1-2002

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

Shiro Koseki
*Mie University*

Yohei Ishihara
*Mie University*

Hiroaki S. Umeda
*Mie University*

Dmitri G. Fedorov
*Iowa State University*

Mark S. Gordon
*Iowa State University*, mgordon@iastate.edu

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


**Abstract**

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.


**Disciplines**

Chemistry

**Comments**


Reprinted (adapted) with permission from *Journal of Physical Chemistry A* 106 (2002): 785, doi:10.1021/jp012644e.

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

**Shiro Koseki,*,†,‡ Yohei Ishihara,† Hiroaki Umeda,†,‡ Dmitri G. Fedorov,§,¶ and Mark S. Gordon*,§**

*Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu 514-8507, Japan, and Department of Chemistry, Iowa State University, Ames, Iowa 50011*

*Received: July 11, 2001; In Final Form: November 6, 2001*

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-$\zeta$ 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 $Z_{\rm eff}$ 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 $Z_{\rm eff}$ 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 $Z_{\rm eff}$ 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

* To whom correspondence should be addressed. E-mail: shiro@ms.cias.osakafu-u.ac.jp. E-mail: mark@si.fi.ameslab.gov.
† Mie University.
‡ Present address: Department of Material Science, College of Integrated Arts and Sciences, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan.
§ Iowa State University.
¶ Present address: University of Tokyo, Japan.

10.1021/jp012644e CCC: $22.00 
Published on Web 01/09/2002

**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 | $D_e$ | $R_e$ | $\omega_e$ | $\chi_e\omega_e$ | $B_e$ | $\alpha_e$ | $\mu$ | 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. $\omega_e$ ($cm^{-1}$) and $\chi_e\omega_e$ ($cm^{-1}$) are the harmonic frequency and anharmonicity, and $B_e$ ($cm^{-1}$) and $\alpha_e$ ($cm^{-1}$) are rotational constants. The dipole moment $\mu$ 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 | $D_e$ | $R_e$ | $\omega_e$ | $\chi_e\omega_e$ | $B_e$ | $\alpha_e$ | $\mu$ | 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 | $D_e$ | $R_e$ | $\omega_e$ | $\chi_e\omega_e$ | $B_e$ | $\alpha_e$ | $\mu$ | 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 $\Omega$ states are given in Tables 2−4, where $\Omega$ 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 $Z_{\text{eff}}$ 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

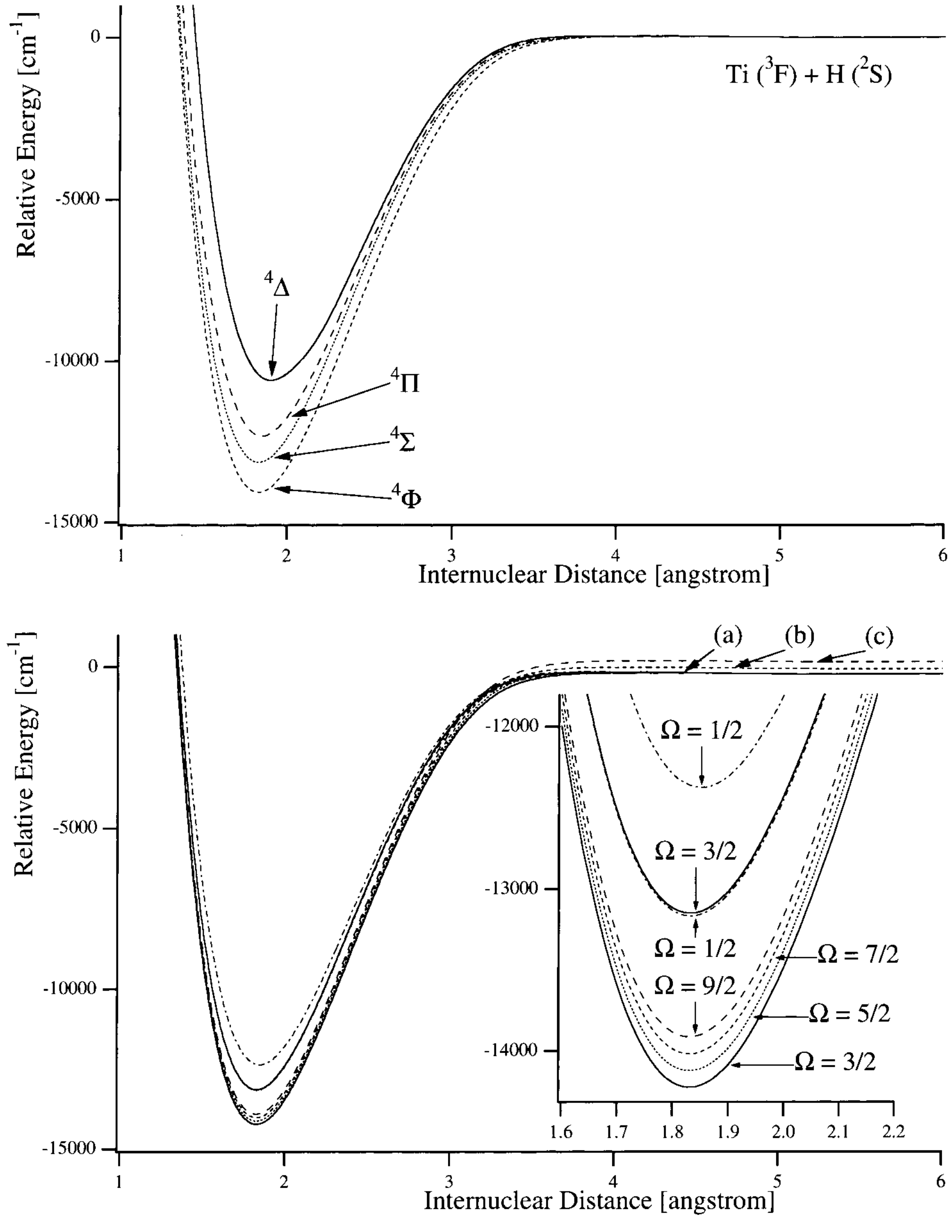


**Figure 1.** Potential energy curves in TiH obtained by using quartet MCSC+SOCI/SBKJC(f,p) wave functions. (top) Low-lying adiabatic states; (bottom) low-lying spin-mixed states. The dissociation limits are (a) $Ti(^3F_2)$ + $H(^2S_{1/2})$; (b) $Ti(^3F_3)$ + $H(^2S_{1/2})$; and (c) $Ti(^3F_4)$ + $H(^2S_{1/2})$. 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 $^3F$ 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 $^3F$ 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 $\Omega$ = 3/2, even though the leading electronic configuration at $R_e$ is different in the three hydrides.

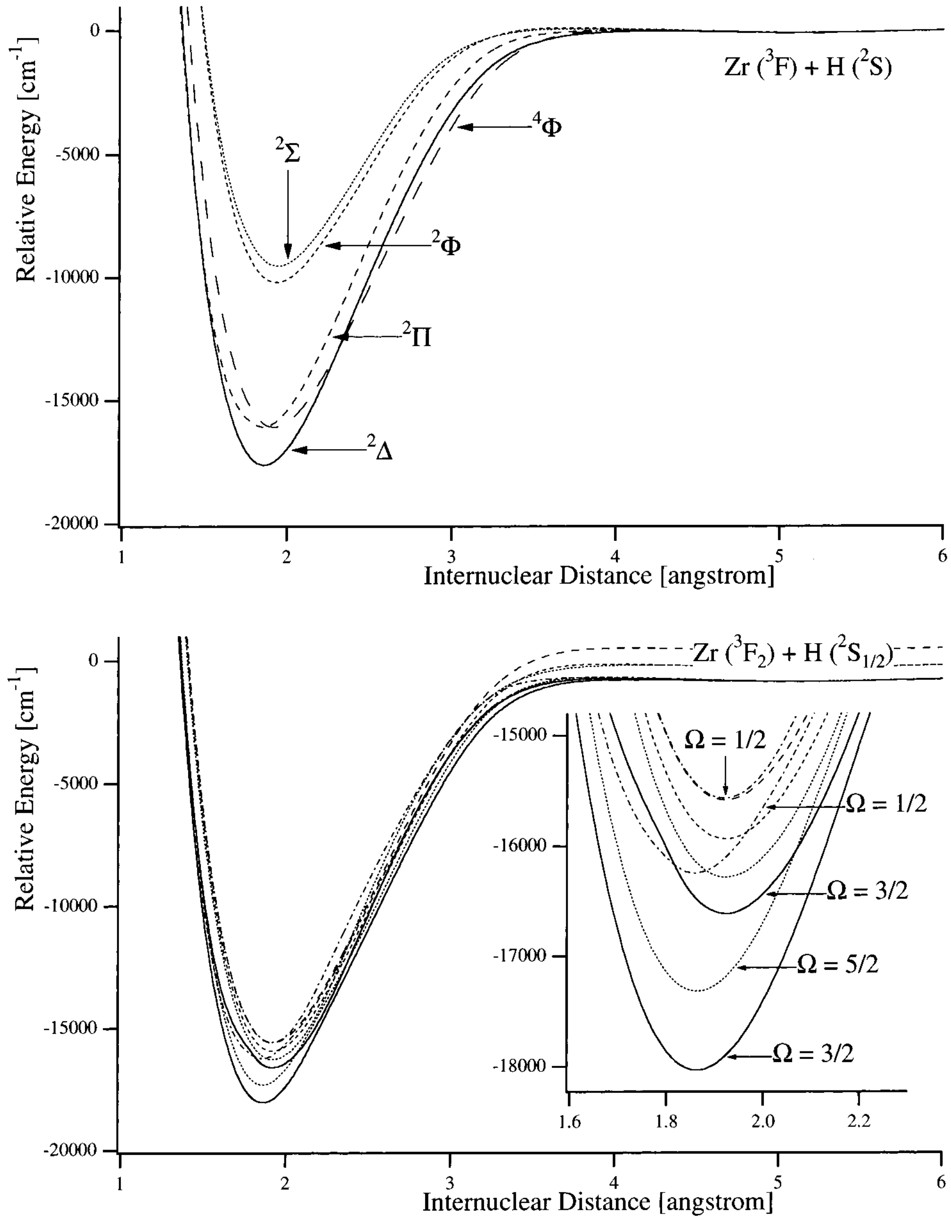


**Figure 2.** Potential energy curves in ZrH obtained by using doublet MCSC+SOCI/SBKJC(f,p) wave functions. (top) Low-lying adiabatic states; (bottom) low-lying spin-mixed states. The inset is a closeup view near the energy minima.

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 $\sigma$, $\pi$, and $\delta$ 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 ($\Omega = 3/2$ 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 ($\Omega = 7/2$) dissociates to the higher [Ti ($^3F_3$) + H ($^2S_{1/2}$)] state, and the fourth spin-mixed TiH state ($\Omega = 9/2$) 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 $\Omega = 3/2$ state has 96% contribution from $^2\Delta_{3/2}$ and 3% from $^2\Pi_{3/2}$, whereas the lowest $\Omega = 5/2$ state has almost 100% contribution from $^2\Delta_{5/2}$. Other low-lying excited states are $\Omega = 3/2$ ($^4\Phi_{3/2}$, >99%), $\Omega = 1/2$ ($^2\Pi_{1/2}$, 97%), $\Omega = 5/2$ ($^4\Phi_{5/2}$, >99%), $\Omega = 3/2$ ($^2\Pi_{3/2}$, 89%), and $\Omega = 7/2$ ($^4\Phi_{7/2}$, >99%) in energetic order. These five states appear in a small 700-cm$^{-1}$ energy range. The ground state ($\Omega = 3/2$) $R_e = 1.883$ 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 ($\sigma$), 1.01 ($\pi$), and 1.00 ($\delta$) in the $^4\Phi$ state, and 3.73 ($\sigma$), 0.19 ($\pi$), and 1.07 ($\delta$) 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 ($\Omega = 3/2$) 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

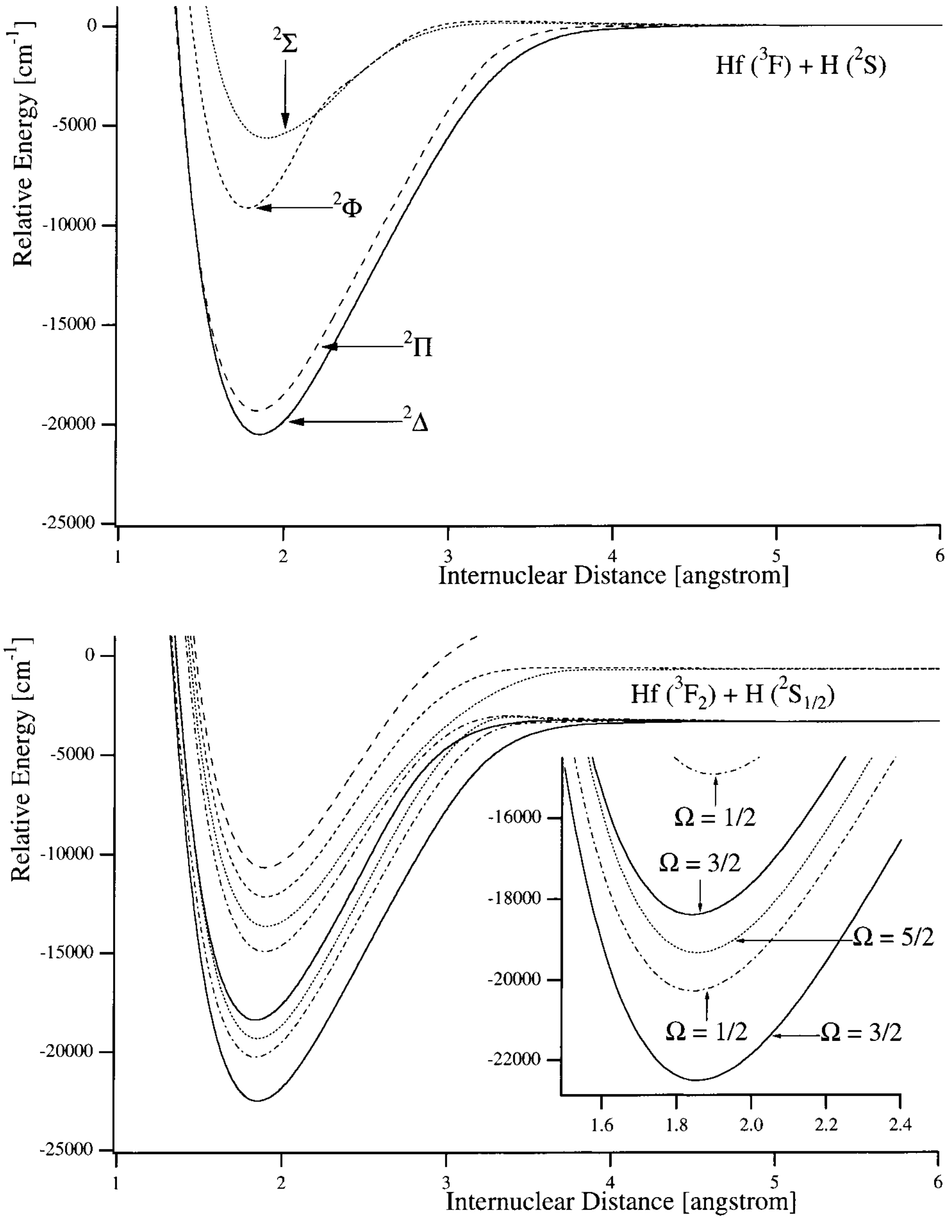


**Figure 3.** Potential energy curves in HfH obtained by using doublet MCSC+SOCI/SBKJC(f,p) wave functions. (top) Low-lying adiabatic states; (bottom) low-lying spin-mixed states. The inset is a closeup view near the energy minima.

**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 $\Omega = 5/2$ state has $^2\Delta_{5/2}$ character of more than 99% because no other $\Omega = 5/2$ 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 $\Omega = 1/2$ 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 $\Omega = 3/2 < 1/2 < 5/2$. 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 $\Omega = 3/2$ state is 82% $^2\Delta$, in good agreement with our results. On the other hand, their lowest $\Omega = 1/2$ and $\Omega = 5/2$ states have are more spin-mixed (72% $^2\Pi$ and 90% $^2\Delta$,

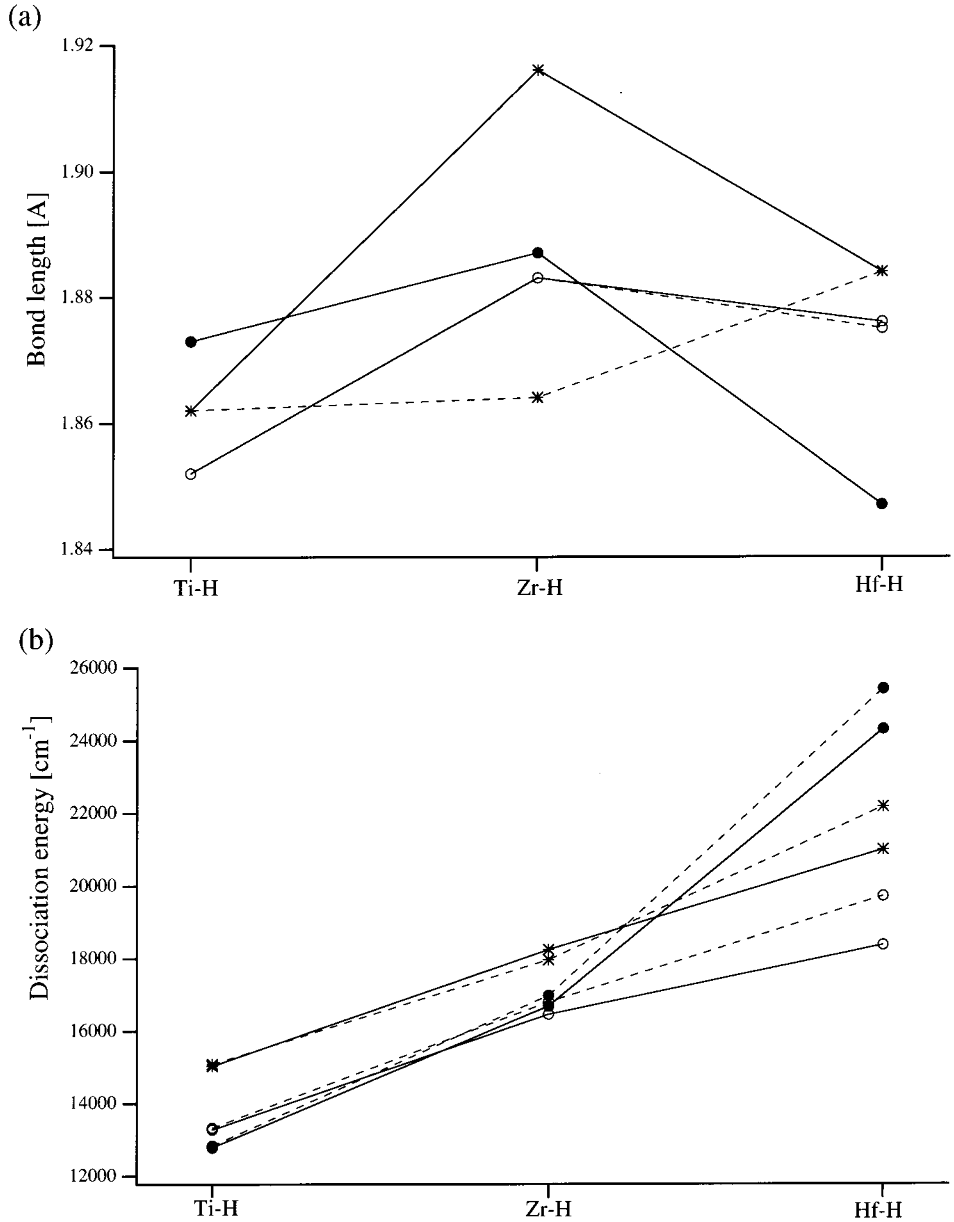


**Figure 4.** (a) Bond lengths and (b) dissociation energies obtained by using the ECP (open circles), AE (astarisks), and AE (RESC) (closed circles) methods. Broken and solid lines indicate adiabatic and spin-mixed results, respectively.

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 $\sigma$, $\pi$, and $\delta$ 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 $\sigma$, $\pi$, and $\delta$ orbitals, respectively. Accordingly, the excitation from $^2\Delta$ to $^2\Pi$ corresponds to the electron promotion from a valence $\delta$ orbital to a valence $\pi$ 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 ($\omega_e$) for the lowest spin-mixed state in TiH, but does slightly change $\omega_e$ in ZrH and HfH. Incorporation of spin−orbit coupling effects increases $\omega_e$ in ZrH and decreases $\omega_e$ in HfH (see Tables 3 and 4). Similar

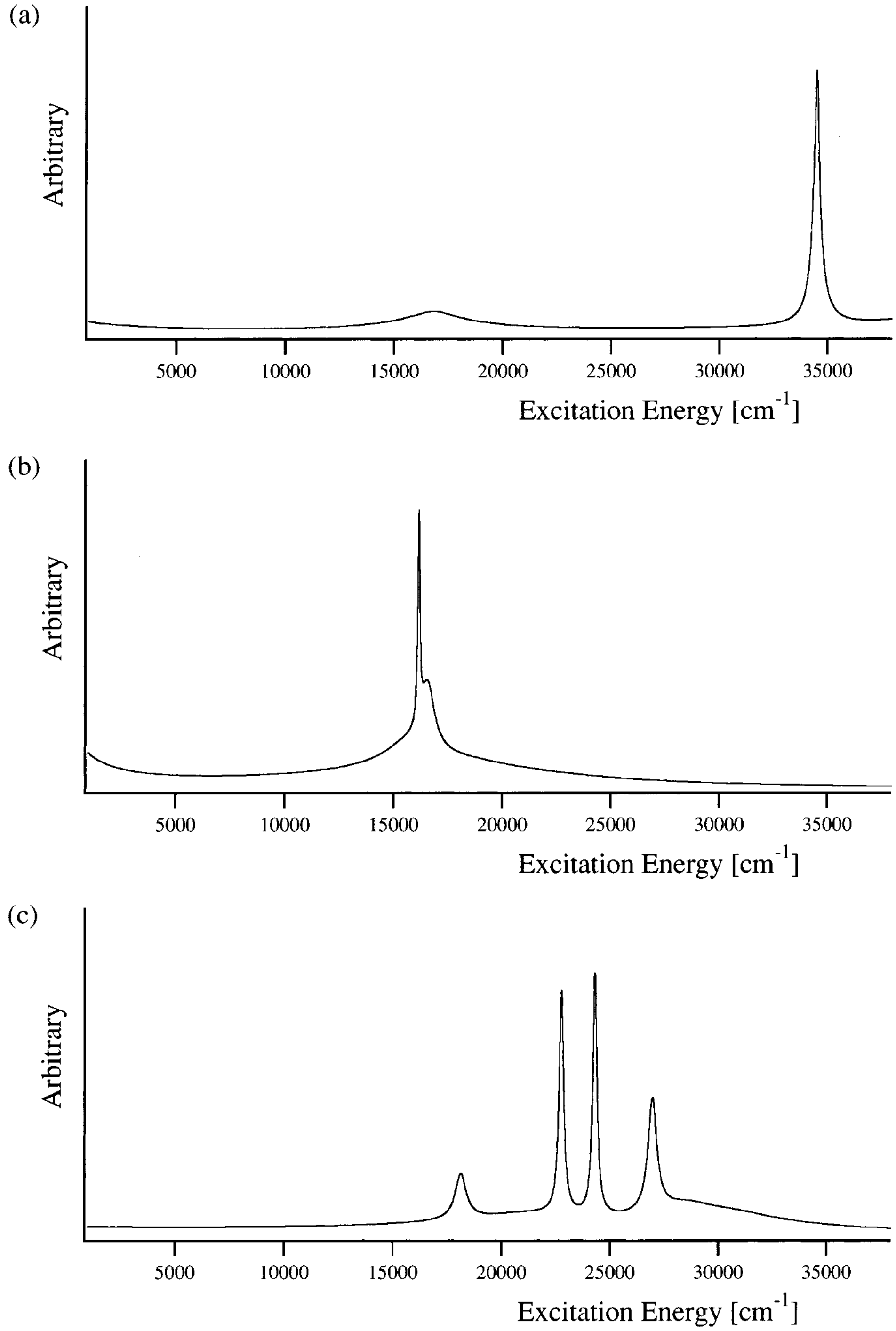


**Figure 5.** Predicted absorption spectra for (a) TiH, (b) ZrH, and (c) HfH.

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

Transition moments ($\mu_{TM}$) 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.

**Acknowledgment.** The authors thank Dr. M. W. Schmidt for helpful discussion. Financial support from a grant-in-aid for Scientific Research (Nos.11166231 and 12042237) from the Ministry in Education, Science, Sports, and Culture, Japan (to S.K.), the DoD CHSSI software development program (to M.S.G.), and a JSPS scholarship award (to D.G.F.) are gratefully acknowledged.

## References and Notes

(1) (a) Carroll, P. K.; McCormack, P. *Astrophys. J. Lett.* **1972**, *177*, L33. (b) Carroll, P. K.; McCormack, P.; O'Connor, S. *Astrophys. J.* **1976,** *208*, 903.

(2) White, N. M.; Wing, R. F. *Astrophys. J.* **1978,** *222*, 209.

(3) Weltner, W., Jr.; McLeod, D., Jr. *J. Phys. Chem.* **1965,** *69*, 3488.

(4) McIntyre, N. S.; Thompson, K. R.; Weltner, W., Jr. *J. Phys. Chem.* **1971,** *75*, 3243.

(5) Balfour, W. J.; Tatum, J. B. *J. Mol. Spectrosc.* **1973,** *48*, 313.

(6) Lauchlan, L. J.; Brom, J. M., Jr.; Broida, H. P. *J. Chem. Phys.* **1976,** *65*, 2672.

(7) Hocking, W.; Gerry, M. C. L.; Merer, A. J. *Can. J. Phys.* **1979,** *57*, 54.

(8) Powell, D.; Brittain, R.; Vala, M. *Chem. Phys.* **1981,** *58*, 355.

(9) Dyke, J. M.; Gravenor, B. W.; Josland, G. D.; Lowis, R. A.; Morris, A. *Mol. Phys.* **1984,** *53*, 465.

(10) Simard, B.; Mitchell, S. A.; Humphries, M. R.; Hackett, P. A. *J. Mol. Spectrosc.* **1988,** *129*, 186.

(11) Steimle, T. C.; Shirley, J. E.; Jung, K. Y.; Russon, L. R.; Scurlock, C. T. *J. Mol. Spectrosc.* **1990,** *92*, 4724.

(12) Gustavson, T.; Amiot, C.; Verges, J. *J. Mol. Spectrosc.* **1991,** *145*, 56.

(13) (a) Bauschlicher, C. W.; Bagus, P. S.; Nelin, C. J. *Chem. Phys. Lett.* **1983,** *101*, 229. (b) Langhoff, S. R.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1988,** *89*, 2160. (c) Langhoff, S. R.; Bauschlicher, C. W., Jr. *Astrophys. J.* **1990,** *349*, 369.

(14) Fehlner, T. P. *Inorganiometallic Chemistry*; Plenum Press: New York, 1992.

(15) Armentrout, P. B.; Sunderlin, L. S. *Acc. Chem. Res.* **1989,** *22*, 315.

(16) Bauschlicher, C. W.; Langhoff, S. R. *Acc. Chem. Res.* **1989,** *22*, 103.

(17) Doetz, K. H.; Fischer, H.; Hoffman, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Chemie Ed.: Deerfield Beach, FL, 1984.

(18) Dyall, K. G. *J. Chem. Phys.* **1993,** *98*, 9678; see also references therein.

(19) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley Inerscience: New York, 1992.

(20) Merer, A. J. *Annu. Rev. Phys. Chem.* **1989,** *40*, 407.

(21) Balasubramanian, K. *J. Chem. Phys.* **1990,** *93*, 8061; see also references therein.

(22) Cheetham, C. J.; Barrow, R. F. *Adv. High Temp. Chem.* **1967,** *1*, 7.

(23) Smith, R. E. *Proc. R. Soc. London, Ser. A* **1973,** *332*, 113.

(24) Scott, P. R.; Richards, W. G. *Chem. Soc. Spec. Period. Rep.* **1976,** *4*, 70.

(25) (a) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991,** *94*, 7221. (b) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993,** *98*, 1293. (c) Frisch, M. J.; Trucks, G. W.; Schlegen, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesman, J. R.; Kieth, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN*; Gaussian Inc.: Pittsburgh, PA. (d) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998,** *109*, 7764. (e) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999,** *110*, 4703.

(26) (a) Fast, P. L.; Sanchez, M. L.; Truhlar, D. G. *Chem. Phys. Lett.* **1999,** *306*, 407. (b) Fast, P. L.; Corchado, J. C.; Truhlar, D. G. *J. Phys. Chem. A* **1999,** *103*, 5129. (c) Fast, P. L.; Truhlar, D. G. *J. Phys. Chem. A* **2000,** *104*, 6111.

(27) (a) Allendorf, M. D.; Melius, C. F. *Surf. Coat. Technol.* **1998,** *108*−*109*, 191. (b) Melius, C. F.; Allendorf, M. D. *J. Phys. Chem. A* **2000,** *104*, 2168.

(28) (a) Jursic, B. S. *J. Phys. Chem. A* **1998,** *102*, 9255; Jursic, B. S. *J. Phys. Chem. A* **1999,** *103*, 5773. (b) Jursic, B. S. *THEOCHEM* **1999,** *459*, 221; Jursic, B. S. *THEOCHEM* **1999,** *467*, 187; Jursic, B. S. *THEOCHEM* **1999,** *490*, 133. (c) Miller, C. E.; Lynton, J. I.; Keevil, D. M.; Francisco, J. S. *J. Phys. Chem. A* **1999,** *103*, 11451. (d) Swihart, M. T.; Girshick, S. L. *Chem. Phys. Lett.* **1999,** *307*, 527. (e) Hrusak, J.; Herman, Z.; Iwata, S. *Int. J. Mass Spectrom.* **1999,** *192*, 165. (f) Jursic, B. S. *Chem. Phys. Lett.* **2000,** *321*, 129; Jursic, B. S. *THEOCHEM* **2000,** *499*, 137; Jursic, B. S. *THEOCHEM* **2000,** *499*, 223; Jursic, B. S. *THEOCHEM* **2000,** *505*, 233. (g) Li, X.; Schlegel, H. B. *J. Chem. Phys.* **2001,** *114*, 8.

(29) Krauss, M.; Stevens, W. J. *Annu. Rev. Phys. Chem.* **1984,** *35*, 357.

(30) for instance, Hess, B. A.; Marian, C. M.; Peyerimhoff, S. D. *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 152.

(31) (a) Koseki, S.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem.* **1992,** *96*, 10768. (b) Koseki, S.; Gordon, M. S.; Schmidt, M. W.; Matsunaga. N. *J. Phys. Chem.* **1995,** *99*, 12764. (c) Matsunaga, N.; Koseki, S.; Gordon. M. S. *J. Chem. Phys.* **1996,** *104*, 7988. (d) Koseki, S. Unpublished results for the sixth-row typical elements: $Z_{eff}$(Cs) = 12 210, $Z_{eff}$(Ba) = 12 432, $Z_{eff}$(Tl) = 9153, $Z_{eff}$(Pb) = 18 204, $Z_{eff}$(Bi) = 18 426, $Z_{eff}$(Po) = 18 648, $Z_{eff}$(At) = 18 870. (e) Koseki, S.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem.* **1998,** *102*, 10430. (f) Koseki, S.; Fedorov, D. G.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **2001,** *105*, 8262.

(32) Fedorov D. G.; Gordon, M. S. *J. Chem. Phys.* **2000,** *112*, 5611.

(33) (a) Nakajima, T.; Hirao, K. *Chem. Phys. Lett.* **1999,** *302*, 383. (b) Nakajima, T.; Koga, K.; Hirao, K. *J. Chem. Phys.* **2000,** *112*, 10142. (c) Witek, H. A.; Nakajima, T.; Hirao, K. *J. Chem. Phys.* **2000,** *113*, 8015. (d) Yanagisawa, S.; Nakajima, T.; Tsuneda, T.; l Hirao, K. *J. Mol. Struct. THEOCHEM* (Fraga Special Issue), in press. (e) Fedorov, D. G.; Nakajima, T.; Hirao, K. *Chem. Phys. Lett.* **2001,** *335*, 183.

(34) (a) Dyall, K. G. *J. Chem. Phys.* **1994,** *100*, 2118−2127. (b) Dyall, K. G. *J. Chem. Phys.* **1997,** *106*, 9618−9626. (c) Dyall, K. G. *J. Chem. Phys.* **1998,** *109*, 4201−4208. (d) Dyall, K. G.; Enevoldsen, T. *J. Chem. Phys.* **1999,** *111*, 10000−10007,

(35) (a) Ruedenberg, K.; Schmidt, M. W.; Dombek, M. M.; Elbert, S. T. *Chem. Phys.* **1982,** *71*, 41, 51, 65. (b) Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998,** *49*, 233.

(36) Lengfield III, B. A.; Jafri, J. A.; Phillips, D. H.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1981,** *74*, 6849.

(37) In ZrH, the lowest $^2\Delta$ and $^4\Phi$ states are very close in energy near the equilibrium nuclear distance. The present calculation shows that the ground state of ZrH is $^2\Delta$, in agreement with previous theoretical results.

(38) (a) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984,** *81*, 6026. (b) Stevens, W. J.; Basch, H.; Krauss, M.; Jasien, P. *Can. J. Chem.* **1992,** *70*, 612. (c) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993,** *98*, 5555−5565. (d) Stevens, W. J.; Krauss, M. *Chem. Phys. Lett.* **1982,** *86*, 320.

(39) (a) Exponents of 1.506, 0.875, and 0.784 are used for f functions on Ti, Zr, and Hf, respectively. (b) The p exponent for H is 1.0.

(40) The effective nuclear charges of Ti, Zr, and Hf atoms are set to 9.57, 192.00, and 1025.28, respectively.

(41) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(42) Three p exponents are set as (0.26, 0.065, 0.01625) on Ti, (0.236, 0.059, 0.01475) on Zr, (0.236, 0.059, 0.01475) on Hf, and (4.0, 1.0, 0.25) on H.

(43) (a) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T. Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, Jr. J. A. *J. Comput. Chem.* **1993,** *14*, 1347−1363. (b) Fletcher, G. D. Schmidt, M. W.; Gordon, M. S. *Adv. Chem. Phys.* (invited), **1999,** *110*, 267. (c) See ref 32.

(44) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1979.

(45) (a) Fisher, E.; Armentrout, P. B. *J. Phys. Chem.* **1990,** *94*, 1674. (b) Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1990,** *94*, 3589. (c) Schultz, R. H.; Armentrout, P. B. *J. Chem. Phys.* **1991,** *94*, 2262. (d) Chen, Y.-M.; Clemmer, D. E.; Armentrout, P. B. *J. Chem. Phys.* **1991,** *95*, 1228. (e) Chen, Y.-M.; Clemmer, D. E.; Armentrout, P. B. *J. Chem. Phys.* **1993,** *98*, 4949.

(46) Chertihin, G. V.; Andrews, L. *J. Am. Chem. Soc.* **1994,** *116*, 8322.

(47) Das, G. *J. Chem. Phys.* **1981,** *74*, 5766.

(48) (a) Walch, S. P.; Bauschlicher, C. W. *J. Chem. Phys.* **1983,** *78*, 4597. (b) Chong, D. P.; Langhoff, S. R.; Bauschlicher, C. W.; Walch, S.; Partridge, H. *J. Chem. Phys.* **1986,** *85*, 2850. (c) Bauschlicher, C. W. *J. Phys. Chem.* **1988,** *92*, 3020. (d) Bauschlicher, C. W.; Taylor, P. R. *Theor. Chim. Acta* **1993,** *86*, 13. (e) Bauschlicher, C. W. *Theor. Chem. Acc.* **1999,** *103*, 141−145.

(49) Wedig, U.; Dolg, M.; Stoll, H.; Preuss, H. *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; Veillard, A., Ed.; Reidel: Dordrecht, 1986; p 79.

(50) (a) Anglada, J.; Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *THEOCHEM (J. Mol. Struct.)* **1983,** *10*, 299. (b) Anglada, J.; Bruna, P. J.; Peyerimhoff, S. D. *Mol. Phys.* **1990,** *69*, 281.

(51) (a) Langhoff, S. R.; Pettersson, L. G. M.; Bauschlicher Jr., C. W.; Partridge, H. *J. Chem. Phys.* **1987,** *86*, 268. (b) Bauschlicher, C. W.; Langhoff, S. R. *Transition Metal Hydrides: Structure and Bonding*; Dedieu, A.. Ed.; VCH Publishers Inc.: New York, 1992; p 103.

(52) Barone, V.; Adamo, C. *Int. J. Quantum Chem.* **1997,** *61*, 443−451.

(53) Colbert, D. T.; Miller, W. H. *J. Chem. Phys.* **1992,** *96*, 1982.

(54) Balasubramanian, K.; Wang, J. Z. *Chem. Phys. Lett.* **1989,** *154*, 525.

(55) Balasubramanian, K. *J. Chem. Phys.* **1990,** *93*, 8061.

(56) Langhoff, S. R.; Pettersson, L. G. M.; Bauschlicher Jr., C. W.; Partridge, H. *J. Chem. Phys.* **1987,** *87*, 268.

(57) Siegbahn, P. E. M. *Theor. Chim. Acta* **1993,** *86*, 219−228.

(58) Reynolds, G. G.; Carter E. A. *J. Phys. Chem.* **1994,** *98*, 8144.

(59) Chertihin, G. V.; Andrews, L. *J. Phys. Chem.* **1995,** *99*, 15004.

(60) The ground state in Hf atom is $^3$F. This state is split into $^3F_2$, $^3F_3$, and $^3F_4$, where $\Delta E(^3F_2 - {}^3F_3) = 2616$ cm$^{-1}$ and $\Delta E(^3F_2 - {}^3F_4) = 5163$ cm$^{-1}$. This splitting leads to the lowering of 3334 cm$^{-1}$ in the ground state ($\Omega = 3/2$) at the dissociation limit of Hf−H.

(61) Balasubramanian, K.; Das, K. K. *J. Mol. Spectrosc.* **1991,** *145*, 142.

(62) Balasubramanian, K. *Relativistic Effects in Chemistry*; John Wiley and Sons: New York, 1997; Parts A and B.

(63) Ram, R. S.; Bernath, P. F. *J. Chem. Phys.* **1994,** *101*, 74.

(64) Wittborn, C.; Wahlgren, U. *Chem. Phys.* **1995,** *201*, 357.

(65) Chertihin, G. V.; Andrews, L. *J. Phys. Chem.* **1995,** *99*, 15004.

(66) Koseki, S.; Ishihara, Y.; Umeda, H.; Fedorov, D.; Gordon, M. S., manuscript in preparation.