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## Raman and Infrared Spectra of $\text{Hf}(\text{BH}_4)_4$ and $\text{Hf}(\text{BD}_4)_4$ . Evidence for Hf-B Bonding<sup>1</sup>

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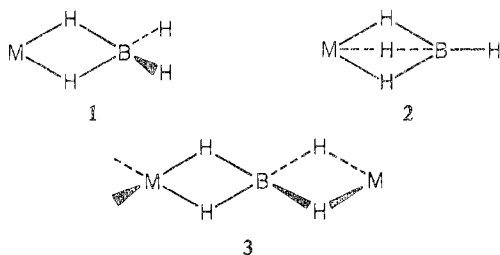
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Raman and infrared spectra are reported for  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BD}_4)_4$ . A normal-coordinate analysis gave reasonable valence force constants and accurate  $A_1$  eigenvectors. The latter were used, in conjunction with measured Raman intensities, to calculate bond polarizabilities and estimate bond orders. A striking feature of the Raman spectrum is a strong polarized Raman band near  $500\text{ cm}^{-1}$ , assignable to a  $\text{HfB}_4$  breathing mode. Analysis of the bond polarizability derivative of this coordinate suggests that Hf-B bonding may be significant in  $\text{Hf}(\text{BH}_4)_4$ .

### Introduction

Structural studies in the past several years have shown that the tetrahydroborate ion,  $\text{BH}_4^-$ , binds to metal ions *via* three-center (M-H-B) bonds of the kind well known for the boron hydrides themselves.<sup>3</sup> Geometries having both two<sup>4</sup> (1) and three<sup>5</sup> (2) hydrogen-bridge bonds have been observed and, in at least two instances,<sup>4e,f</sup> the tetrahydroborate ligand is known to link metal atoms in a polymer having backbone structure 3. Despite the availability of this structural in-



formation, however, several important points need to be clarified, including the strength of the hydrogen-bridge bonds and the extent of direct metal-boron bonding in structures 1-3. In addition, coordination of the tetrahydroborate ion to a metal ion is usually accompanied by changes in its vibrational spectrum that are characteristic of the mode of attachment.<sup>6</sup> The assignment of the vibrational frequencies is not always straightforward, however, and the need for a more detailed vibrational analysis is apparent.

Raman spectroscopy has been shown to be a sensitive technique for the evaluation of bonding interactions in metal complexes.<sup>7</sup> A study of  $\text{Hf}(\text{BH}_4)_4$  and its deuterated analog by infrared and Raman spectroscopy was therefore carried out in conjunction with a normal-coordinate analysis in order to provide additional information pertaining to the points mentioned above for a simple molecule having structural attachment 2. During the course of this work, infrared and Raman spectra of  $\text{Zr}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BH}_4)_4$  were reported and assigned.<sup>6,8,9</sup> The present treatment is more extensive, however, being aided by the availability of the  $\text{Hf}(\text{BD}_4)_4$  Raman spectrum which is reported here for the first time and by the normal-coordinate analysis.

### Experimental Section

Hafnium borohydride was synthesized by the method of Reid, Bish, and Brenner.<sup>10</sup> Raman spectra were obtained for pure single crystals, neat liquids, and neopentane solutions of  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BD}_4)_4$ . Concentrations of the solution samples were estimated from the relative volumes of solvent and solute using known densities. The samples were sealed in thin-walled quartz tubes of  $\sim 3\text{-mm}$  i.d. Spectra were excited with the  $4880\text{-\AA}$  line of a Coherent Radiation CR-5 argon laser. The Raman spectrometer was based on a Spex 1401 double monochromator. The light was detected by dc amplification of the photocurrent of a cooled IIT FW130 photomultiplier. The scattered

light was analyzed with a Polaroid disk. Intensities of the Raman bands of the neopentane solutions were measured from the recorded spectra using a polar planimeter. Intensities were placed on an absolute scale by comparison with  $\nu_1$  ( $459\text{ cm}^{-1}$ ) of  $\text{CCl}_4$  in a mixture of neopentane and  $\text{CCl}_4$ .

Infrared spectra were obtained from  $600$  to  $200\text{ cm}^{-1}$  on gas-phase  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BD}_4)_4$ . Spectra were obtained at less than saturation vapor pressure ( $<10$  Torr) in a  $10\text{-cm}$  cell fitted with polyethylene windows. A Beckman IR-12 spectrophotometer purged with dry  $\text{N}_2$  gas was used to record the spectra.

### Results and Discussion

**Spectra and Assignments.** The structure of crystalline  $\text{Hf}(\text{BH}_4)_4$ <sup>4c</sup> is shown in Figure 1. From an examination of Raman and infrared spectra, Davies, *et al.*,<sup>9</sup> concluded that this  $T_d$  structure is maintained in liquid and gas phases, as do we. Fifty-seven normal modes of vibration are expected for  $\text{M}(\text{BH}_4)_4$ , classifying as

$$\Gamma_{\text{vib}} = 4 A_1 + 5 E + 9 T_2 + 1 A_2 + 5 T_1$$

The Raman spectrum should contain  $A_1$  (polarized),  $E$  (depolarized), and  $T_2$  (depolarized) modes, while the infrared spectrum should contain only the  $T_2$  modes. The  $A_2$  and  $T_1$  modes are inactive.

Our vibrational assignments are given in Table I (*cf.* ref 9). The Raman spectra of single crystals of  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BD}_4)_4$  are shown in Figures 2 and 3. Assignment to the three symmetry classes  $A_1$ ,  $E$ , and  $T_2$  can in principle be obtained directly from single-crystal spectra,<sup>11</sup> but the proper orientation is difficult to achieve for air-sensitive materials sealed in capillaries. The arbitrary orientations used for the spectra shown reproduce qualitatively the depolarization ratios found in solution. The four  $A_1$  modes can immediately be recognized as the four polarized bands, at  $2572$ ,  $2193$ ,  $1287$ , and  $552\text{ cm}^{-1}$ . A medium-intensity depolarized Raman band at  $1088\text{ cm}^{-1}$  for the hydride and  $812\text{ cm}^{-1}$  for the deuteride has no ir counterpart<sup>9</sup> and is assigned to an  $E$  mode. A strong depolarized Raman band is found at  $224\text{ cm}^{-1}$  for the hydride and  $207\text{ cm}^{-1}$  for the deuteride. Associated with these features are weak components at  $209\text{ cm}^{-1}$  (hydride) and  $195\text{ cm}^{-1}$  (deuteride). The ir spectra (Figure 4) show a peak at  $211\text{ cm}^{-1}$  for the hydride and rising absorption of  $200\text{ cm}^{-1}$  (the spectrometer limit) for the deuteride. The weak Raman components are therefore tentatively assigned to  $T_2$  and the strong ones to  $E$  symmetry.

The solution Raman spectra in perpendicular polarization show components underlying the  $A_1$  modes, which should vanish ( $\rho = 0$  for  $A_1$  modes in  $T_d$  symmetry). Strong ir bands are found<sup>9</sup> corresponding to Raman components at  $2570$ ,  $2197$ ,  $2123$ ,  $1218$ , and  $480\text{ cm}^{-1}$  for the hydride and at  $1930$ ,  $1633$ ,  $1551$ ,  $918$ ,  $468$ , and  $398\text{ cm}^{-1}$  for the deuteride. These are therefore assigned to  $T_2$  modes. Remaining Raman components are tentatively assigned to  $E$  and  $T_2$  modes as indicated in Table I, on the basis of the normal-coordinate calculations.

Table I. Frequencies ( $\text{cm}^{-1}$ ) and Assignments of  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BD}_4)_4$ 

Symmetry	Normal mode	$\text{Hf}(\text{BH}_4)_4$		$\text{Hf}(\text{BD}_4)_4$		Major internal coordinates
		Obsd <sup>a</sup>	Calcd <sup>b</sup>	Obsd <sup>a</sup>	Calcd <sup>b</sup>	
$A_1$	$\nu_1$	2572	2572	1917	1923	$\nu_{\text{BH}_t}$
	$\nu_2$	2193	2202	1551	1564	$\nu_{\text{BH}_b}$
	$\nu_3$	1287	1286	955	936	$\delta_{\text{HBH}}, \nu_{\text{MH}}$
	$\nu_4$	552	552	510	505	$\nu_{\text{MB}}$
$A_2$	$\nu_5$		397 <sup>d</sup>		281 <sup>d</sup>	
$E$	$\nu_6$	(2227)	2125	(1669)	1586	$\nu_{\text{BH}_b}$
	$\nu_7$	(1290)	1278	(910)	904	$\delta_{\text{HBH}}, \nu_{\text{MH}}$
	$\nu_8$	1088	1079	812	787	$\delta_{\text{HBH}}$
	$\nu_9$	(570)	575	(430)	435	$\nu_{\text{MH}}, \delta_{\text{HBH}}$
	$\nu_{10}$	(224)	192	(207)	166	$\delta_{\text{HMH}}$
$T_1$	$\nu_{11}$		2122		1583	
	$\nu_{12}$		1246		882	
	$\nu_{13}$		1014		762	
	$\nu_{14}$		531		382	
	$\nu_{15}$		486		347	
$T_2$	$\nu_{16}$	2570	2573	1930	1926	$\nu_{\text{BH}_t}$
	$\nu_{17}$	2197	2199	1633 <sup>c</sup>	1626	$\nu_{\text{BH}_b}$
	$\nu_{18}$	2123	2128	1551	1522	$\nu_{\text{BH}_b}$
	$\nu_{19}$	(1290)	1289	(940)	938	$\delta_{\text{HBH}}, \nu_{\text{MH}}$
	$\nu_{20}$	1218	1264	918	895	$\delta_{\text{HBH}}, \nu_{\text{MH}}$
	$\nu_{21}$	(1140)	1092	(830)	814	$\delta_{\text{HBH}}$
	$\nu_{22}$	(570)	572	468	475	$\nu_{\text{MH}}, \delta_{\text{HBH}}$
	$\nu_{23}$	480	495	398	409	$\nu_{\text{MB}}, \nu_{\text{MH}}$
	$\nu_{24}$	(211)	208	(195)	183	$\delta_{\text{HMH}}$

<sup>a</sup> Observed frequencies are those of the single crystals. The values in parentheses are tentatively assigned and were *not* used in the least-squares fit of calculated frequencies. <sup>b</sup> Values calculated with force constants in Table III. <sup>c</sup> Average value of two bands apparently in Fermi resonance (see ref 9). <sup>d</sup> Values based solely on  $k_{\text{HMH}(\text{tor})}$  which is essentially undetermined.

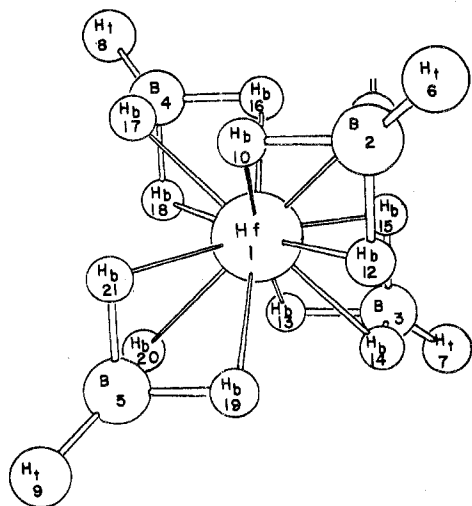


Figure 1. Computer drawing of the  $\text{Hf}(\text{BH}_4)_4$  geometry, determined in the 24°K crystal structure analysis<sup>5c</sup> showing the labeling scheme used in the text and normal-coordinate analysis.

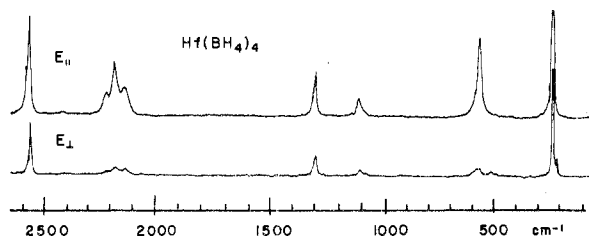


Figure 2. Polarized Raman spectrum of a  $\text{Hf}(\text{BH}_4)_4$  single crystal at room temperature observed with 4880-Å excitation.

**Normal-Coordinate Analysis.** An approximate normal-coordinate analysis was carried out to clarify the nature of the normal modes. Schachtschneider's programs<sup>12</sup> GMAT and FPERT were used to construct the  $G$  matrix and to solve the secular equations, with least-squares adjustment of the force constants to fit the hydride and deuteride frequencies simultaneously. All atoms in the structure were included; the molecular pa-

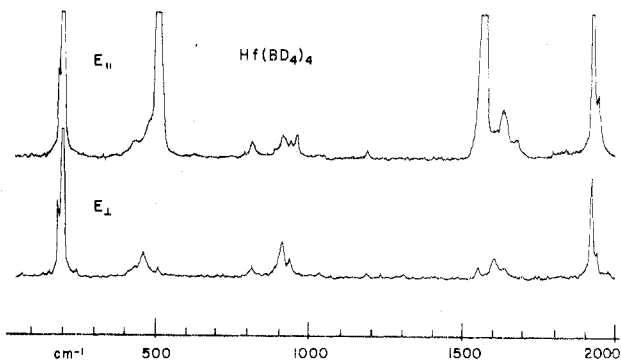


Figure 3. Polarized Raman spectrum of a  $\text{Hf}(\text{BD}_4)_4$  single crystal at room temperature observed with 4880-Å excitation.

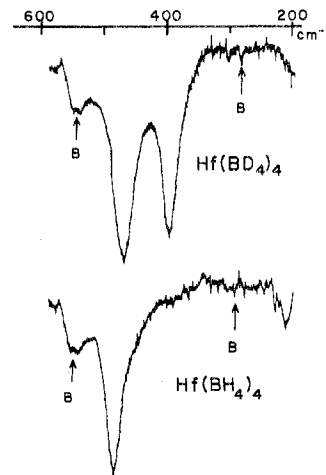


Figure 4. Room-temperature infrared spectra of  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BD}_4)_4$  from 600 to 200  $\text{cm}^{-1}$ , using a 10-cm path of unsaturated vapor. Features designated with a "B" are also present in scans of background (empty cell).

rameters are given in Table II. Symmetry coordinates were constructed from the internal coordinates by the usual method.<sup>13</sup> The internal coordinate set included B-H<sub>t</sub> ( $t =$

**Table II.** Molecular Parameters for  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BD}_4)_4$  Used in This Calculation<sup>a</sup>

Atoms	Dist, Å	Atoms	Angle, deg
Hf-B	2.31	H <sub>t</sub> -B-H <sub>b</sub>	109.5
B-H <sub>b</sub>	1.27	Hf-H <sub>b</sub> -B	94.1
B-H <sub>t</sub>	1.18	H <sub>b</sub> -B-H <sub>b</sub>	108.4
Hf-H <sub>b</sub>	2.21		

<sup>a</sup> Values for  $\text{Zr}(\text{BH}_4)_4$ <sup>sb</sup> were used rather than the results of the neutron study of  $\text{Hf}(\text{BH}_4)_4$ <sup>sc</sup> since the latter were obtained at 24°K and the present study was performed at room temperature. The conclusions of the present analysis are not strongly dependent upon the choice of these parameters.

**Table III.** Adjusted Force Constants<sup>a</sup> for  $\text{Hf}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BD}_4)_4$ 

Primary force const	Value	Interactn const	Value
$\nu_{\text{BH}_t}$	3.55		
$\nu_{\text{BH}_b}$	2.38		
$\nu_{\text{MH}_b}$	0.45		
$\nu_{\text{MB}}$	1.08		
$\delta_{\text{H}_t\text{BH}_b}$	0.35		
$\delta_{\text{H}_b\text{BH}_b}$	0.35	$\nu_{\text{BH}_b}-\nu_{\text{BH}_b}$	0.07
$\delta_{\text{H}_b\text{MH}_b(\text{ext})}$	0.50	$\delta_{\text{H}_t\text{BH}_b}-\delta_{\text{H}_b\text{BH}_b}$	0.03
$\delta_{\text{H}_b\text{MH}_b(\text{tor})}$	0.10	$\nu_{\text{MB}}-\delta_{\text{H}_b\text{MH}_b(\text{ext})}$	0.15

<sup>a</sup> Units are mdyn/Å for stretching and mdyn Å for bending force constants and mdyn for stretch-bend interaction.

terminal), B-H<sub>b</sub> (b = bridging), M-H, and M-B stretching, H<sub>t</sub>-B-H<sub>b</sub> and H<sub>b</sub>-B-H<sub>b</sub> bending, and two kinds of H-M-H bending: H-M-H(ext) involving adjacent hydrogen atoms from different BH<sub>4</sub> units (e.g., the atoms numbered 10 and 17 in Figure 1) and H-M-H(tor) involving hydrogen atoms related by a twofold rotation (e.g., atoms 10 and 19 in Figure 1). Only the latter contribute to the A<sub>2</sub> torsion mode.

Because of cyclic redundancies within the MH<sub>3</sub>B groups, the choice of internal coordinates is not unique. In particular, the M-B stretching coordinate could have been omitted in favor of including M-H-B and internal H-M-H bending coordinates. It has been shown<sup>14</sup> that in such cases the form of the eigenvectors is little affected by the choice of the internal coordinates, as long as the frequencies are accurately calculated. The choice of M-B stretching coordinate in this study was dictated by our aim of evaluating the M-B polarizability derivative from the eigenvectors and the Raman intensities. It is stressed that a unique determination of the force field is not possible.

Preliminary values of the principal force constants for the various internal coordinates were transferred from related molecules<sup>15,16</sup> and adjusted to fit the data. The H<sub>t</sub>-B-H<sub>b</sub> and H<sub>b</sub>-B-H<sub>b</sub> bending constants were highly correlated and could not be varied independently. They were therefore constrained to the same value, which trial calculations indicated to be 0.35 mdyn Å. The H-M-H(tor) bending constant is sensitive mainly to the value of the A<sub>2</sub> frequency, which is unobserved. This force constant was arbitrarily set at 0.10 mdyn Å. After initial optimization, a minimum number of interaction constants were introduced to improve the fit. The final calculations used eight primary valence force constants and three interaction constants, listed in Table III, to calculate ten hydride and eleven deuteride frequencies. Table I shows that the A<sub>1</sub> frequencies are calculated to within experimental error, while the E and T<sub>2</sub> frequencies are reasonably well calculated. Remaining discrepancies in the latter two symmetry blocks could have been reduced by inclusion of further interaction constants, but since little significance could be attached to them, they were not introduced.

The potential energy distribution showed the A<sub>1</sub> and T<sub>2</sub> modes at ~2570 cm<sup>-1</sup> in the hydride and ~1920 cm<sup>-1</sup> in the deuteride to be pure (>90%) B-H<sub>t</sub> stretching and the complex of modes at ~2200 cm<sup>-1</sup> in the hydride and 1500-1600 cm<sup>-1</sup> in the deuteride to be pure (>90%) B-H<sub>b</sub> stretching. The

**Table IV.** A<sub>1</sub> Intensities and Molecular Polarizability Derivatives

$\nu$ , cm <sup>-1</sup>	R <sup>a</sup>	$\rho_1$ <sup>b</sup>	$\bar{\alpha}'_{\text{Q}}$ <sup>c</sup>	$\bar{\alpha}'_{\text{Q}}(\text{calcd})$ <sup>d</sup>
			$\text{Hf}(\text{BH}_4)_4$	
2572	21.59	0.22	±3.05	+2.85
2193	15.45	0.04	±2.66	+2.86
1287	9.17	0.42	±0.98	+0.98
552	20.17	0.00	±1.30	+1.30
			$\text{Hf}(\text{BD}_4)_4$	
1917	8.24	0.22	±1.53	+1.69
1551	18.87	0.00	±2.39	+2.22
955	2.17	0.37	±0.43	+0.44
510	20.46	0.00	±1.24	+1.24

<sup>a</sup> R is the measured intensity relative to the 2710-cm<sup>-1</sup> (A<sub>1</sub>) band of the neopentane solvent. <sup>b</sup>  $\rho_1$  is the depolarization ratio for polarized incident light and analyzed scattered light. (Note  $\rho_1 = 0$  for A<sub>1</sub> modes in the T<sub>d</sub> point group. Observed nonzero values reflect contributions from underlying non-A<sub>1</sub> modes. The determination of  $\bar{\alpha}'_{\text{Q}}$  is unaffected by this.) <sup>c</sup>  $\bar{\alpha}'_{\text{Q}}$  is the mean molecular polarizability derivative obtained from R by the equation

$$(\bar{\alpha}'_1)^2 = \frac{(\nu_0 - \Delta\nu_2)^4}{(\nu_0 - \Delta\nu_1)^4} \left( \frac{\Delta\nu_1 [1 - \exp(h\Delta\nu_1/kT)]}{\Delta\nu_2 [1 - \exp(h\Delta\nu_2/kT)]} \right) \left( \frac{3}{3 - 4\rho_2} \right) \times \left( \frac{3 - 4\rho_1}{3} \right) (\bar{\alpha}'_2)^2 R$$

where the subscript 1 refers to the tabulated band and the subscript 2 refers to the 2710-cm<sup>-1</sup> band of neopentane, for which  $\rho = 0.00$  and  $\bar{\alpha}'_2 = 0.812$ , measured with respect to the 450-cm<sup>-1</sup> band of CCl<sub>4</sub>.<sup>16</sup>  $\nu_0$  is the excitation frequency, 19,436 cm<sup>-1</sup>, and  $\Delta\nu$  is the Raman shift. <sup>d</sup> Calculated  $\nu$  via  $\bar{\alpha}'_{\text{Q}} = \sum_j N_j^{1/2} l_{ij} \bar{\alpha}'_{\text{Q}j}$  using the eigenvector elements given in Table V and the following bond polarizability derivatives:  $\bar{\alpha}'_{\text{B-H}_t} = 1.75$ ,  $\bar{\alpha}'_{\text{B-H}_b} = 0.61$ ,  $\bar{\alpha}'_{\text{M-H}} = 0.39$ , and  $\bar{\alpha}'_{\text{M-B}} = 1.46$  Å<sup>2</sup>. These values are arrived at from eq 1 and the observed  $\bar{\alpha}'_{\text{Q}}$ . (See discussion in text.)

bands between 1300 and 570 cm<sup>-1</sup> in the hydride and between 960 and 435 cm<sup>-1</sup> in the deuteride are mixtures of H<sub>t</sub>-B-H<sub>b</sub> and H<sub>b</sub>-B-H<sub>b</sub> bending and M-H stretching. The A<sub>1</sub> and T<sub>2</sub> modes at 552 and 495 cm<sup>-1</sup> are mainly M-B stretching with some M-H stretching. The modes near 200 cm<sup>-1</sup> are mainly H-M-H(ext) bending.

The force constants (Table III) all have reasonable values. The B-H<sub>t</sub> stretching constant, 3.55 mdyn/Å, is the same as that found for B<sub>2</sub>H<sub>6</sub>, 3.54 mdyn/Å.<sup>15</sup> The MH<sub>3</sub>B bridging system has a unique geometry and the associated force constants are not directly comparable to those of previously studied systems. They are, however, in the same range as previous analogs. The B-H<sub>b</sub> stretching constant, 2.38 mdyn/Å, is larger than that found for B<sub>2</sub>H<sub>6</sub>, 1.68 mdyn/Å, but smaller than the B-H constant for ionic BH<sub>4</sub><sup>-</sup>, 3.19 mdyn/Å.<sup>16</sup> The M-H stretching constant, 0.45 mdyn/Å, is low, reflecting partial bond character (see below). The H<sub>t</sub>-B-H<sub>b</sub> bending constant, 0.35 mdyn Å, is the same as that used for B<sub>2</sub>H<sub>6</sub>, 0.34 mdyn Å,<sup>15</sup> while the H-M-H(ext) bending constant, 0.50 mdyn Å, is somewhat high, possibly reflecting nonbonding interactions in the crowded Hf coordination sphere, containing 12 hydrogen atoms. No particular significance can be attached to the M-B stretching constant, 1.08 mdyn/Å, since it could have been replaced by angle-bending constants. We note that an even larger force constant, 2.51 mdyn/Å, was used for the B-B stretching coordinate in B<sub>2</sub>H<sub>6</sub>.<sup>15</sup>

**Polarizability Derivatives.** From the measured intensities and depolarization ratios for the A<sub>1</sub> Raman bands, given in Table IV, normal-mode mean polarizability derivatives,  $\bar{\alpha}'_{\text{Q}}$ , were calculated in the usual manner.<sup>17</sup> These derivatives were then connected to internal coordinate bond polarizability derivatives  $\bar{\alpha}'_{\text{u}}$  via the transformation<sup>17</sup>

$$\bar{\alpha}'_{\text{Q}_i} = \sum_j N_j^{1/2} l_{ij} \bar{\alpha}'_{\text{u}_j} \quad (1)$$

Table V. A<sub>1</sub> Eigenvector Elements (*l<sub>ij</sub>* in Eq 1)

<i>v</i> (calcd), cm <sup>-1</sup>	BH <sub>t</sub>	BH <sub>b</sub>	MH	MB
		Hf(BH <sub>4</sub> ) <sub>4</sub>		
2572	1.032	-0.200	0.007	-0.100
2202	0.140	0.998	0.116	0.032
1286	-0.028	-0.006	0.959	-0.074
552	0.015	0.049	0.244	0.276
		Hf(BD <sub>4</sub> ) <sub>4</sub>		
1923	0.750	-0.233	0.013	-0.144
1564	0.154	0.699	0.076	0.034
936	-0.042	0.001	0.649	-0.101
505	0.023	0.037	0.263	0.246

where *l<sub>ij</sub>* is the eigenvector element connecting the *i*th normal mode *Q<sub>i</sub>* with the A<sub>1</sub> symmetry coordinate *S<sub>j</sub>* made up from the *j*th internal coordinate *u<sub>j</sub>*, and *N<sub>j</sub>* is the number of internal coordinates in the set. The components *l<sub>ij</sub>* are given in Table V, and *N<sub>j</sub>* = 4 for *j* = BH<sub>t</sub> and MB, and *N<sub>j</sub>* = 12 for *j* = BH<sub>b</sub> and MH.

There are four A<sub>1</sub> modes and four simultaneous forms of eq 1. The A<sub>1</sub> eigenvectors contain contributions from the four bond-stretching and from the angle-bending internal coordinates, so that the equations are underdetermined. Contributions to the mean polarizability derivative from angle bending are expected to be quite small however<sup>15,19,20</sup> and are neglected in the present case. Because Raman intensity is proportional to ( $\bar{\alpha}'$ )<sup>2</sup>, the sign of  $\bar{\alpha}'$ Q is undetermined. The four simultaneous equations therefore have 16 possible solutions, comprised of eight pairs which differ only in sign. Only one pair of solutions was found, however, which gave physically reasonable values for the bond polarizability derivatives and which reproduced the isotope effect on  $\bar{\alpha}$ Q (see Table IV). The positive solution is  $\bar{\alpha}'_{B-H_t} = 1.75$ ,  $\bar{\alpha}'_{B-H_b} = 0.61$ ,  $\bar{\alpha}'_{M-H} = 0.39$ , and  $\bar{\alpha}'_{M-B} = 1.46 \text{ \AA}^2$ .

These bond polarizability derivatives can be used to estimate bond orders according to the  $\delta$  function potential equation of Long and Plane<sup>18</sup>

$$\bar{\alpha}'_u = \frac{3}{2}(g\sigma/za_0)(n/2)r^3 \quad (2)$$

where *r* is the internuclear distance, *n*/2 is the number of electron pairs in the bond (bond order), *a*<sub>0</sub> is the Bohr radius, *g* is the  $\delta$  function strength (estimated as  $\chi$ , where  $\chi$  is the Pauling electronegativity),  $\sigma$  is the Pauling covalent character  $\exp[-1/4(\chi_A - \chi_B)^2]$ , and *z* is the effective nuclear charge (taken as the atomic number minus the number of inner-shell electrons). For heteronuclear bonds, the geometric mean of *g*/*z* is taken. Bond orders calculated with eq 2 are 1.04 for B-H<sub>t</sub>, 0.21 for B-H<sub>b</sub>, 0.06 for Hf-H, and 0.30 for Hf-B. Equation 2 seems to work well for terminal bonds, and the unit bond order calculated for B-H<sub>t</sub> is reassuring. For skeletal bonds, however, eq 2 is often found to give values between two and three times lower than expected, although related kinds of bonds give consistent results.<sup>7,11,18</sup> This pattern holds in the present case, since each HfH<sub>3</sub>B unit should contain three

bonding electron pairs, but the total bond order  $3(n/2_{B-H_b}) + 3(n/2_{Hf-H}) + n/2_{Hf-B}$  is only 1.32, which is too low by a factor of 2.3. If each calculated bond order is multiplied by this factor, the following corrected estimates are obtained: 0.48 for B-H<sub>b</sub>, 0.13 for Hf-H, and 0.69 for Hf-B. These may be compared with the estimates of Plato and Hedberg,<sup>5b</sup> who applied Pauling's empirical bond order equation to the internuclear distances in Zr(BH<sub>4</sub>)<sub>4</sub> to obtain 0.66 for B-H<sub>b</sub>, 0.18 for Zr-H, and 0.66 for Zr-B. The agreement between these two estimates may be fortuitous, but it does appear that the present interpretation of the Raman intensity patterns is at least reasonable. Thus Hf-B bonding may well be significant in Hf(BH<sub>4</sub>)<sub>4</sub> and could account for something on the order of one-fourth of the total bonding in each HfH<sub>3</sub>B unit. In another perspective, Hf-B bonding, as modeled with the present force field, is about 80% greater than Hf-H bonding in the Hf coordination sphere.

Registry No. Hf(BH<sub>4</sub>)<sub>4</sub>, 53608-70-1; Hf(BD<sub>4</sub>)<sub>4</sub>, 37354-63-5.

### References and Notes

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