monomeric dimethylberyllium at 727 cm^{-1}.[10]

The 585-cm^{-1} band of dimeric dimethylberyllium vapor is very likely the BeC_2Be asymmetric bridge stretch which occurs at 587 and 534–565 cm^{-1} in methylberyllium borohydride dimer and solid dimethylberyllium, respectively.[20]

Additional support that the 754- and 587-cm^{-1} bands arise from a portion of the molecule which is moderately distant from the borohydride group is apparent from the low deuterium shift ratio of 1.01 and the low boron-10 shift range of 6–9 cm^{-1}. These moderately low isotopic shifts are consistent with vibrations involving the carbon. Both the asymmetric BeC_2Be stretch and the perpendicular methyl rocking mode should exhibit considerable carbon movement.

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