Vibrational Spectra of Zirconium Tetrahydroborate and Related Molecules

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The i.r. spectra of $Zr(BH_4)_4$, $Zr(BD_4)_4$, $Hf(BH_4)_4$, $Hf(BD_4)_4$, and $U(BH_4)_4$ have been interpreted in conjunction with the Raman spectra of benzene solutions of $Zr(BH_4)_4$ and $Hf(BH_4)_4$. In all cases the results are strongly indicative of a triple hydrogen bridge structure of symmetry point group T_d.

The vapour-phase i.r. spectrum of zirconium tetrahydroborate, $Zr(BH_4)_4$, was initially interpreted on the assumption of a double hydrogen bridge structure.[1] Since then, a low-temperature (−160 °C) *X*-ray diffraction study of the solid [2] and electron-diffraction studies of the vapour [3] have both been interpreted on the basis of a tetrahedral ZrB_4 'skeleton', with three bridging hydrogen atoms between each boron and the central zirconium atom. It has been noted [4] that the overall pattern of the i.r. spectrum of $Zr(BH_4)_4$ in the vapour phase is more consistent with triple hydrogen bridging than with double bridging and the Raman spectrum has been given a brief interpretation [5] in terms of a triply bridged structure of T_d molecular symmetry.

In the present work, the vapour-phase i.r. spectra of $Zr(BH_4)_4$ and $Zr(BD_4)_4$ have been reinvestigated. The i.r. spectra of $Hf(BD_4)_4$ and $U(BH_4)_4$ (vapours) and the Raman spectra of $Hf(BH_4)_4$ (benzene solution) are presented for the first time. The structural implications of the vibrational spectra will be discussed, a reasonable choice of bands corresponding to fundamentals presented, the symmetry types of these fundamentals determined and, as far as possible, descriptions of the modes corresponding to the observed frequencies applied.

EXPERIMENTAL AND RESULTS

Preparations.—Zirconium and hafnium tetrahydroborates were prepared by the method of Reid *et al.*[6] and purified by trap-to-trap distillation *in vacuo*.[7] The deuterioborate analogues were prepared in a similar manner from lithium deuterioborate (Koch-Light Laboratories) of isotopic purity >98%.

Uranium tetrahydroborate, obtained as green crystals volatile at 40 °C, was prepared from the reaction of anhydrous UF_4 with excess of aluminium tetrahydroborate in a sealed tube [8] (Found: H, 5·20. Calc. for UB_4H_{16}: H, 5·37%). The mass spectrum of the solid showed a peak at *m/e* 298, corresponding to $U(BH_4)_4^+$.

All compounds were handled by use of conventional synthetical high-vacuum lines and nitrogen-filled glove-boxes.

Spectra.—Spectra were obtained on a number of different instruments at the various institutions. Spectra were always reproducible although the accuracy and quality varied slightly.

Zirconium compounds. The vapour-phase i.r. spectra of $Zr(BH_4)_4$ and $Zr(BD_4)_4$ contained in 10 cm pathlength gas cells fitted with KBr windows and the i.r. spectrum of a Nujol solution of $Zr(BH_4)_4$ between KBr plates were recorded on a Perkin-Elmer 225 instrument. In these spectra, band contours were closely examined. Frequencies reported are expected to be accurate to ±1 cm^{-1} for sharp bands. [It should, however, be noted that the bands observed represent the unresolved superimposition of bands due to various isotopic molecules, $Zr(^{11}B_n{}^{10}B_{4-n})H_{16}$; see later.] The low-energy i.r. spectrum (400—20 cm^{-1}) of a Nujol solution of $Zr(BH_4)_4$ between polyethylene plates was obtained with the Research and Industrial Instruments Corp. interferometer at the University of Newcastle upon Tyne. The Raman spectrum of a *ca.* 2·5M solution of $Zr(BH_4)_4$ in benzene was recorded on a Perkin-Elmer LR-1 spectrophotometer (He–Ne laser source, 632·8 nm, 8 mW).

Hafnium compounds. The i.r. spectrum of $Hf(BH_4)_4$ vapour was obtained with a Unicam SP 100 spectrophotometer. Frequencies in this case are expected to be accurate to ±3 cm^{-1}. The Raman spectrum was obtained from a concentrated solution in benzene on the University of Newcastle upon Tyne Cary 81 instrument fitted with a Toronto arc exciting source emitting the 435·8 nm mercury line.

Uranium tetrahydroborate. The i.r. spectrum of $U(BH_4)_4$ was obtained by introducing crystals of the compound into a nitrogen-filled gas cell, evacuating, and maintaining the cell at 40—50 °C in the beam of a Perkin-Elmer Infracord instrument by use of a heating coil. Peak positions are expected to be accurate only to *ca.* ±5 cm^{-1} and, in view of the limited volatility of the compound in comparison with the zirconium and hafnium analogues, only the strongest bands appear in the spectrum.

In all cases, care was taken to exclude any diborane (or B_2D_6) produced by thermal decomposition of the parent compounds. This was accomplished by evacuating the cell whilst the compound was trapped at −80 °C in a side-arm. In no case, within the duration of the experiments, was any reaction observed with the i.r. cell windows.

The i.r. frequencies of $Zr(BH_4)_4$ and $Zr(BD_4)_4$ are in Table 1. The spectra are shown in Figure 1.

I.r. frequencies for $Hf(BH_4)_4$, $Hf(BD_4)_4$, and $U(BH_4)_4$ vapours are in Table 2 and Raman frequencies of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ in Table 3. The major features of the benzene solution i.r. spectrum (Perkin-Elmer 457 instrument) of $Zr(BH_4)_4$ [2562s, 2480w, 2415w, 2179s, 2117s, 1285w, 1212s, 1098vw, 561vvw(sh), 501s] are comparable with the gas-phase spectrum, although the bands generally

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TABLE 1

Vapour-phase i.r. spectra of $Zr(BH_4)_4$ and $Zr(BD_4)_4$

Assignment	$Zr(BH_4)_4$ [a]	ν_H/ν_D [b]	$Zr(BD_4)_4$ [a]	Assignment
			3145vvw	1545 + 1603 = 3148
			3078vvw	2 × 1545 = 3090
			2925vvw	1545 + 922 + 484 = 2951
			2850vvw	1927 + 922 = 2849
			2576vw	$ZrB_4D_{15}H$, $\nu B-H_t$
			2465vvw	1545 + 922 = 2467
			2169w	$ZrB_4D_{15}H$, $\nu B-H_b$
$\nu B-H_t$	2575s	1·34	1927s	$\nu B-D_t$
1218 + 1288 = 2506	2493w			
2 × 1218 = 2436	2431w		1838vw	2 × 922 = 1844
$\nu B-H_b$	2194s	1·35	1638w	$\nu B-D_b$; in Fermi resonance with 2 × 812?
			1603w	
$\nu B-H_b$	2133s	1·38	1545s	$\nu B-D_b$
1288 + 507 = 1795	1785vw		1367vvw	
			1244vw	$ZrB_4D_{15}H$
			1191w	
1218 + 213 = 1431	1416vw		1096vvw	
Fundamental?	1288w		1020vvw	
$\nu Zr-H$?	1218vs	1·32	922s	$\nu Zr-D$?
	1155w			
Fundamental	1034w		812vvw	
	560sh,vw			
$\nu Zr-B$	507s	1·05	484s	$\nu Zr-B$
			419w	922 − 484 = 438 in Fermi resonance with 484
δZrB_4?	213m,[c]			

[a] In wavenumbers/cm^{-1}; where fine structure is apparent, only the fundamental frequency is given. [b] These ratios should be taken cautiously. Except for the 2194 cm^{-1} band, no allowance has been made for Fermi resonance. [c] From Nujol solution.

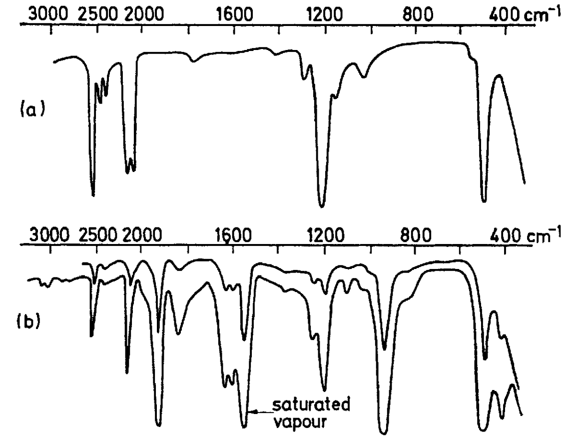

FIGURE 1 I.r. spectrum of (a), $Zr(BH_4)_4$; (b), $Zr(BD_4)_4$

TABLE 2

Vapour-phase i.r. spectra of $Hf(BD_4)_4$, $Hf(BH_4)_4$, and $U(BH_4)_4$ in cm^{-1} [a]

$Hf(BD_4)_4$	$Hf(BH_4)_4$	$U(BH_4)_4$
2188vw		
1934s	2581s	2570s
	2509w	
1850w	2447w	
1650w	2207s	2155s
1620w		
1558vs	2146s	2090s
1203w		
	1300vw	
945m,sh?		
923vs	1228vs	1230vs
	1140vw	1110vw
830vw	1020vw	
473vs	487vs	478s
407m		

[a] The assignments presented for the fundamentals, overtones, and combination and difference bands in $Zr(BH_4)_4$ and $Zr(BD_4)_4$ are applicable to the corresponding bands here.

occur slightly to lower frequency. Additional weak features at 1778, 1170, and 1050 cm^{-1} can be observed in Nujol solution.

TABLE 3

Raman spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ in cm^{-1}

$Hf(BH_4)_4$	$Zr(BH_4)_4$	Assignments
2570s,P	2570m,P	A_1, $\nu B-H_t$
	2215sh,vw	E, $\nu B-H_b$
2195s,P	2180m,P	A_1, $\nu B-H_b$
2144m,sh	2125sh,vw	T_2, $\nu B-H_b$
1290s,P	1285s,P	A_1, $\nu M-H$
1088w,dP	1077w,dP	E,
552s,P	549vs,P	A_1, $\nu M-B$
488m,sh,dP	510?vw	T_2, $\nu M-B$
217s,dP	216s,dP	T_2, δMB_4? [a]

P = polarized, dP = depolarized.

[a] Perhaps coincident with the corresponding E mode.

DISCUSSION

In view of the X-ray and electron-diffraction evidence on the $Zr(BH_4)_4$ molecule, the vibrational spectra of this and related compounds were examined further. As a result, a more satisfactory interpretation of the structural implications of the vibrational data than was previously possible [1] now becomes feasible. The simplicity of the observed spectra, even with allowance for the possibility of accidental degeneracies, is indicative of high molecular symmetry. The highest possible symmetry for the $Zr(BH_4)_4$ molecule is T_d, consistent with a tetrahedral array of boron atoms bonded through triple hydrogen bridges to zirconium, for which just $9T_2$ i.r.-active and $4A_1 + 5E + 9T_2$ Raman-active modes are expected. Other possible structural models involving a tetrahedral or a square planar ZrB_4 ' skeleton ' and triple or double hydrogen bridging are of lower symmetry and predict much more complex i.r. and Raman spectra than are observed. That just four polarized

Raman lines are observed is consistent only with the structure of T_d symmetry. In fact, it will be seen from the following interpretation that the number and symmetry species of the observed fundamentals correspond well with the predictions of the T_d model.

That the corresponding i.r. and Raman spectra of the zirconium, hafnium, and uranium compounds are extremely similar implies that all molecules (in the phases studied) conform with the T_d structure. In the following discussion, reference will be made only to the spectra of the zirconium compounds and the frequencies quoted are those listed in Table 1 and 3. The arguments applied and conclusions reached can confidently be extended to the hafnium and uranium compounds, where the corresponding data have been reported.

In the Raman spectrum, the four polarized lines are assigned to A_1 fundamentals. Lines at 2125 and 216 cm^{-1} appear coincident with i.r. bands and may therefore be assigned to T_2 modes. The 2215 and 1077 cm^{-1} Raman bands do not appear to have any i.r. coincidences and thus are probably E vibrations. In the Raman spectrum of $Hf(BH_4)_4$ (Table 3), the feature at 488 cm^{-1} is ascribed to a T_2 mode since it coincides with the 487 cm^{-1} i.r. band.

All i.r.-active modes must be of T_2 symmetry. In the i.r. spectrum of $Zr(BH_4)_4$, the six strong lines at 2576, 2194, 2133, 1218, 507, and 213 cm^{-1} can reasonably be ascribed to fundamentals. However, the assignment of the remaining T_2 fundamentals from the weak lines of the spectrum is less certain. The weak 1034 cm^{-1} band which is considerably removed from any of the strong bands in the spectrum is probably associated with the 1077 cm^{-1} Raman line and is therefore ascribed to a fundamental. A weak band at 2431 cm^{-1} is well fitted by the overtone 2 × 1218 = 2436 cm^{-1}, as is its counterpart in the borodeuteride spectrum (2 × 922 = *ca.* 1838 cm^{-1}). Possible combination frequencies are suggested in Table 1 to account for three of the remaining weak features. Two of these involve the 1288 cm^{-1} band, which may also be a fundamental.

The correlation of hydride and deuteride i.r. frequencies is shown in Table 1. Figure 1 shows that the pattern of strong lines in the hydride spectrum undergoes two changes on passing to the deuteride. First, in the deuteride region which corresponds to the single hydride band at 507 cm^{-1}, two bands are found, one at 484 cm^{-1} together with a weaker feature at 419 cm^{-1}. This is interpreted as being due to Fermi resonance in the deuteride spectrum between the fundamental (484 cm^{-1}) and a suitable overtone, combination, or difference band which occurs close to the fundamental and borrows intensity from it. A suitable difference band which would not experience intensity enhancement in the hydride spectrum but may do so in the deuteride spectrum is $922 - 484 = 438$ cm^{-1}. The second spectral change may have a similar origin in that two equally intense bands at 2133 and 2194 cm^{-1} in the hydride spectrum are replaced by three bands in the corresponding region of the deuteride spectrum, a strong one at 1545 cm^{-1} and two weaker bands at 1603 and 1638 cm^{-1}, of approximately equal intensity. The most suitable frequency that could be found to account for this result was $2 \times 812 = 1624$ cm^{-1} in resonance with the deuteride counterpart of the 2194 cm^{-1} hydride band.

It is expected that some of the weaker features of the deuteride spectrum may be due to a hydride impurity. This will be almost entirely in the form of $ZrB_4D_{15}H$ in which there is three times the probability that the proton will reside in a bridging position than in a terminal position. This molecule should exhibit single hydrogen stretching frequencies [9] in the vicinity of the hydrogen stretching frequencies observed for $Zr(BH_4)_4$ (see below). The bands at 2576 and 2169 cm^{-1} and at least one of 1244 and 1191 cm^{-1} are therefore ascribed to $ZrB_4D_{15}H$. Possible explanations for the remaining weak features in the deuteride spectrum are given as overtones and combinations in Table 1.

Although the vibrational spectrum of no other triple hydrogen bridged molecule has been treated in detail, some elucidation of the nature of the modes represented by the observed frequencies can be gained from a comparison with other boron hydride species.

In the present hydride spectra, the region above 2000 cm^{-1} separates into two sections, consistent with observations in double bridge molecules,[10,11] in which the higher-frequency region contains terminal B–H stretching modes and the lower region bridge B–H stretches. This is reflected in the electron-diffraction data for $Zr(BH_4)_4$, $Al(BH_4)_3$, and B_2H_6 in all of which $r_{B-H_b} > r_{B-H_t}$.[3,12,13] Thus the 2576 cm^{-1} (i.r., T_2) and 2570 cm^{-1} (R, A_1) bands are assigned to the boron–terminal hydrogen stretching frequencies. Their small separation implies very little coupling between the terminal stretching modes, as is expected from the large separation of the $B-H_t$ bonds in the molecule. This has also been observed [14,15] for the terminal stretching modes in $Al(BH_4)_3$. That the i.r. and Raman spectra each contain just one such mode is indicative of both a triple bridging structure and a T_d molecular symmetry. It follows that the 2100—2225 cm^{-1} region of the hydride i.r. and Raman spectra are assigned to $B-H_b$ stretching modes.

The 507 cm^{-1} (T_2) hydride i.r. band shows only a small shift on deuteriation to *ca.* 484 cm^{-1} (ν_H/ν_D = *ca.* 1·05). This implies that there can be little H(D) motion involved in the vibration. That the corresponding Raman mode at 549 cm^{-1} is totally symmetric means

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that these bands can only be ascribed to Zr–B stretching vibrations. Similar modes have been observed in other boron hydride systems, *e.g.*, B_2H_6 ($\nu_H/\nu_D = 1{\cdot}14$),[16] solid $Be(BH_4)_2$ ($\nu_H/\nu_D = 1{\cdot}04$),[11] and $Al(BH_4)_3$ ($\nu_H/\nu_D = 1{\cdot}10$, $1{\cdot}06$).[15] The hydride band at 213 cm^{-1} (i.r.)/216 cm^{-1} (R) may be assigned to a skeletal deformation mode, but the possibility that it is a low-frequency bridge mode cannot be discounted in the absence of the necessary deuteride data.

The remaining observed fundamentals lie in the region 1000—1300 cm^{-1}. For a number of zirconium hydride compounds containing Zr–H(D)–Zr bridges, Wailes and Weigold[17] assigned frequencies from 1240 to 1520 cm^{-1} and 905 to 1100 cm^{-1} to Zr–H and Zr–D bridge stretches respectively. It is probable that in the Raman spectrum of $Zr(BH_4)_4$ the totally symmetric mode at 1285 cm^{-1} can be described as a Zr–H stretch in a Zr–H–B bridge. In the spectrum of solid $Be(BH_4)_2$, bands at 1543 cm^{-1} and 1440 cm^{-1} were interpreted as Be–H stretches in a Be–H–B bridge, though a ^{11}B–^{10}B isotope effect in the former band was taken to indicate substantial mixing of the totally symmetric bridge modes.[11]

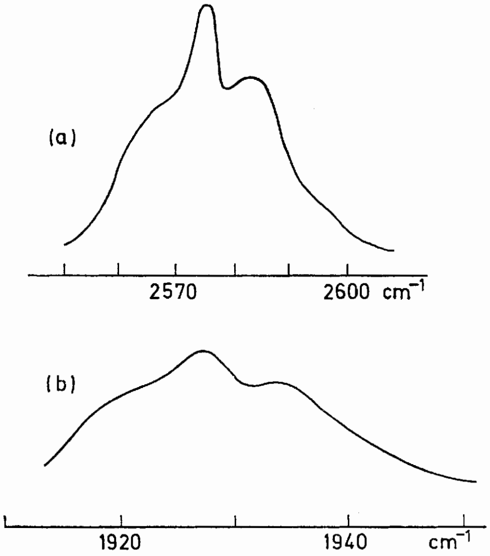

FIGURE 2 Feature of i.r. spectrum of (a), $Zr(BH_4)_4$; (b), $Zr(BD_4)_4$

All sharp hydride and deuteride i.r. bands show rotational fine structure of the *PQR* type. Where the modes concerned involve significant motion of the boron atom, the band contours are expected to be affected by the natural occurrence of ^{10}B and ^{11}B isotopes in the molecule. Table 4 shows the natural abundances of the isotopic species $Zr^{11}B_n{}^{10}B_{4-n}$, where ^{11}B and ^{10}B are assumed to have the natural abundances 81·17 and 18·83% respectively. The qualitative effect of substituting ^{10}B for ^{11}B is to shift the mode to higher frequency. Thus the 2575 cm^{-1} hydride i.r. band displayed a high-frequency asymmetry [Figure 2(a)] which persisted in the Nujol solution spectrum and is also apparent in the corresponding deuteride 1927 cm^{-1} band [Figure 2(b)], and an asymmetry in the deuteride band at 1545 cm^{-1} is similarly ascribed to the boron isotope effect. These observations are consistent with our descriptions of these modes as B–H(D) stretching frequencies. Analogous effects have been observed for boron isotope-labelled diboranes.[18] The 1218 cm^{-1} hydride and 922 cm^{-1} deuteride bands occur in the regions expected for Zr–H(D) stretching [*cf.* 1285 cm^{-1} (R) and ref. 17]. It is interesting that neither band shows any evidence of a boron isotope effect. The Zr–B stretching frequencies would also be expected to show significant ^{11}B–^{10}B shifts. However, the band contours could not be ascertained reliably owing to interference from absorption due to the potassium bromide cell windows.

TABLE 4

Natural abundances (%) of isotopic species $M^{11}B_n{}^{10}B_{4-n}$

$M^{11}B_4$	43·4	$M^{11}B^{10}B_3$	2·2
$M^{11}B_3{}^{10}B$	40·3	$M^{10}B_4$	0·0
$M^{11}B_2{}^{10}B_2$	14·0		

Possible assignments made so far are summarized in Tables 1 and 3. The number and symmetries of fundamentals observed correspond well with the predictions for a T_d structure, as listed in Table 5. A reasonable assignment of four A_1, seven T_2, and two E fundamentals has been given. This represents the first reinterpretation of the vibrational spectra of the $M(BH_4)_4$ molecules in terms consistent with the triply bridged structure.

TABLE 5

Number and symmetries of fundamentals for T_d molecules, $M(BH_4)_4$

Approximate descriptions	Number and symmetries of fundamentals	
	Expected [a]	Observed [b]
νB–H$_t$	$A_1 + T_2$	$A_1 + T_2$
νB–H$_b$	$A_1 + E + 2T_2 + T_1$	$A_1 + E + 2T_2$
νM–H$_b$	$A_1 + E + 2T_2 + T_1$	$A_1 + T_2$
νM–B	$A_1 + T_2$	$A_1 + T_2$
δMB_4	$E + T_2$	T_2
τMBH_4	$A_2 + T_1$	
Additional	$2E + 2T_2 + 2T_1$	$E + T_2$ [c]

[a] A_2 and T_1 modes are i.r.- and Raman-inactive. [b] See Tables 1 and 3 for observed frequencies. [c] 1077 cm^{-1} (R) and 1034 cm^{-1} (i.r.) respectively.

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