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Raman and Infrared Spectra of $Hf(BH_4)_4$ and $Hf(BD_4)_4$. Evidence for Hf–B Bonding[1]

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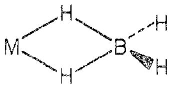
Raman and infrared spectra are reported for $Hf(BH_4)_4$ and $Hf(BD_4)_4$. A normal-coordinate analysis gave reasonable valence force constants and accurate A_1 eigenvectors. The latter were used, in conjunction with measured Raman intensities, to calculate bond polarizabilities and estimate bond orders. A striking feature of the Raman spectrum is a strong polarized Raman band near 500 cm^{-1}, assignable to a HfB_4 breathing mode. Analysis of the bond polarizability derivative of this coordinate suggests that Hf–B bonding may be significant in $Hf(BH_4)_4$.

Introduction

Structural studies in the past several years have shown that the tetrahydroborate ion, BH_4^-, binds to metal ions *via* three-center (M–H–B) bonds of the kind well known for the boron hydrides themselves.[3] Geometries having both two[4] (**1**) and three[5] (**2**) hydrogen-bridge bonds have been observed and, in at least two instances,[4e,f] the tetrahydroborate ligand is known to link metal atoms in a polymer having backbone structure **3**. Despite the availability of this structural information, 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.[6] The assignment of the vibrational frequencies is not always straightforward, however, and the need for a more detailed vibrational analysis is apparent.



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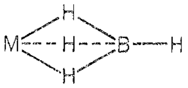

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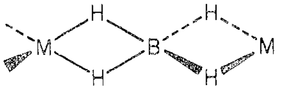

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Raman spectroscopy has been shown to be a sensitive technique for the evaluation of bonding interactions in metal complexes.[7] A study of $Hf(BH_4)_4$ and its deuterated analog by infrared and Raman spectroscopy was therefore carried out in conjunction 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 $Zr(BH_4)_4$ and $Hf(BH_4)_4$ were reported and assigned.[6,8,9] The present treatment is more extensive, however, being aided by the availability of the $Hf(BD_4)_4$ 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.[10] Raman spectra were obtained for pure single crystals, neat liquids, and neopentane solutions of $Hf(BH_4)_4$ and $Hf(BD_4)_4$. 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 ~3-mm i.d. Spectra were excited with the 4880-Å 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 ITT 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 ν_1 (459 cm^{-1}) of CCl_4 in a mixture of neopentane and CCl_4.

Infrared spectra were obtained from 600 to 200 cm^{-1} on gas-phase $Hf(BH_4)_4$ and $Hf(BD_4)_4$. Spectra were obtained at less than saturation vapor pressure (<10 Torr) in a 10-cm cell fitted with polyethylene windows. A Beckman IR-12 spectrophotometer purged with dry N_2 gas was used to record the spectra.

Results and Discussion

Spectra and Assignments. The structure of crystalline $Hf(BH_4)_4$[5c] is shown in Figure 1. From an examination of Raman and infrared spectra, Davies, *et al.*,[9] 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 $M(BH_4)_4$, classifying as

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

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 $Hf(BH_4)_4$ and $Hf(BD_4)_4$ 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,[11] 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 cm^{-1}. A medium-intensity depolarized Raman band at 1088 cm^{-1} for the hydride and 812 cm^{-1} for the deuteride has no ir counterpart[9] and is assigned to an E mode. A strong depolarized Raman band is found at 224 cm^{-1} for the hydride and 207 cm^{-1} for the deuteride. Associated with these features are weak components at 209 cm^{-1} (hydride) and 195 cm^{-1} (deuteride). The ir spectra (Figure 4) show a peak at 211 cm^{-1} for the hydride and rising absorption of 200 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[9] corresponding to Raman components at 2570, 2197, 2123, 1218, and 480 cm^{-1} for the hydride and at 1930, 1633, 1551, 918, 468, and 398 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 (cm^{-1}) and Assignments of $Hf(BH_4)_4$ and $Hf(BD_4)_4$

		$Hf(BH_4)_4$		$HF(BD_4)_4$		
Symmetry	Normal mode	Obsd[a]	Calcd[b]	Obsd[a]	Calcd[b]	Major internal coordinates
A_1	ν_1	2572	2572	1917	1923	ν_{BH_t}
	ν_2	2193	2202	1551	1564	ν_{BH_b}
	ν_3	1287	1286	955	936	δ_{HBH}, ν_{MH}
	ν_4	552	552	510	505	ν_{MB}
A_2	ν_5		397[d]		281[d]	
E	ν_6	(2227)	2125	(1669)	1586	ν_{BH_b}
	ν_7	(1290)	1278	(910)	904	δ_{HBH}, ν_{MH}
	ν_8	1088	1079	812	787	δ_{HBH}
	ν_9	(570)	575	(430)	435	ν_{MH}, δ_{HBH}
	ν_{10}	(224)	192	(207)	166	δ_{HMH}
T_1	ν_{11}		2122		1583	
	ν_{12}		1246		882	
	ν_{13}		1014		762	
	ν_{14}		531		382	
	ν_{15}		486		347	
T_2	ν_{16}	2570	2573	1930	1926	ν_{BH_t}
	ν_{17}	2197	2199	1633[c]	1626	ν_{BH_b}
	ν_{18}	2123	2128	1551	1522	ν_{BH_b}
	ν_{19}	(1290)	1289	(940)	938	δ_{HBH}, ν_{MH}
	ν_{20}	1218	1264	918	895	δ_{HBH}, ν_{MH}
	ν_{21}	(1140)	1092	(830)	814	δ_{HBH}
	ν_{22}	(570)	572	468	475	ν_{MH}, δ_{HBH}
	ν_{23}	480	495	398	409	ν_{MB}, ν_{MH}
	ν_{24}	(211)	208	(195)	183	δ_{HMH}

[a] 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. [b] Values calculated with force constants in Table III. [c] Average value of two bands apparently in Fermi resonance (see ref 9). [d] Values based solely on $k_{HMH(tor)}$ which is essentially undetermined.

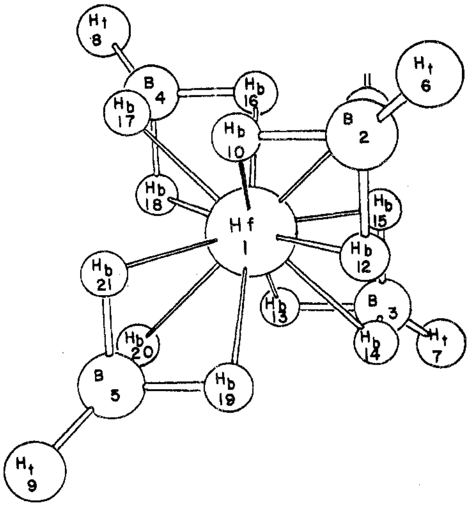

Figure 1. Computer drawing of the $Hf(BH_4)_4$ geometry, determined in the 24°K crystal structure analysis[5c] showing the labeling scheme used in the text and normal-coordinate analysis.

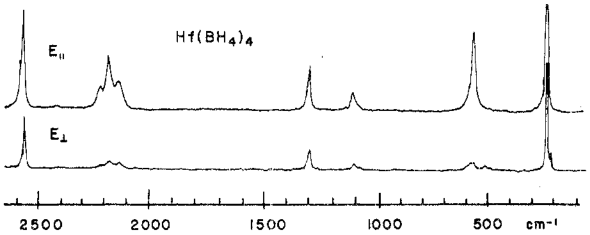

Figure 2. Polarized Raman spectrum of a $Hf(BH_4)_4$ single crystal at room temperature observed with 4880-Å excitation.

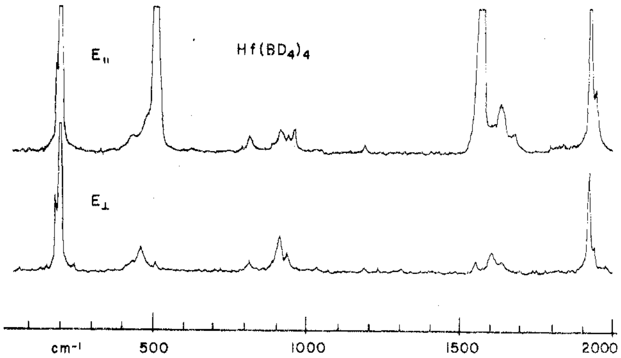

Figure 3. Polarized Raman spectrum of a $Hf(BD_4)_4$ single crystal at room temperature observed with 4880-Å excitation.

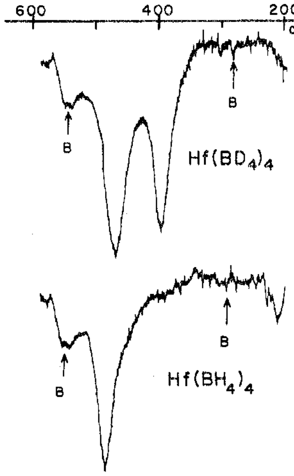

Figure 4. Room-temperature infrared spectra of $Hf(BH_4)_4$ and $Hf(BD_4)_4$ from 600 to 200 cm^{-1}, using a 10-cm path of unsaturated vapor. Features designated with a "B" are also present in scans of background (empty cell).

Normal-Coordinate Analysis. An approximate normal-coordinate analysis was carried out to clarify the nature of the normal modes. Schactschneider's programs[12] 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 parameters are given in Table II. Symmetry coordinates were constructed from the internal coordinates by the usual method.[13] The internal coordinate set included B–H_t (t =

Table II. Molecular Parameters for $Hf(BH_4)_4$ and $Hf(BD_4)_4$ Used in This Calculation[a]

Atoms	Dist, Å	Atoms	Angle, deg
Hf–B	2.31	H_t–B–H_b	109.5
B–H_b	1.27	Hf–H_b–B	94.1
B–H_t	1.18	H_b–B–H_b	108.4
Hf–H_b	2.21		

[a] Values for $Zr(BH_4)_4$[5b] were used rather than the results of the neutron study of $Hf(BH_4)_4$,[5c] 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[a] for $Hf(BH_4)_4$ and $Hf(BD_4)_4$

Primary force const	Value	Interacn const	Value
ν_{BH_t}	3.55		
ν_{BH_b}	2.38		
ν_{MH_b}	0.45		
ν_{MB}	1.08		
$\delta_{H_tBH_b}$	0.35		
$\delta_{H_bBH_b}$	0.35	ν_{BH_b}–ν_{BH_b}	0.07
$\delta_{H_bMH_b(ext)}$	0.50	$\delta_{H_tBH_b}$–$\delta_{H_bBH_b}$	0.03
$\delta_{H_bMH_b(tor)}$	0.10	ν_{MB}–$\delta_{H_bMH_b(ext)}$	0.15

[a] Units are mdyn/Å for stretching and mdyn Å for bending force constants and mdyn for stretch–bend interaction.

terminal), B–H_b (b = bridging), M–H, and M–B stretching, H_t–B–H_b and H_b–B–H_b bending, and two kinds of H–M–H bending: H–M–H(ext) involving adjacent hydrogen atoms from different BH_4 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_2 torsion mode.

Because of cyclic redundancies within the MH_3B 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[14] 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[15,16] and adjusted to fit the data. The H_t–B–H_b and H_b–B–H_b 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_2 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_1 frequencies are calculated to within experimental error, while the E and T_2 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_1 and T_2 modes at ~2570 cm^{-1} in the hydride and ~1920 cm^{-1} in the deuteride to be pure (>90%) B–H_t stretching and the complex of modes at ~2200 cm^{-1} in the hydride and 1500–1600 cm^{-1} in the deuteride to be pure (>90%) B–H_b stretching. The bands between 1300 and 570 cm^{-1} in the hydride and between 960 and 435 cm^{-1} in the deuteride are mixtures of H_t–B–H_b and H_b–B–H_b bending and M–H stretching. The A_1 and T_2 modes at 552 and 495 cm^{-1} are mainly M–B stretching with some M–H stretching. The modes near 200 cm^{-1} are mainly H–M–H(ext) bending.

Table IV. A_1 Intensities and Molecular Polarizability Derivatives

ν, cm^{-1}	R^a	$\rho_1{}^b$	$\bar{\alpha}'_Q{}^c$	$\bar{\alpha}'_Q$(calcd)^d
		$Hf(BH_4)_4$		
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
		$Hf(BD_4)_4$		
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

[a] R is the measured intensity relative to the 2710-cm^{-1} (A_1) band of the neopentane solvent. [b] ρ_1 is the depolarization ratio for polarized incident light and analyzed scattered light. (Note $\rho_1 = 0$ for A_1 modes in the T_d point group. Observed nonzero values reflect contributions from underlying non-A_1 modes. The determination of $\bar{\alpha}'_Q$ is unaffected by this.) [c] $\bar{\alpha}'_Q$ 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^{-1} band of neopentane, for which $\rho = 0.00$ and $\bar{\alpha}'_2 = 0.812$, measured with respect to the 450-cm^{-1} band of CCl_4.[18] ν_0 is the excitation frequency, 19,436 cm^{-1}, and $\Delta\nu$ is the Raman shift. [d] Calculated *via* $\bar{\alpha}'_Q = \Sigma_j N_j{}^{1/2} l_{ij} \bar{\alpha}'_{uj}$ using the eigenvector elements given in Table V and the following bond polarizability derivatives: $\bar{\alpha}'_{B-H_t} = 1.75$, $\bar{\alpha}'_{B-H_b} = 0.61$, $\bar{\alpha}'_{M-H} = 0.39$, and $\bar{\alpha}'_{M-B} = 1.46$ $Å^2$. These values are arrived at from eq 1 and the observed $\bar{\alpha}'_Q$. (See discussion in text.)

The force constants (Table III) all have reasonable values. The B–H_t stretching constant, 3.55 mdyn/Å, is the same as that found for B_2H_6, 3.54 mdyn/Å.[15] The MH_3B 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_b stretching constant, 2.38 mdyn/Å, is larger than that found for B_2H_6, 1.68 mdyn/Å, but smaller than the B–H constant for ionic BH_4^-, 3.19 mdyn/Å.[16] The M–H stretching constant, 0.45 mdyn/Å, is low, reflecting partial bond character (see below). The H_t–B–H_b bending constant, 0.35 mdyn Å, is the same as that used for B_2H_6, 0.34 mdyn Å,[15] 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_2H_6.[15]

Polarizability Derivatives. From the measured intensities and depolarization ratios for the A_1 Raman bands, given in Table IV, normal-mode mean polarizability derivatives, $\bar{\alpha}'_Q$, were calculated in the usual manner.[17] These derivatives were then connected to internal coordinate bond polarizability derivatives $\bar{\alpha}'_u$ *via* the transformation[17]

$$\bar{\alpha}'_{Q_i} = \Sigma N_j{}^{1/2} l_{ij} \bar{\alpha}'_{u_j} \tag{1}$$

Table V. A_1 Eigenvector Elements (l_{ij} in Eq 1)

ν(calcd), cm^{-1}	BH_t	BH_b	MH	MB
		$Hf(BH_4)_4$		
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
		$Hf(BD_4)_4$		
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_{ij} is the eigenvector element connecting the ith normal mode Q_i with the A_1 symmetry coordinate S_j made up from the jth internal coordinate u_j, and N_j is the number of internal coordinates in the set. The components l_{ij} are given in Table V, and $N_j = 4$ for j = BH_t and MB, and $N_j = 12$ for j = BH_b and MH.

There are four A_1 modes and four simultaneous forms of eq 1. The A_1 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[15,19,20] and are neglected in the present case. Because Raman intensity is proportional to $(\bar{\alpha}')^2$, 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 $\bar{\alpha}'_{B-H_t} = 1.75$, $\alpha'_{B-H_b} = 0.61$, $\bar{\alpha}'_{M-H} = 0.39$, and $\bar{\alpha}'_{M-B} = 1.46$ Å^2.

These bond polarizability derivatives can be used to estimate bond orders according to the δ function potential equation of Long and Plane[18]

$$\overline{\alpha}'_u = {}^3/_2(g\sigma/za_0)(n/2)r^3 \qquad (2)$$

where r is the internuclear distance, $n/2$ is the number of electron pairs in the bond (bond order), a_0 is the Bohr radius, g is the δ function strength (estimated as χ, where χ is the Pauling electronegativity), σ 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_t, 0.21 for B–H_b, 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_t 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.[7,11,18] This pattern holds in the present case, since each HfH_3B 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_b, 0.13 for Hf–H, and 0.69 for Hf–B. These may be compared with the estimates of Plato and Hedberg,[5b] who applied Pauling's empirical bond order equation to the internuclear distances in $Zr(BH_4)_4$ to obtain 0.66 for B–H_b, 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 $Hf(BH_4)_4$ and could account for something on the order of one-fourth of the total bonding in each HfH_3B 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. $Hf(BH_4)_4$, 53608-70-1; $Hf(BD_4)_4$, 37354-63-5.

References and Notes

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