Infrared Spectra of ZrH_4 and HfH_4 in Solid Argon

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One of the most interesting characteristics of third-row transition metal chemistry is lanthanide contraction where the 4f subshell electrons are contracted by the additional nuclear charge with the well-known result of decreasing atomic size. This is dramatically illustrated in the chemistry of Ti, Zr, and Hf where oxide frequencies decrease from Ti and Zr and are essentially unchanged for Hf.[1] In addition, the bonds to heavy atoms are shortened by relativistic effects.[2–5] The tetrahydrides have been examined theoretically, and slightly shorter bonds are predicted for tetrahedral HfH_4 (190.7 pm) than for ZrH_4 (191.2 pm) including the relativistic bond-length contraction.[2,3] The heavy transition metal tetrahydrides are good subjects for experimental verification of the predicted bond-length contraction as revealed by vibrational frequencies since there is little heavy metal atom contribution to the reduced mass of the vibration.

Pulsed-laser ablation has proven to be an effective method for producing metal atoms for reaction with hydrogen where some activation energy is required for the metal atom insertion reaction with hydrogen. The metal dihydride molecules so produced are then trapped in solid argon for infrared spectroscopic examination. Cases in point include Al, Ti, Be, and Mg.[6–9] The experimental methods have been described[10,11] and are essentially the same as used for Ti and H_2 studies.[7]

Figure 1 contrasts the spectra for Zr and Hf reacting with isotopic hydrogen samples in the stretching regions of interest here. Table 1 collects the absorption band positions. The strongest absorption in Zr/H_2 experiments at 1623.6 cm^{-1} shifts to 1166.6 cm^{-1} with D_2. Although water contributes to absorptions in the 1600 cm^{-1} region, the weak 1589.9 cm^{-1} water band shows that water makes only a minor contribution to the 1623.6 cm^{-1} band. The most important observation is *four product bands* at 1656.4, 1623.7, 1183.1, and 1167.4 cm^{-1} in the Zr/HD reaction, which increase together on broad-band photolysis and decrease together on annealing to 30–40 K.

Likewise the strongest absorption at 1678.4 cm^{-1} in Hf/H_2 experiments shifts to 1201.7 cm^{-1} with D_2. Again *four product bands* were observed for the HD reaction, with Hf now at 1706.7, 1677.2, 1219.3, and 1203.0 cm^{-1}. The same four bands were observed for H_2–D_2 mixtures.

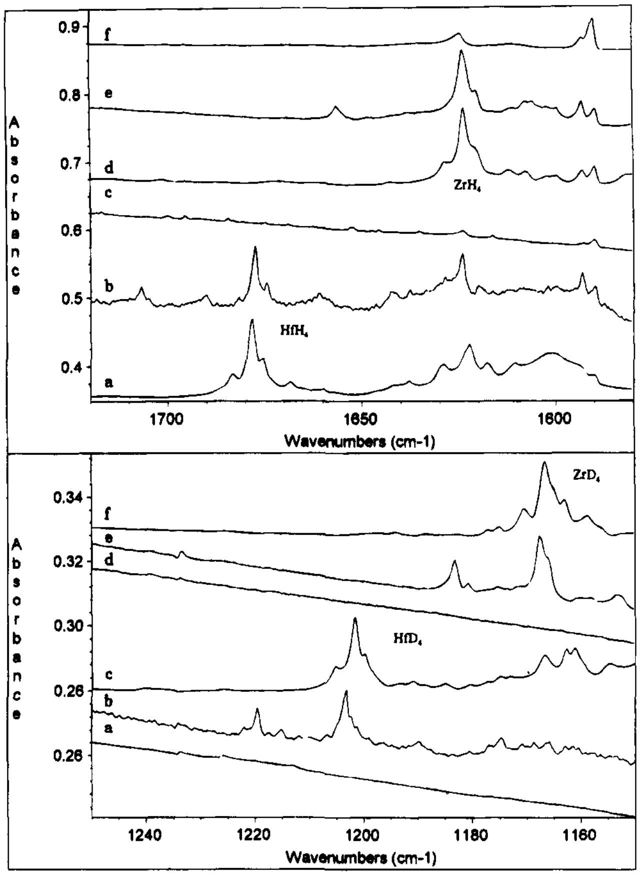

Figure 1. Infrared spectra in the 1720-1580 and 1250-1150 cm^{-1} regions for reactions of pulsed-laser-ablated metal atoms with hydrogen (5%) in argon during condensation at 10 K. (a) Hf + H_2, (b) Hf + HD, (c) Hf + D_2, (d) Zr + H_2, (e) Zr + HD, and (f) Zr + D_2.

Table 1. Absorptions (cm^{-1}) Observed for Zirconium and Hafnium Tetrahydrides in Metal Atom Reactions with Isotropic Hydrogen Molecules

	H_2	D_2	HD[a]	assignment
Zr			1656.4	sym Zr–H_2
	1623.6		1623.7	antisym Zr–H_2
			1183.1	sym Zr–D_2
		1166.6	1167.4	antisym Zr–D_2
Hf			1706.7	sym Hf–H_2
	1678.4		1677.2	antisym Hf–H_2
			1219.3	sym Hf–D_2
		1201.7	1203.0	antisym Hf–D_2

[a] Same bands observed for H_2–D_2 mixtures.

The strongest 1623.6 and 1678.4 cm^{-1} bands are assigned to the triply-degenerate antisymmetric Zr–H and Hf–H stretching fundamental of the tetrahedral ZrH_4 and HfH_4 molecules, respectively. The H/D ratios 1.3917 and 1.3967, respectively, reveal the slightly decreased participation of the heavier metal atom in the vibrational mode. The two pairs of strong bands in the HD reactions are assigned to symmetric and antisymmetric MH_2 and MD_2 stretching fundamentals in the ZrH_2D_2 and HfH_2D_2 molecules of C_{2v} symmetry with four active stretching modes. Note that the stronger antisymmetric stretching mode in each pair agrees (within 1.3 cm^{-1}) with the antisymmetric mode for the MH_4 and MD_4 molecules, and that the new symmetric MH_2 stretching counterpart is higher by 32.7 cm^{-1} for ZrH_2D_2 and by 28.3 cm^{-1} for HfH_2D_2. These small symmetric–antisymmetric mode separations show that there is little stretch–stretch interaction through the heavy metal atom, which is even less for Hf than for Zr. The observation of four metal–hydrogen (deuterium) stretching modes for the metal atom–HD reaction products, also observed with H_2–D_2 mixtures, confirms the metal tetrahalide identification.

Like titanium,[7,12] the reaction of Zr and Hf atoms with H_2 requires activation energy, which is provided by excess kinetic energy in the laser-ablated metal atoms.[13,14] Broad-band photolysis also increased the yield of products. Other weaker

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absorptions will be identified as MH_3 and MH_2 species in a later publication with supporting ab initio calculations. The highly exothermic reaction of ZrH_2 with H_2 has been predicted by electronic structure calculations,[15] which underscore the stability of ZrH_4 and its observation in the present reaction system.

Several comparisons in the Ti, Zr, and Hf hydride family are noteworthy. For Ti, the major product is TiH_2 and not TiH_4;[7,12] TiH_3 was a more significant product than TiH_4.[7] Such is not the case with Zr and Hf: the tetrahydrides dominate the product spectrum, and the trihydrides are weaker than the dihydrides. These trends are expected from the increased stability of the higher oxidation states for the heavier transition metals. Finally, the antisymmetric metal–hydrogen stretching fundamental decreases from 1663.8 cm^{-1} for TiH_4 to 1623.6 cm^{-1} for ZrH_4 and then increases to 1678.4 cm^{-1} for HfH_4. The higher fundamental for HfH_4 is due to the larger relativistic bond-length contraction for Hf predicted by Pyykko et al.,[3] which leads to the close chemical similarity of Zr and Hf.

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