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Dissociation Potential Curves of Low-Lying States in Transition Metal Hydrides. I. Hydrides of Group 4

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The dissociation energy curves of low-lying spin-mixed states for Group 4 hydrides, TiH, ZrH, and HfH, have been calculated using both effective core potential and all-electron approaches. A comprehensive set of theoretical results including the dissociation energies, equilibrium distances, harmonic frequencies, anharmonicities, rotational constants, and dipole moments are reported for these molecules. We present results for both ground and a few excited states, filling a considerable gap in available data for these molecules. Absorption spectra are also predicted on the basis of the results. The present study uses three methods, all based on the multiconfigurational self-consistent field (MCSCF) method, augmented by second-order configuration interaction (SOCI), with either an effective core potential basis set (SBKJC) or a double-ζ basis set (MIDI): (*i*) MCSCF+SOCI/SBKJC(f,p) with a one-electron approximation using effective nuclear charges, (*ii*) MCSCF+SOCI/MIDI(3p,3p) with the full Breit−Pauli Hamiltonian, and (*iii*) MCSCF +SOCI/MIDI(3p,3p) with the relativistic elimination of the small component scheme and full Breit−Pauli Hamiltonian. The results are compared with previous theoretical studies and available experimental data reported previously. Good agreement is obtained between the results obtained when the first and third methods are used.

1. Introduction

The electronic spectra of simple transition metal-containing molecules provide the necessary data required to understand the role of d electrons in chemical bond formation.[1−24] Transition metal-containing molecules are also of astrophysical importance, and several transition metal oxides and hydrides have been observed in the spectra of the sun and other stars.[1−13] Furthermore, diatomic transition metal hydrides also serve as useful models for the study of metal−hydrogen bonding in inorganic chemistry[14] and in surface science,[15,16] and have important practical applications in heterogeneous catalysis[17−19] where, e.g., hydrocarbons are hydrogenated or re-formed. In recent years, an increasing number of theoretical and experimental studies on transition metal-containing molecules have been reported,[20−24] and several review papers have been published on the oxides and the hydrides.[22−24] For theoreticians, prediction of the spectroscopic properties of these molecules has been challenging, because the molecules possess numerous closely packed electronic states with high spin multiplicities and large orbital angular momenta. Consequently, both relativistic and electron correlation effects need to be taken into account in ab initio molecular orbital studies of these molecules.

Because of recent advances in theory and code development, it is becoming straightforward to estimate the effects of electron correlation with such methods as perturbation theory, configuration interaction, multiconfiguration self-consistent field, coupled clusters, and their combined methods. It has become possible to estimate the effects of both static and dynamic correlation even in large molecular systems. Many theoretical studies reveal the general features of correlation effects, and useful empirical correction methods[25−28] have been proposed, to avoid performing full configuration interaction calculations.

The relativistic effective core potential (RECP) method, an extension of the nonrelativistic effective core potential (ECP) approach, has been reviewed by Krauss and Stevens.[29] In the present series of investigations on relativistic effects, an ECP-based method using the Breit−Pauli Hamiltonian (BPH)[30] has been chosen for the estimation of spin−orbit coupling effects. Initially, only the one-electron parts of the BPH were calculated, to simplify the computations. In those calculations, effective nuclear charges Z_{eff} were used for the second- through sixth-row main group elements[31a,b,d] and for the first- through third-row transition elements[31e] to approximately account for the missing two-electron components of the BPH. The Z_{eff} values were chosen to reproduce experimental spin−orbit splittings of low-lying states in diatomic main-group hydrides or spectral terms of atomic transitions. This one-electron Z_{eff} method generally results in errors on the order of 30% or less, and seems to be less useful for transition elements than for main-group elements, mainly because nodeless orbitals are used for 4d and 5d orbitals and partly because the shapes of atomic orbitals are different in each atomic state.

Recently, Fedorov and Gordon developed the methodology for calculating the two-electron parts of the BPH and investigated their effects on several diatomic and triatomic molecules by using all-electron (AE) basis sets.[32] Full BPH studies on transition elements have been performed by these methods with both AE and ECP basis sets.[31e] This analysis revealed that ECP basis sets are apparently inappropriate in full BPH studies

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TABLE 1: Numbers of Configuration State Functions Used in MCSCF+SOCI Calculations, and Numbers of Adiabatic States Included in Spin−Orbit Coupling Matrixes[a]

			TiH			ZrH			HfH		
sym[b]	CSFs	total	ECP	AE	AE (RESC)	ECP	AE	AE (RESC)	ECP	AE	AE (RESC)
$^2A_1$	23 325		6	6	6	6	7	6	11	10	11
$^2A_2$	22 726		6	6	6	6	8	6	11	11	11
$^2B_1$	22 987		6	6	6	6	8	6	11	10	11
$^2B_2$	22 987	92 025	6	6	6	6	8	6	11	10	11
			24	24	24	24	31	24	44	41	44
$^4A_1$	15 708		7	5	6	4	5	4	8	9	7
$^4A_2$	16 004		11	7	9	8	11	8	11	12	9
$^4B_1$	15 878		10	7	8	7	10	7	11	12	9
$^4B_2$	15 878	63 468	10	7	8	7	10	7	11	12	9
			38	26	31	26	36	26	41	45	34
$^6A_1$	3 042		6	4	5	3	3	3	3	5	2
$^6A_2$	3 160		8	4	6	5	6	5	5	6	3
$^6B_1$	3 070		7	4	5	4	5	4	4	6	2
$^6B_2$	3 070	12 342	7	4	5	4	5	4	4	6	2
			28	16	21	16	19	16	16	23	9

[a] An energy tolerance for state selection is set to 92 (TiH), 75 (ZrH), or 88 (HfH) mhartree in the dissociation limit. The estimated errors caused by the state selection are about 1 (TiH), 21 (ZrH), and 288 (HfH) cm^{-1}, respectively, on the basis of perturbation theory by using the largest matrix elements. [b] Molecular symmetry (sym) is set to C_{2v}, instead of $C_{\infty v}$.

TABLE 2: Spectroscopic Parameters in the Low-lying States of TiH[a]

state	method	D_e	R_e	ω_e	$\chi_e\omega_e$	B_e	α_e	μ	ref
$^4\Phi$	ECP	13 335	1.852	1471	25.59	5.08	0.22	1.823	
	AE	15 083	1.862	1504	20.2	5.01	0.19	1.855	
	AE (RESC)	12 832	1.873	1444	13.8	4.95	0.19	1.714	
$\Omega = 3/2$	ECP	13 277	1.852	1471	25.59	5.08	0.22		
	AE	15 037	1.862	1511	24.61	4.99	0.17		
	AE (RESC)	12 786	1.873	1444	13.96	4.95	0.19		
	expt	12 906						0.987	44
	expt	16 778							45
		15 809							
	expt			1385					46
	ECP	13 713	1.905	1331					47
	AE	17 100	1.83	1407					48a
	AE	15 326	1.781	1407					48b
		−17 100							
	AE	14 922							49
	AE	15 810	1.789	1572					48c−e
		17 157	1.784	1543				0.881	
	AE	15 406	1.836	1498	22.2	5.08	0.12		50
	AE	16 616	1.82	1548				2.19	51
	AE		1.849	1471					46
	AE	21 020	1.744	1601					52
$\Omega = 5/2$	ECP	13 174	1.852	1471	25.6	5.08	0.22		
	AE	14 953	1.863	1521	25.04	4.98	0.17		
	AE (RESC)	12 706	1.873	1444	13.85	4.95	0.19		
$\Omega = 7/2$	ECP	13 233	1.852	1471	25.6	5.08	0.22		
	AE	14 966	1.873	1602	11.22	4.97	0.27		
	AE (RESC)	12 752	1.873	1444	13.82	4.95	0.19		
$\Omega = 9/2$	ECP	13 340	1.851	1471	25.59	5.08	0.22		
	AE	15 087	1.862	1506	20.29	5.01	0.19		
	AE (RESC)	12 837	1.872	1444	13.79	4.95	0.19		

[a] D_e is the dissociation energy (cm^{-1}) corrected for the zero-point vibrational energy. R_e is the equilibrium internuclear distance ((angstrom) obtained as the expectation value of the lowest vibrational state. ω_e (cm^{-1}) and $\chi_e\omega_e$ (cm^{-1}) are the harmonic frequency and anharmonicity, and B_e (cm^{-1}) and α_e (cm^{-1}) are rotational constants. The dipole moment μ is in Debye. These properties were obtained by using a root-mean-square fit to the energies of the lowest vibrational states obtained by the discrete variable representation (ref 53).

because of the use of nodeless orbitals. In addition, it was concluded that in AE calculations, scalar relativistic corrections, such as those provided by the relativistic elimination of the small component (RESC) or normalized elimination of the small component[34] methods, are needed to obtain reasonable energetic ordering of low-lying adiabatic states before the inclusion of spin−orbit effects. In this study, we examine the reliability and capability of the Z_{eff} method and the AE method with the RESC scheme by applying these methods to the study of several properties of transition metal hydrides. These properties include the relativistic dissociation energy curves and several spectroscopic parameters in low-lying electronic states of the Group 4 hydrides (TiH, ZrH, and HfH).

2. Methods of Calculation

Both ECP and AE calculations have been performed by using multiconfiguration self-consistent field (MCSCF) wave functions[35] followed by second-order configuration interaction (SOCI) calculations.[36] The MCSCF active space includes the orbitals corresponding to the *n*d and $(n + 1)$sp orbitals of the transition elements and the 1s orbital of hydrogen. The orbitals were optimized by using the state-averaged MCSCF approach with equal weight for the lowest four states: $^4\Sigma$, $^4\Pi$, $^4\Delta$, and $^4\Phi$ in TiH, $^2\Sigma$, $^2\Pi$, $^2\Delta$, and $^2\Phi$ in ZrH and HfH.[37] These states correlate with the ground state (^3F) of the metal atom $(nd)^2[(n + 1)s]^2$ ($n = 3$, 4, and 5) in the dissociation limit.

TABLE 3: Spectroscopic Parameters in the Low-lying Spin-mixed States of ZrH[a]

state	method	D_e	R_e	ω_e	$\chi_e\omega_e$	B_e	α_e	μ	ref
$^2\Delta$	ECP	16 798	1.883	1634	27.81	4.86	0.18	0.845	
	AE	17 963	1.864	1433	6.54	4.95	0.19	1.064	
	AE (RESC)	16 980	1.887	1583	17.47	4.83	0.16	0.768	
$\Omega = 3/2$	ECP	16 456	1.883	1646	38.23	4.88	0.2		
	AE	18 240	1.916	1332	5.71	4.71	0.17		
	AE (RESC)	16 682	1.887	1587	19.13	4.83	0.17		
	AE	19 762	1.857	1483				1.23	51
	AE	19 586	1.86						57
	RECP	21 294 −23 392	1.77	1777					54
	RECP	19 923	1.811	1784					55
	RECP	18 152							58
	ECP	17 872	1.852						58
	ECP		1.823	1591					59
$\Omega = 5/2$	ECP	15 742	1.884	1632	41.48	4.86	0.21		
	AE	17 904	1.923	1368	5.76	4.61	0.13		
	AE (RESC)	16 058	1.887	1591	21.98	4.84	0.18		
	RECP		1.77	1779					54
	RECP		1.811	1817					55
$\Omega = 3/2$	ECP	15 121	1.94	1433	18.25	4.61	0.14		
	AE	17 587	1.89	1504	29.03	4.78	0.18		
	AE (RESC)	14 186	1.943	1252	2.73	4.58	0.15		
	RECP		1.82	1604					54
	RECP		1.897	1569					55
$\Omega = 1/2$	ECP	14 715	1.883	1466	27.11	4.87	0.2		
	AE	17 317	1.916	1320	6.61	4.73	0.19		
	AE (RESC)	14 132	1.893	1457	21.33	4.78	0.19		
	RECP		1.78	1740					54

[a] See the footnote to Table 2.

TABLE 4: Spectroscopic Parameters in the Low-lying Spin-mixed States of HfH[a]

state	method	D_e	R_e	ω_e	$\chi_e\omega_e$	B_e	α_e	μ	ref
$^2\Delta$	ECP	19 715	1.875	1605	24.34	4.87	0.19	0.752	
	AE	22 177	1.884	1594	19.43	4.82	0.13	0.884	
	AE (RESC)	25 419	1.847	1534	12.68	4.95	0.11	0.758	
$\Omega = 3/2$	ECP	18 378	1.876	1590	23.58	4.87	0.19		
	AE	21 004	1.884	1581	19.66	4.82	0.13		
	AE (RESC)	24 306	1.847	1532	13.28	4.95	0.11		
	expt		1.831			5.02	0.12		63
	AE	22 818	1.857						64
	AE	24 584	1.857						
	RECP	22 585	1.854	1704				0.66	61
	RECP	23 231	1.852						62
	RECP	22 521	1.852						64
	RECP	24 343	1.852						
	ECP		1.835	1682					65
$\Omega = 1/2$	ECP	16 153	1.864	1578	24	4.96	0.2		
	AE	18 226	1.885	1469	20.83	4.82	0.15		
	AE (RESC)	20 873	1.835	1522	20	5.02	0.11		
	RECP		1.853	1651				0.81	61
$\Omega = 5/2$	ECP	15 195	1.875	1605	24.64	4.87	0.19		
	AE	17 809	1.89	1585	29.27	4.81	0.16		
	AE (RESC)	21 645	1.847	1536	13.04	4.95	0.11		
	RECP		1.853	1701				0.67	61
$\Omega = 3/2$	ECP	14 257	1.862	1596	24.13	4.94	0.2		
	AE	17 449	1.952	1454	27.34	4.5	0.12		
	AE (RESC)	19 353	1.835	1525	19.2	5.02	0.11		
	RECP		1.855	1654				0.89	61

[a] See the footnote to Table 2.

The MCSCF-optimized orbitals were used in SOCI calculations to construct doublet, quartet, and sextet wave functions and to estimate spin−orbit couplings among these wave functions. The external space of the SOCI calculations includes one set of transition element virtual d, s, and p orbitals and one set of hydrogen s and p orbitals, where these external orbitals are the lowest eigenvectors of the standard MCSCF Fock operator. The total numbers of configuration-state functions (CSFs) in the SOCI calculations are 92 025, 63 468, and 12 342 for doublets, quartets, and sextets, respectively. The spin−orbit coupling matrixes were constructed on the basis of the lowest SOCI states. The number of states used for each molecule is given in Table 1. All states within a certain energy range were included; thus, the number of states varied slightly for each method (see Table 1, footnote *a*). For each molecule, the ground state within the L−S coupling scheme and the lowest spin-mixed Ω states are given in Tables 2−4, where Ω is the *z* component of the total angular momentum quantum number.

The ECP calculations used the SBKJC basis set,[38] augmented by a set of f functions[39a] for transition metal elements and the 31G basis set augmented by a set of p functions for hydrogen.[39b] With use of the SOCI wave functions, the spin−orbit splittings of low-lying states were estimated within the Z_{eff} approximation.[31e,40] This method is referred to simply as ECP in the following discussion.

The AE calculations used the MIDI basis set[41] augmented by three sets of $(n + 1)$p functions in both the transition element and hydrogen;[42] this is referred to as MIDI(3p,3p). The MCSCF

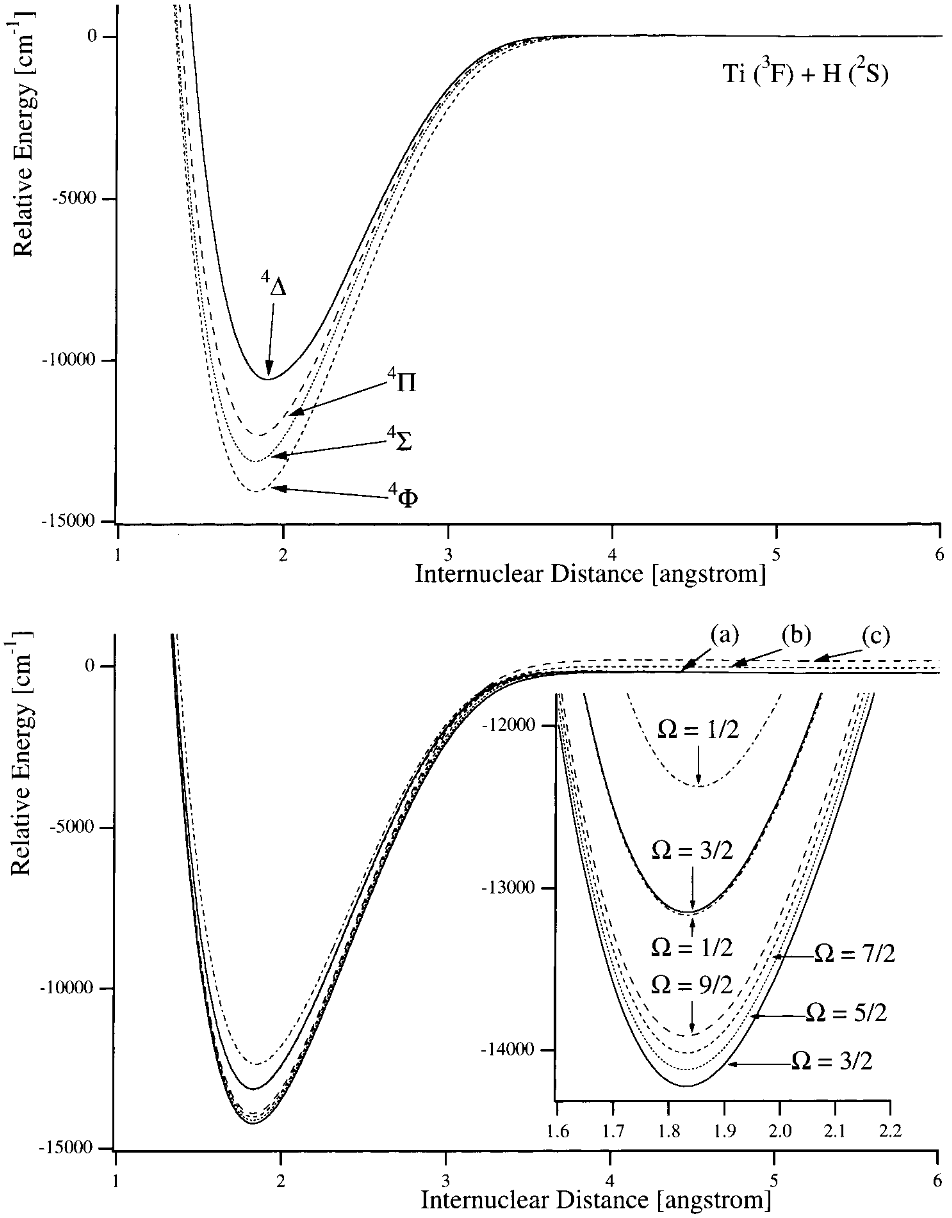

Figure 1. Potential energy curves in TiH obtained by using quartet MCSC+SOCI/SBKJC(f,p) wave functions. (top) Low-lying adiabatic states; (bottom) low-lying spin-mixed states. The dissociation limits are (a) Ti($^3F_2$) + H($^2S_{1/2}$); (b) Ti($^3F_3$) + H($^2S_{1/2}$); and (c) Ti($^3F_4$) + H($^2S_{1/2}$). The inset is a closeup view near the energy minima.

orbitals were optimized by two different methods: without relativistic corrections and with the RESC scheme.[33] Spin−orbit configuration interaction matrixes were constructed by using the SOCI wave functions and BPH including both one- and two-electron terms. These methods are referred to simply as AE and AE (RESC), respectively.

All calculations have been performed using the GAMESS suite of program codes.[43]

3. Results and Discussion

Potential Energy Curves Obtained by the ECP Method. Within the adiabatic scheme with the ECP method, the ground state is $^4\Phi$ in TiH, and $^2\Delta$ in both ZrH and HfH. The R_e in these adiabatic ground states are calculated to be 1.852 Å in TiH, 1.883 Å in ZrH, and 1.875 Å in HfH, respectively (Tables 2−4). The dissociation energies from these ground states are estimated to be 13 335 (TiH), 16 798 (ZrH), and 19 715 (HfH) cm^{-1}. The first excited state is $^4\Sigma$ in TiH and the 0−0 $^4\Phi$−$^4\Sigma$ energy gap is only 927 cm^{-1}. The corresponding state and gap are calculated to be $^4\Phi$ and 1464 cm^{-1} ($^2\Delta$ −$^4\Phi$) in ZrH, and $^2\Pi$ and 1199 cm^{-1} ($^2\Delta$ −$^2\Pi$) in HfH. These adiabatic energy splittings are fairly small. Because the spin−orbit splittings in the ^{3}F ground state of the transition elements ($^3F_2$ − $^3F_3$ and $^3F_2$ − $^3F_4$) in the dissociation limit are calculated to be 163 and 379 cm^{-1} in atomic Ti, 572 and 1269 cm^{-1} in Zr, and 2616 and 5163 cm^{-1} in Hf,[31e,f] the energetic order of spin-mixed states near R_e is expected to be affected strongly by the spin−orbit splittings. Note that the leading configuration in the Ti, Zr, and Hf ^{3}F ground states is $(nd)^2[(n + 1)s]^2$ (n = 3, 4, 5).

Figures 1−3 illustrate potential energy curves of low-lying spin-mixed states in the hydrides. A few low-lying adiabatic states are included in the top of each figure for comparison. The inset to the right in each of the bottom figures is an enlargement of the region near R_e. The lowest spin-mixed state near R_e has Ω = 3/2, even though the leading electronic configuration at R_e is different in the three hydrides.

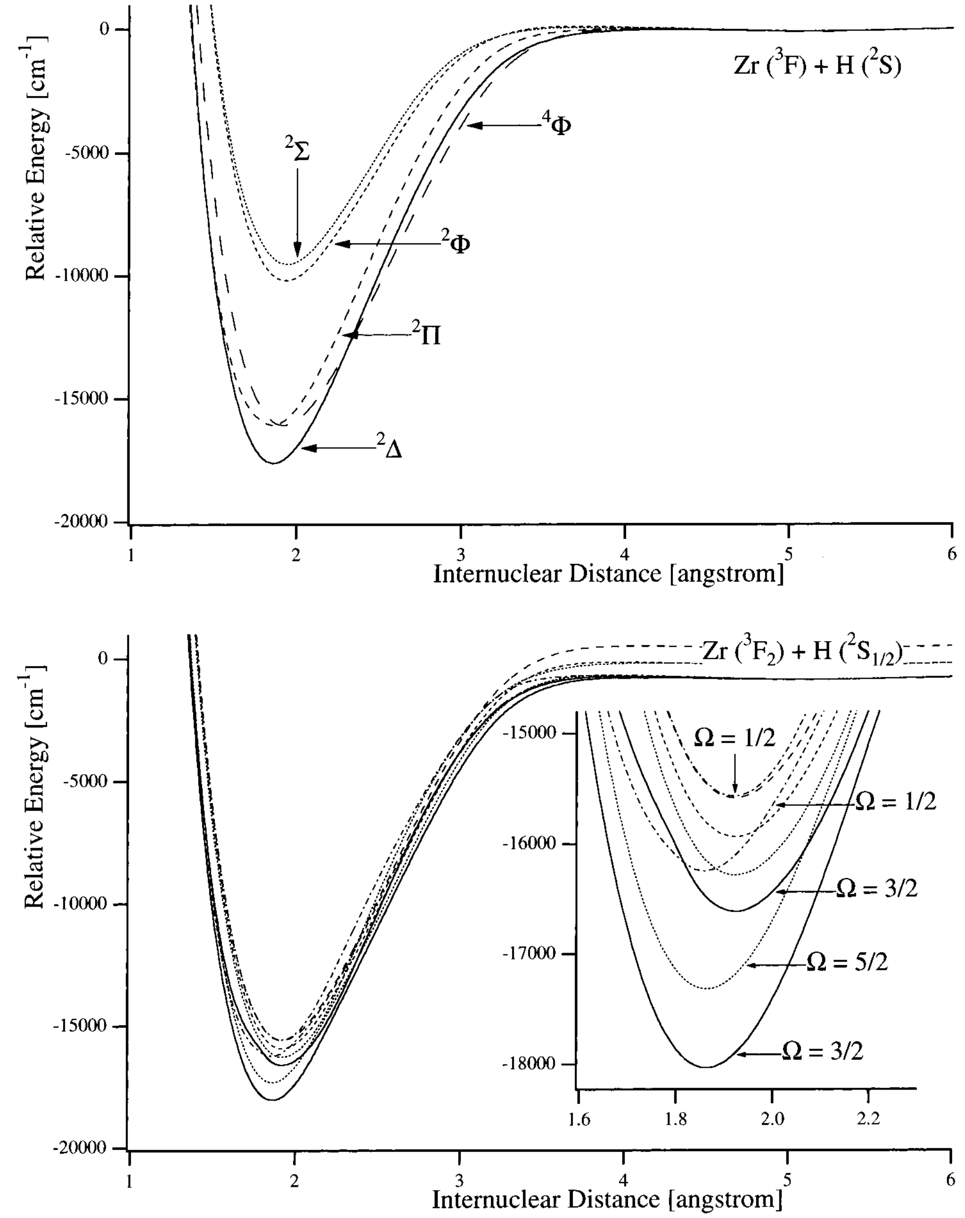

Figure 2. Potential energy curves in ZrH obtained by using doublet MCSC+SOCI/SBKJC(f,p) wave functions. (top) Low-lying adiabatic states; (bottom) low-lying spin-mixed states. The inset is a closeup view near the energy minima.

Before the inclusion of spin−orbit effects, the lowest TiH $^4\Phi$ state has total occupation numbers of 2.99, 1.01, and 1.00 for the valence σ, π, and δ orbitals, and the Mulliken populations are 2.35 (3d), 0.95 (4s), and 0.48 (4p), respectively. After the spin−orbit coupling effects are considered, the four lowest spin-mixed TiH states have >99% contributions from $^4\Phi_{3/2}$, $^4\Phi_{5/2}$, $^4\Phi_{7/2}$, and $^4\Phi_{9/2}$, respectively (Table 5), and the $^4\Phi_{5/2}$−$^4\Phi_{3/2}$, $^4\Phi_{7/2}$−$^4\Phi_{3/2}$, and $^4\Phi_{9/2}$−$^4\Phi_{3/2}$ energy splittings are 103, 208, and 314 cm^{-1}. The lowest two spin-mixed states (Ω = 3/2 and 5/2; Figure 1) correlate with the lowest state in the dissociation limit, Ti ($^3F_2$) and H ($^2S_{1/2}$). The third state (Ω = 7/2) dissociates to the higher [Ti ($^3F_3$) + H ($^2S_{1/2}$)] state, and the fourth spin-mixed TiH state (Ω = 9/2) dissociates to Ti ($^3F_4$) + H ($^2S_{1/2}$).

The spin−orbit mixing is complicated in ZrH (Figure 2). The mixing occurs mainly among the lowest $^2\Delta$, $^2\Pi$, and $^4\Phi$ states. As shown in Table 5, the lowest Ω = 3/2 state has 96% contribution from $^2\Delta_{3/2}$ and 3% from $^2\Pi_{3/2}$, whereas the lowest Ω = 5/2 state has almost 100% contribution from $^2\Delta_{5/2}$. Other low-lying excited states are Ω = 3/2 ($^4\Phi_{3/2}$, >99%), Ω = 1/2 ($^2\Pi_{1/2}$, 97%), Ω = 5/2 ($^4\Phi_{5/2}$, >99%), Ω = 3/2 ($^2\Pi_{3/2}$, 89%), and Ω = 7/2 ($^4\Phi_{7/2}$, >99%) in energetic order. These five states appear in a small 700-cm^{-1} energy range. The ground state (Ω = 3/2) R_e = 1.883 Å is almost unchanged by spin−orbit coupling effects. Spin−orbit coupling slightly decreases the dissociation energy (16 798−16 456 cm^{-1}). The spin−orbit splittings are 717 cm^{-1} ($^2\Delta_{3/2}$−$^2\Delta_{5/2}$), 1050 cm^{-1} ($^4\Phi_{3/2}$−$^4\Phi_{9/2}$), and 286 cm^{-1} ($^2\Pi_{1/2}$−$^2\Pi_{3/2}$). The first two splittings are 20−30% larger than those obtained by Balasubramanian et al.[54] Without the spin−orbit effects, the dipole moments [0.85 D ($^2\Delta$) and 2.28 D ($^4\Phi$)] are comparable with those reported in refs 55 and 56. The occupation numbers are computed to be 2.99 (σ), 1.01 (π), and 1.00 (δ) in the $^4\Phi$ state, and 3.73 (σ), 0.19 (π), and 1.07 (δ) in the $^2\Delta$ state. The atomic-orbital populations are 2.66 (4d), 0.80 (5s), and 0.37 (5p) in the $^4\Phi$ state, and 2.32 (4d), 1.10 (5s), and 0.47 (5p) in the $^2\Delta$ state. Because the ground state (Ω = 3/2) is 96% $^2\Delta$, its chemical properties should be almost equal to those of the adiabatic $^2\Delta$ state.

In HfH, strong spin−orbit coupling is observed between the lowest $^2\Delta$ and $^2\Pi$ states, because the adiabatic states are close

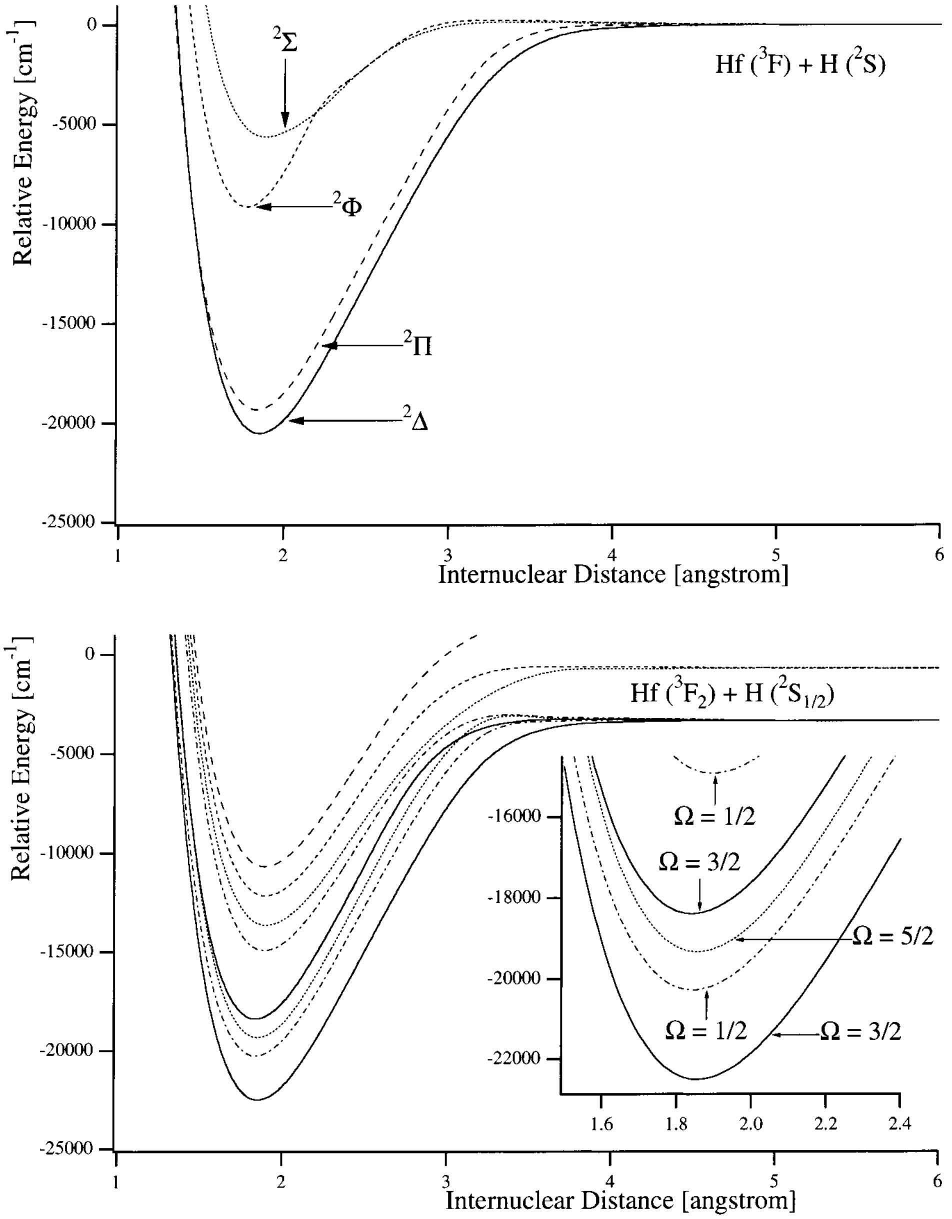

Figure 3. Potential energy curves in HfH obtained by using doublet MCSC+SOCI/SBKJC(f,p) wave functions. (top) Low-lying adiabatic states; (bottom) low-lying spin-mixed states. The inset is a closeup view near the energy minima.

TABLE 5: Percentages of MCSCF+SOCI/SBKJC(f,p) Adiabatic States in Low-lying Spin-mixed States

mol.	W	energy (cm^{-1})	components
TiH	3/2	0	$^4\Phi_{3/2}$ (>99%)
	5/2	103.4	$^4\Phi_{5/2}$ (>99%)
	7/2	208.0	$^4\Phi_{7/2}$ (>99%)
	9/2	313.8	$^4\Phi_{9/2}$ (>99%)
ZrH	3/2	0	$^2\Delta_{3/2}$ (96%), $^2\Pi_{3/2}$ (3%)
	5/2	717.4	$^2\Delta_{5/2}$ (>99%)
	3/2	1560.5	$^4\Phi_{3/2}$ (>99%)
	1/2	1788.1	$^2\Pi_{1/2}$ (97%), $^2\Sigma_{1/2}$ (2%)
	5/2	1891.4	$^4\Phi_{5/2}$ (>99%)
	3/2	2073.8	$^2\Pi_{3/2}$ (89%), $^2\Sigma_{1/2}$ (6%), $^2\Delta_{3/2}$ (3%)
	7/2	2233.5	$^4\Phi_{7/2}$ (>99%)
HfH	3/2	0	$^2\Delta_{3/2}$ (86%), $^2\Pi_{3/2}$ (14%)
	1/2	2241.2	$^2\Pi_{1/2}$ (94%), $^2\Sigma_{1/2}$ (5%)
	5/2	3179.4	$^2\Delta_{5/2}$ (>99%)
	3/2	4131.6	$^2\Pi_{3/2}$ (84%), $^2\Delta_{3/2}$ (14%)

in energy to each other (the main picture in Figure 3). The calculated results show that the lowest spin-mixed state is 86% $^2\Delta_{3/2}$ and 14% $^2\Pi_{3/2}$ near R_e (see Table 5). On the other hand, the lowest Ω = 5/2 state has $^2\Delta_{5/2}$ character of more than 99% because no other Ω = 5/2 state is close in energy to this state. Even though the spin−orbit splitting of the $^2\Delta$ state in HfH is calculated to be about 3200 cm^{-1}, R_e is almost unchanged by spin−orbit coupling effects (Table 4: 1.875−1.876 Å). The dissociation energy from the lowest spin-mixed state decreases somewhat (19 715−18 378 cm^{-1}), because the spin−orbit lowering near R_e is smaller than that in the dissociation limit.[60] The first excited spin-mixed state is Ω = 1/2 with leading configuration $^2\Pi_{1/2}$ (94%). The largest component of the third state is $^2\Delta_{5/2}$. The large spin−orbit splitting of the $^2\Delta$ state and the small energy difference between the lowest $^2\Delta$ and $^2\Pi$ states leads to the energetic order Ω = 3/2 < 1/2 < 5/2. Note that the spin−orbit coupling constants of the $^2\Delta$ and $^2\Pi$ states of HfH are estimated to be 3179 and 1890 cm^{-1}, respectively, at the energy minimum of the lowest spin-mixed state. The corresponding splittings are 4742 and 114 cm^{-1} for the lowest $^2\Delta$ and $^2\Pi$ states in refs 61 and 62. These authors found that the lowest Ω = 3/2 state is 82% $^2\Delta$, in good agreement with our results. On the other hand, their lowest Ω = 1/2 and Ω = 5/2 states have are more spin-mixed (72% $^2\Pi$ and 90% $^2\Delta$,

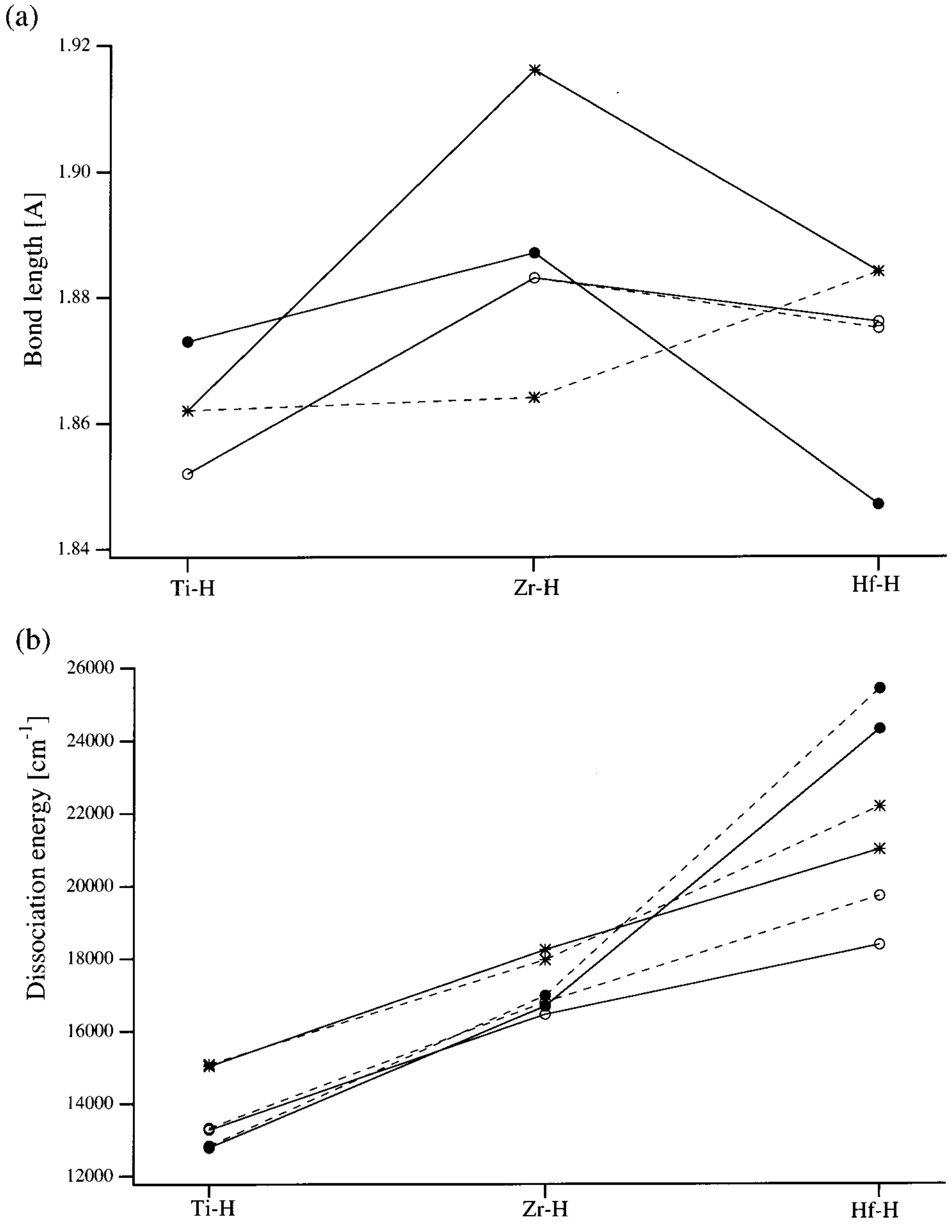

Figure 4. (a) Bond lengths and (b) dissociation energies obtained by using the ECP (open circles), AE (astarisks), and AE (RESC) (closed circles) methods. Broken and solid lines indicate adiabatic and spin-mixed results, respectively.

respectively). This is partly because the energy gap (7107 cm^{-1}) of the lowest $^2\Delta$ and $^2\Sigma$ states is smaller than ours (13 688 cm^{-1}), and partly because more spin-mixed states were included in spin–orbit coupling matrixes in refs 61 and 62.

The Mulliken population analyses at R_e of the ground state $^2\Delta$ in HfH show that the occupation numbers of valence σ, π, and δ orbitals are 3.81, 0.22, and 0.96, whereas the first excited state $^2\Pi$ has occupation numbers of 3.82, 1.10, and 0.07 for valence σ, π, and δ orbitals, respectively. Accordingly, the excitation from $^2\Delta$ to $^2\Pi$ corresponds to the electron promotion from a valence δ orbital to a valence π orbital. The atomic-orbital populations are 2.14 (5d), 1.16 (6s), and 0.49 (6p) in the $^2\Delta$ state, and 2.25 (5d), 1.10 (6s), and 0.45 (6p) in the $^2\Pi$ states, so that Hf has a positive charge of 0.20 e in both states. The dipole moments are 0.75 D in $^2\Delta$ and 0.94 D in $^2\Pi$, and are somewhat larger than those obtained by Balasubramanian and Das.[61] Because, after consideration of spin–orbit coupling, the ground spin-mixed state has the composition 86% $^2\Delta$ and 14% $^2\Pi$, the dipole moment is estimated to be 0.78 D in the ground spin-mixed state, a somewhat larger value than that (0.66 D) reported in ref 61.

Spectroscopic Parameters. The energies and wave functions of vibrational states have been obtained for low-lying spin-mixed states on the basis of the numerical analyses of dissociation energy curves.[53] Tables 2–4 list several spectroscopic parameters in the lowest spin-mixed state ($\Omega = 3/2$), together with those obtained for the lowest adiabatic state. As discussed above, the equilibrium internuclear distance (R_e) is almost unchanged by the spin–orbit effects, whereas the dissociation energy (D_e) tends to decrease slightly. The RECP results in ref 61 predict the dissociation energy of HfH increases slightly because of the spin–orbit coupling effects. Note that R_e in ZrH is longer than that in *both* TiH and HfH (Figure 4a). This can be recognized as the Lanthanide contraction.[62] Spin–orbit coupling does not change the vibrational frequency (ω_e) for the lowest spin-mixed state in TiH, but does slightly change ω_e in ZrH and HfH. Incorporation of spin–orbit coupling effects increases ω_e in ZrH and decreases ω_e in HfH (see Tables 3 and 4). Similar

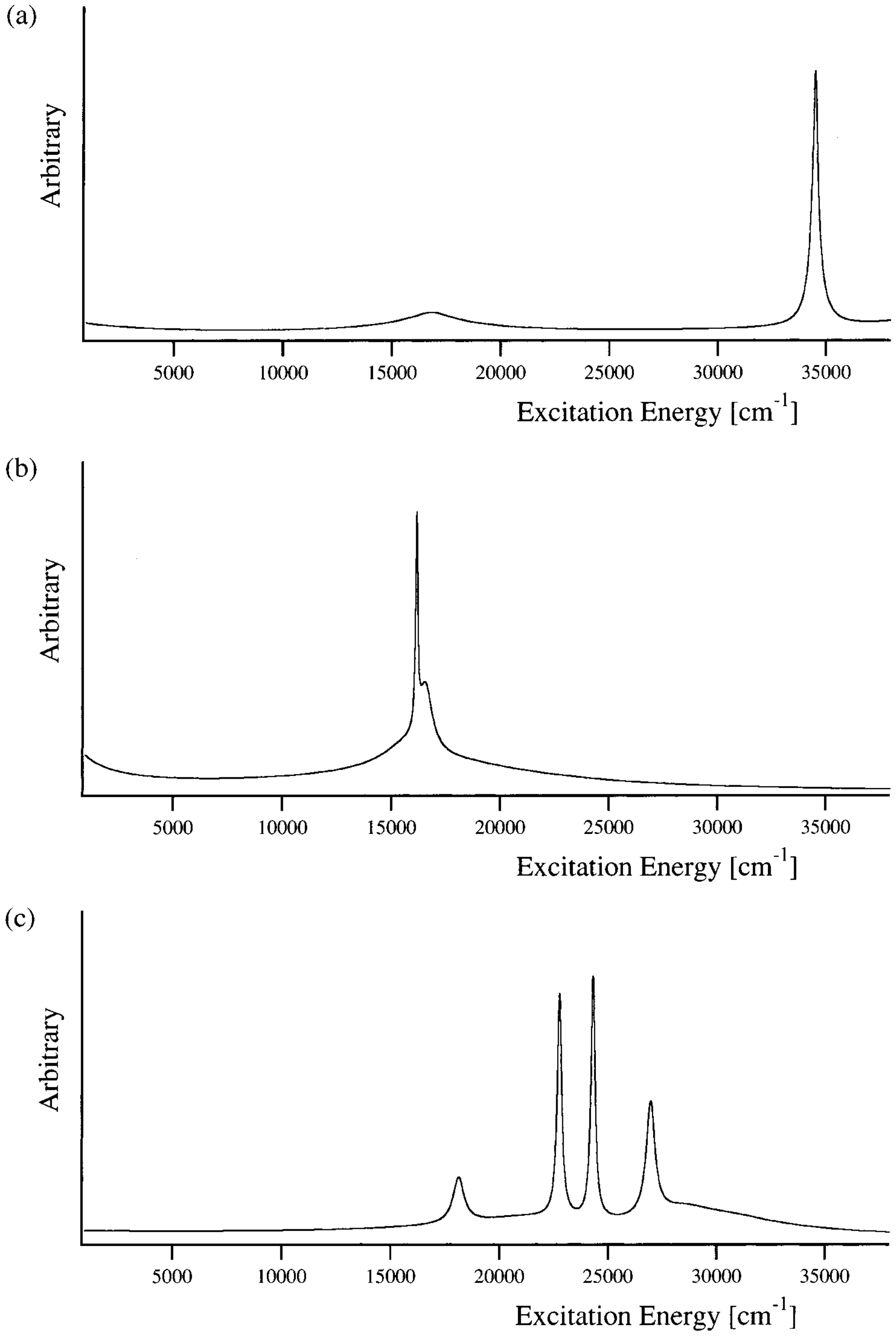

Figure 5. Predicted absorption spectra for (a) TiH, (b) ZrH, and (c) HfH.

trends are observed for the anharmonicity ($\chi_e\omega_e$) and the rotation constant (B_e).

Transition moments (μ_{TM}) connecting spin-mixed states have also been investigated. Assuming that each spectral envelope is expressed by a Lorentz function, that the temperature is 300 K, and that no vibrational transition occurs, Figure 5 illustrates predicted absorption spectra for the hydrides. The sharp large peak around 35000 cm^{-1} in Figure 5(a) corresponds principally to the electronic transition from the ground spin-mixed state to the $\Omega = 3/2$ spin state consisting predominantly of the third $^4\Phi$ state ($^4\Phi_{3/2}$) in TiH. Surprisingly, this peak has a large contribution of the transition from the ground state to the energetically high $^4\Sigma_{3/2}$ state. The broad small peak around 17000 cm^{-1} in Figure 5(a) is attributed to the electronic transitions from the ground state to the $\Omega = 3/2$ spin state consisting of the lowest $^4\Gamma$ and the second $^4\Phi$ states. An overlap of two large peaks appears at the energy of 16000 cm^{-1} for ZrH (Figure 5(b)). These peaks correspond to the transition from the ground state to a $\Omega = 3/2$ state consisting essentially of the fourth $^2\Pi_{3/2}$ state and the transition to the third $^2\Delta_{3/2}$ state. In HfH (Figure 5(c)), the electronic transitions from the ground state to the $\Omega = 3/2$ spin state consisting of the second, fourth, fifth, and sixth $^2\Delta_{3/2}$ states provide four sharp peaks in the range of 18000−28000 cm^{-1}, respectively. The intensity is quite small for the transition to the third $^2\Delta_{3/2}$ state. Even though the shapes of absorption spectra become more complicated when vibrational and rotational excitation are considered, each hydride is predicted to have characteristic absorption spectra.

Comparison with AE and Literature Results. The MIDI-(3p,3p) basis sets have been used in AE calculations so that basis sets of similar quality can be used for the first- through third-row elements.[51] MCSCF calculations that do not use the RESC method predict the ground state of the three hydrides to be $^4\Phi$. This is not consistent with the ECP results. RECP and experimental results[51,54,55,61−63] also suggest that the ZrH and HfH ground states are $^2\Delta$. Even when spin−orbit coupling effects are included and the MCSCF active space and the SOCI external space are the same as those in the ECP calculations, the energetic order obtained by the AE method are not correct. This suggests that when the AE method is used, it is very important to include spin-free scalar relativistic effects with use of the RESC approximation[33] to obtain reliable results. Consequently, both one- and two-electron parts of the RESC spin-dependent Hamiltonian are used in the present AE studies.

The AE and AE (RESC) results are shown in Tables 2−4. Figure 4 plots the equilibrium internuclear distances (R_e) and the dissociation energies (D_e) of the hydrides, together with the ECP results. Spin−orbit coupling has little effect on the R_e or on the trend in D_e calculated by using the ECP and AE (RESC) methods. Additionally, with respect to other spectroscopic parameters, except for $\chi_e\omega_e$, the AE (RESC) results are in surprisingly good agreement with the ECP results. This suggests that for the hydrides TiH, ZrH, and HfH in the region close to the equilibrium separation, the spin-free relativistic corrections accounted for by either ECP or RESC are more important than the spin−orbit interaction.

Several experimental and theoretical results on these hydrides have been reported previously. Huber and Herzberg[44] have reported $D_e = 12\,906$ cm^{-1} for TiH (see Table 2). This is close to the present results, but Chen et al.[45d] obtained a larger value experimentally in 1991. To our knowledge, only AE computational results on TiH have been reported to date,[46,48−52] except for ref 47. All reported values for D_e are in the range of 13 700−17 100 cm^{-1}. No experimental measurements of R_e have been reported. The values predicted for R_e in the present work are in good agreement with those obtained by a pseudopotential method,[47] but somewhat longer than those predicted by previous AE calculations. Some of the previous calculations used MCSCF wave functions with the same active space as in this work, followed by MRCI.[46,48d,50b] Others used the CCSD[48e] and MCPF[48e] methods.

Unfortunately, no experimental report on ZrH has been found so far, but both AE and RECP calculations have been performed previously (see Table 3). The D_e predicted by Langhoff et al.[51] and Siegbahn[57] are 19 762 and 19 586 cm^{-1}, respectively. They also predict a longer R_e than that found in the present work. Balasubramanian et al.[54,55] recalculated both properties by using RECP basis sets and reported somewhat larger D_e and shorter R_e. Recently, Reynolds and Carter[58] and Chertihin and Andrews[59] reported a smaller D_e and an R_e that is intermediate in length among the previously reported results. Their reported D_e values are similar to the present results.

Only one experimental report[61] has been found for HfH, giving R_e =1.831 Å. This is slightly longer than the values obtained previously by using both AE and RECP methods,[62−65] as can be seen in Table 4. The values for R_e obtained in the present work are longer than the experimental one by more than 0.04 Å. The best estimate for D_e, based on the previous AE and RECP results, is about 23 000 cm^{-1}. Accordingly, it can be concluded that the ECP method underestimates D_e by about 4000 cm^{-1}, and the AE (RESC) method overestimates it slightly.

Apparently, a considerable lack of both theoretical and experimental data for the excited states exists. Calculated spectroscopic parameters for several low-lying states are given in Tables 3−5. They presumably have similar quality to our results for the ground states, but no other data are available for comparison.

4. Summary

The dissociation energy curves of low-lying spin-mixed states for Group 4 hydrides, TiH, ZrH, and HfH, have been computed. Many chemical properties, such as the dissociation energies, equilibrium distances, harmonic frequencies, anharmonicities, rotational constants, and dipole moments have been calculated, because a lack of both experimental and theoretical data currently exists for many properties of these molecules, most notably dipole moments and rotational constants. It is difficult to estimate the quality of our results because of the considerable disagreement among different experimental data for TiH, no reported data for ZrH, and very scarce data on HfH, so that it is difficult to estimate the quality of our results.

In comparison with the available data, we estimate that both the ECP and AE (RESC) methods tend to underestimate the dissociation energies (D_e) by at most 4000 cm^{-1} and to overestimate the equilibrium internuclear distances (R_e) by at most 0.01−0.04 Å. The dissociation energy obtained with the semiempirical Z_{eff} method agrees with the AE methods to within 500−1000 cm^{-1} for TiH and ZrH and to within 3000−4000 cm^{-1} for HfH. Thus, we conclude that the Z_{eff} method performed very well for the two lighter molecules; the agreement is somewhat worse for HfH. For TiH and HfH, the equilibrium distances obtained by the Z_{eff} method are shorter than the AE results by about 0.02−0.03 Å, whereas the values are very similar for ZrH. Predicted $\chi_e\omega_e$ values seem to be much more sensitive to the method used than dissociation energies and equilibrium distances. Nevertheless, these methods should be applicable to investigation of relativistic effects in general molecular systems, because the calculated results are qualitatively correct and sometimes semiquantitatively reliable when their errors are kept in mind. More investigations on transition metal hydrides[66] are in progress in our laboratories.

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