

# Spin-orbit effects on the transactinide $p$ -block element monohydrides MH (M=element 113–118)

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(Received 12 October 1999; accepted 16 November 1999)

Spin-orbit effects on the bond lengths and dissociation energies of sixth- and seventh-row  $p$ -block element monohydrides MH (M=TI–Rn and element 113–118) are evaluated using relativistic effective core potentials at the coupled-cluster level of theory. Spin-orbit effects play a dominant role in the determination of molecular properties for the seventh-row hydrides. Spin-orbit effects on the bond lengths and dissociation energies of seventh-row hydrides are qualitatively similar to, but substantially larger than those of the sixth-row homologs due to the enormous spin-orbit splitting of  $7p$  orbitals. Spin-orbit interactions change the bond lengths of sixth- and seventh-row hydrides by  $-0.02 \sim +0.03$  Å and  $-0.21 \sim +0.21$  Å, respectively. Spin-orbit interactions usually elongate the bond lengths except for the molecules of the  $(p_{1/2})^1$ -valence atoms, i.e., TIH and (113)H. The maximum elongation is predicted for (115)H, where the element 115(eka-bismuth) has the  $(7p_{3/2})^1$  configuration outside the inner  $(7p_{1/2})^2$  closed-shell. The spin-orbit coupling weakens the bondings between the heavy element and the hydrogen except for BiH and changes the dissociation energies by  $-0.71 \sim +0.08$  eV and  $-2.18 \sim -0.23$  eV for sixth- and seventh-row hydrides, respectively. The dissociation energy of the (114)H molecule is merely 0.39 eV, because the element 114(eka-lead) has a closed-shell electronic structure in the  $jj$ -coupling scheme. The bonding between the element 118(eka-radon), which is another closed-shell atom, and hydrogen is very weak and can be regarded as a pure van der Waals bond. But with highly electronegative elements the element 118 seems to form more stable compounds than other closed-shell atoms such as the element 112(eka-mercury) or the element 114. © 2000 American Institute of Physics.

[S0021-9606(00)30606-7]

## I. INTRODUCTION

Researchers at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia, reported creating two atoms of element 114 that lasted for as long as 30 s before flickering out.<sup>1,2</sup> Lawrence Berkeley National Laboratory (LBNL) in the U.S. forged the heaviest element yet, element 118,<sup>3</sup> and when it decayed, it morphed into element 116, then an isotope of 114 with even fewer neutrons than Dubna's. It lasted for milliseconds. The discoveries have no practical applications as far as today's scientists know, but it is thrilling for academics. Chemists can be, also for academic reasons, interested in the properties and chemistry of the transactinide  $p$ -block elements. Since quantum calculations are presently the only way to accurately predict the physical and chemical behaviors of the transactinide elements, applications of quantum chemical calculations for molecules have been progressing rapidly in the field of transactinide element chemistry. Recent reviews on transactinide element chemistry have been given by Schwerdtfeger *et al.*<sup>4</sup> and Pershina.<sup>5</sup>

Spin-orbit effects are essential to the accurate theoretical descriptions of the electronic structures of such molecules containing the superheavy elements, for which the  $jj$ -coupling is more appropriate than the  $ls$ -coupling. For instance, in the (118)F<sub>4</sub> molecule<sup>6,7</sup> of the element 118, which has the  $(7p_{1/2})^2(7p_{3/2})^4$ -valence configuration, spin-orbit contributions make the tetrahedral geometry another stable structure with the energy comparable to that of the

square-planar structure. The tetrahedral structure, which can be called as "a spin-orbit induced isomer" was confirmed to be a local minimum by a normal-mode analysis.<sup>8</sup> The structure is what is expected from four  $(7p_{3/2})^4$ -valence electrons and stereochemically inactive  $7s^2$  and  $(7p_{1/2})^2$  electron pairs.

Spin-orbit effects on molecules have been investigated extensively for the molecules containing the sixth-row  $p$ -block elements. Among them, the simplest monohydride systems have been studied using various all-electron and relativistic effective core potential (RECP) approaches. The hydrogen atom can be used as an instrument to probe features of  $\sigma$ -bonding in the heavy elements. Dolg *et al.*<sup>9,10</sup> calculated MH (M=TI, Pb, Bi, Po, and At) using the energy-adjusted RECPs at the CIPSI (Ref. 11)/CIPSO (Ref. 12) and spin-orbit configuration interaction (CI) levels of theory.<sup>13,14</sup> Seijo<sup>15</sup> calculated the molecules using *ab initio* model potentials (AIMP) at the spin-orbit CI level. Dilabio *et al.*<sup>16</sup> performed the spin-orbit CI calculations for the molecules using the shape-consistent RECPs. All-electron scalar relativistic zero-order regular approximation (SRZORA)/two-component ZORA calculations and all-electron spin-orbit CI calculations for TIH were carried out by Lenthe *et al.*<sup>17</sup> and Marian *et al.*,<sup>18</sup> respectively. Nash *et al.* calculated PbH (Ref. 6) and AtH (Ref. 19) using the shape-consistent RECPs at the spin-orbit CI level of theory. Saue *et al.*<sup>20</sup> performed, for AtH, a first-order perturbation esti-

mate of the mass-velocity and Darwin term (MVD) and four-component Dirac-Hartree-Fock (DHF) calculations. Only a few calculations for molecules containing seventh-row  $p$ -block elements have been reported. Seth<sup>21,22</sup> calculated (113)H at all-electron one-component Douglas-Kroll (DK) CC singles and doubles with a perturbative triple contributions (CCSD(T)) and DHF-CCSD(T) levels of theory as well as the spin-orbit CI levels using the energy-adjusted RECPs. Nash *et al.* calculated (114)H (Ref. 6) and (117)H (Ref. 19) at the spin-orbit CI level using the shape-consistent RECPs. Saue *et al.*<sup>20</sup> calculated (117)H at the MVD and DHF levels of theory. To the authors' knowledge, there are no published results for RnH, (115)H, (116)H, and (118)H.

In the present work, one- and two-component calculations are performed using RECPs for the monohydride systems of the sixth- and seventh-row  $p$ -block elements and the results are compared with the previously reported theoretical results and available experimental data. The present work aims to present spin-orbit effects on the seventh-row  $p$ -block element hydrides and to explore if there are any unusual chemical behaviors and anomalies in periodic trends related with spin-orbit effects. In particular, the stabilities on the molecules containing closed-shell "noble" atoms, elements 114 and 118, are discussed. The multiconfiguration DHF calculations<sup>23</sup> for the element 114 showed that the coefficients of the configuration state wave functions are 0.9957 for the  $(p_{1/2})^2$  configuration, hence the ground state clearly has a closed-shell configuration. Then it will be interesting to determine to what extent the closed-shell nature in the element 114 resembles a closed-shell atom in the traditional sense, i.e., a rare gas atom. Another interesting point is that how far the spin-orbit destabilization of  $7p_{3/2}$  spinors in the element 118 causes the deviation in reactivity from the trend of the rare gas group. The results are also compared with those on analogues containing element 112, which is a closed-shell  $d$ -block transactinide element. The methods, basis sets, and RECPs we used are described in Sec. II. The results are presented and discussed in Sec. III, and our conclusions are summarized in Sec. IV.

## II. CALCULATIONAL DETAILS

There can be many variations in the form of RECPs and the present RECP(REP) is expressed by the following form:<sup>24</sup>

$$U^{\text{REP}} = U_{LJ}^{\text{REP}}(r) + \sum_{l=0}^{L-1} \sum_{j=|l-\frac{1}{2}|}^{l+\frac{1}{2}} \sum_{m=-j}^j [U_{lj}^{\text{REP}}(r) - U_{LJ}^{\text{REP}}(r)] \times |ljm\rangle\langle ljm|, \quad (1)$$

where  $|ljm\rangle\langle ljm|$  represents a two-component projection operator. Molecular spinors which are one-electron eigenfunctions of the Hamiltonian containing the above REP have two components. The  $U^{\text{REP}}$  which is referred to as REP here can be expressed as the sum of the scalar relativistic effective core potential (AREP),  $U^{\text{AREP}}$ , and the effective one-electron spin-orbit (ESO) operator,<sup>24</sup>  $U^{\text{SO}}$ , as

$$U^{\text{REP}} = U^{\text{AREP}} + U^{\text{SO}}. \quad (2)$$

The spin-orbit effects here are defined as the difference between AREP and REP results calculated with the same basis set at the given level of theory. We have shown that the differences between AREP and REP calculations are in good agreement with those between all-electron one-component DK- and four-component DHF-based results for (113)H, demonstrating that the potential average scheme is useful for obtaining the scalar relativistic ECPs even for the  $p$ -block transactinide elements.<sup>25</sup>

We have developed two-component Kramers' restricted Hartree-Fock (KRHF) (Ref. 26) method which includes spin-orbit interaction at the HF level of theory using the REPs. The KRHF program utilizes the REPs as a whole at the HF level and produces molecular spinors obeying double group symmetry. The KRHF method can be a starting point for many correlated methods of treating spin-orbit interactions. We have implemented CC methods on the basis of the KRHF molecular spinors and designated them as KRCC (Ref. 27) methods. In the present work, the bond lengths and dissociation energies of sixth- and seventh-row  $p$ -block element monohydrides using AREP and REPs were calculated at the CCSD(T) level of theory. The dissociation energies were evaluated using results of separate calculations of atoms. The  $F_2$  elimination energies for (114) $F_2$  and (118) $F_2$  were also evaluated using the HF optimized geometries at the CCSD(T) level of theory.

The  $dsp$ -type 13~18 valence electrons (VE) (Ref. 28) and  $spdsp$ -type 21~26 VE shape-consistent RECPs (Ref. 29) with corresponding valence basis sets were used for sixth- and seventh-row  $p$ -block elements, respectively. The  $spdsp$ -type shape-consistent RECPs were also employed for Tl(21VE) (Ref. 30) and Pb(22VE).<sup>6</sup> The basis sets were used as uncontracted forms and were augmented by one  $f$  polarization functions. The  $(5s2p)/[3s2p]$  basis set was used for the hydrogen atom.<sup>31</sup> Although the quality of the basis sets used here may not be good enough to guarantee accurate bond lengths and dissociation energies, we believe that major conclusions of the present work, especially those on spin-orbit effects, will be affected only slightly by the enlarged basis sets. The  $F_2$  elimination energies of (114) $F_2$  and (118) $F_2$  were evaluated at the scalar relativistic level using  $9p7sd3f$  basis sets with the shape-consistent RECP for element 114 and 118 and aug-cc-pVTZ (Ref. 31) for  $F$  atoms. The AREP calculations were carried out with the GAUSSIAN94 (Ref. 32) and the MOLPRO98 (Refs. 33-35) and the REP calculations with a modified two-component version of the MOLFDIR packages.<sup>36,37</sup> All occupied and virtual orbitals (or spinors) were included at the CCSD(T) level of theory.

## III. RESULTS AND DISCUSSION

Tables I and II show the bond lengths ( $R_e$ ) of sixth- and seventh-row  $p$ -block element monohydrides, respectively, which are also plotted in Fig. 1. The spin-orbit effects ( $\Delta_e(\text{SO})$ ) evaluated by several theoretical approaches and available experimental data are included in the tables for comparison. The REP bond lengths for the sixth-row hydrides at the CCSD(T) level are in good agreement with

TABLE I. AREP and REP bond lengths ( $R_e$  in Å) and spin-orbit effects( $\Delta R_e(\text{SO})$ ) at the CCSD(T) level of theory.<sup>a</sup>

	AREP	REP	$\Delta R_e(\text{SO})$	DiLabio <i>et al.</i> <sup>b</sup> spin-orbit CI	Seijo <sup>c</sup> spin-orbit CI	Dolg <i>et al.</i> <sup>d</sup> CIPSI/CIPSO	
TIH	1.948	1.927	-0.021	-0.024	-0.028	-0.014	-0.031 <sup>e</sup>
	1.899	1.877	-0.022				
PbH	1.883	1.884	0.001	-0.002	-0.005	0.001	0.002 <sup>f</sup>
	1.824	1.826	0.002				
BiH	1.817	1.836	0.019	0.016	0.011	0.015	
PoH	1.753	1.784	0.031	0.030	0.019	0.027	
AtH	1.711	1.742	0.031	0.029	0.018	0.028 <sup>g</sup>	0.032 <sup>h</sup>

<sup>a</sup>The second rows for TIH and PbH are results of calculations with 21VE and 22VE RECPs for Tl and Pb, respectively.

<sup>b</sup>The REP bond lengths at the multireference spin-orbit CISD level of theory are 1.912, 1.881, 1.832, 1.785, and 1.752 Å for TIH, PbH, BiH, PoH, and AtH, respectively, Ref. 16. Available experimental values for bond length are TIH, 1.870 Å ; PbH, 1.839 Å ; BiH, 1.805 Å .-Ref. 45.

<sup>c</sup>Reference 15.

<sup>d</sup>Reference 9.

<sup>e</sup>SRZORA/ZORA result obtained with functional of the generalized gradient approximation(GGA) type, Ref. 17.

<sup>f</sup>Spin-orbit CI result, Ref. 6.

<sup>g</sup>Two-component Kramers' restricted CISD result, Ref. 10.

<sup>h</sup>MVD/DHF result, Ref. 20.

those at the multireference (MR) CI singles and doubles (CISD) level of theory using same RECPs and the basis sets similar to this work.<sup>16</sup> The bond lengths from MRCI calculations are given as footnotes in Table I. Spin-orbit effects at the spin-orbit CI are in excellent agreement with our results indicating that the active spaces used in their work are sufficient to describe the orbital relaxations due to spin-orbit interactions. The present spin-orbit effects for the sixth-row hydrides are also in overall good agreement with those evaluated by the spin-orbit CI calculations<sup>15</sup> using AIMP and those by the CIPSI/CIPSO calculations<sup>9,10</sup> using energy-adjusted RECPs. All-electron SRZORA/ZORA calculations for TIH showed that the spin-orbit coupling contracts the Tl-H bond by 0.031 Å,<sup>17</sup> which is in good agreement with the RECP results. The TIH molecule was also calculated by all-electron spin-orbit CI energy extrapolation technique (SOCIEX),<sup>18</sup> but the spin-orbit effects on the bond length (-0.05 Å) and harmonic vibrational frequency (+193 cm<sup>-1</sup>) seem to be somewhat exaggerated compared with other results.<sup>27</sup> The spin-orbit elongation of the bond length

for AtH(+0.032 Å)<sup>20</sup> estimated from the difference between MVD and DHF results is in good agreement with the RECP results.

The spin-orbit changes of bond lengths for (114)H (Ref. 6) and (117)H (Ref. 19) estimated by the spin-orbit CI calculations are somewhat smaller than those by the CCSD(T) calculations, although the same RECPs and the basis sets of similar quality were used for the elements 114 and 117. The bond length contraction for (113)H at the spin-orbit CI level is also smaller than that of the present calculations or all-

TABLE II. AREP and REP bond lengths ( $R_e$  in Å) and spin-orbit effects [ $\Delta R_e(\text{SO})$ ] at the CCSD(T) level of theory.

	AREP	REP	$\Delta R_e(\text{SO})$	Spin-orbit CI	
(113)H	1.965	1.759	-0.206	-0.160 <sup>a</sup>	-0.217 <sup>b</sup>
(114)H	1.892	1.960	0.068	0.030 <sup>c</sup>	
(115)H	1.878	2.084	0.206		
(116)H	1.817	1.988	0.171		
(117)H	1.778	1.949	0.171	0.135 <sup>d</sup>	0.196 <sup>e</sup>

<sup>a</sup>References 21, 22.

<sup>b</sup>DK/DHF-CCSD(T) result, Refs. 21, 22.

<sup>c</sup>Reference 6.

<sup>d</sup>Reference 19.

<sup>e</sup>MVD/DHF result, Ref. 20.

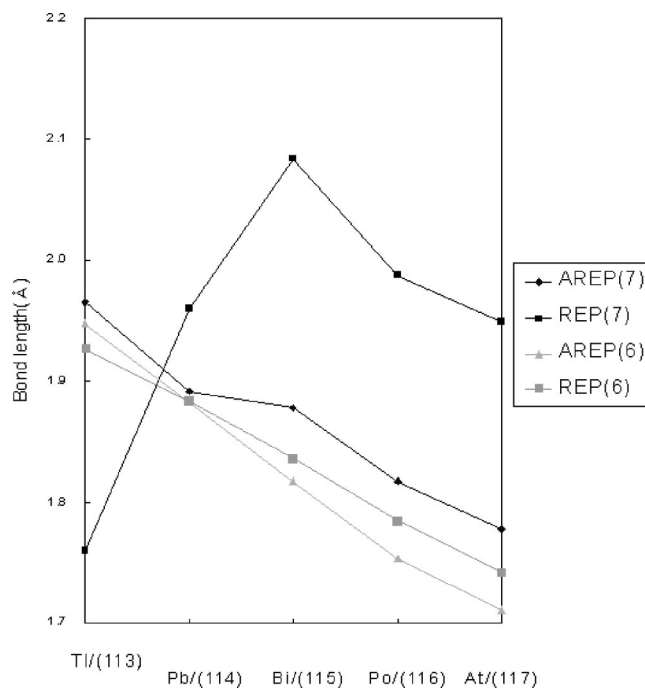


FIG. 1. Bond lengths of sixth- and seventh-row element monohydrides MH (M=TI-At and element 113-117).

electron DK/DHF-CCSD(T) calculations.<sup>21</sup> The all-electron MVD/DHF calculations for (117)H provide somewhat larger  $\Delta R_e(\text{SO})$  value (+0.196 Å) than our result (+0.179 Å) at the HF level and we believe that employing variational calculations in place of the MVD calculations could lead to a closer agreement. In Table I, the spin-orbit effects on bond lengths at the spin-orbit CI level are very similar to KRCC ones when the same RECPs are employed. We think that the larger differences for the seventh-row hydrides may originate from the limited CI spaces in the spin-orbit CI calculations. Orbital relaxations due to the spin-orbit interactions are expected to become sizable for the seventh-row elements, which cause the spin-orbit CI calculations employing the molecular orbitals from the scalar relativistic calculations to suffer slow convergences. Even in TIH,<sup>38,39</sup> it was found that spin-orbit CI calculations recover only one half of the spin-orbit bond contraction compared with the two-component Kramers' restricted CI (Ref. 40) at the single-reference CISD level.

Spin-orbit interactions elongate the bond lengths of all sixth-row hydrides but the TIH molecule. The bond length elongation is negligible for PbH(+0.001 Å) and becomes somewhat larger (+0.02–0.03 Å) for the remaining hydrides. The  $\Delta R_e(\text{SO})$  values for PbH have positive and negative signs depending upon the type of calculations but are always very small in magnitude. Spin-orbit interactions elongate bond lengths by 0.016 Å, 0.023 Å, 0.023 Å, and 0.023 Å for PbF, PbCl, PbBr, and PbI, respectively, at the CCSD(T) level of theory for the Pb–X(X=F, Cl, Br, and I) molecules which have open-shell configurations.<sup>41</sup> However, spin-orbit interactions contract the bond lengths by 0.013 Å, 0.003 Å, 0.004 Å, and 0.001 Å, respectively, at the HF level for the PbH<sub>2</sub>, PbH<sub>4</sub>, PbF<sub>2</sub>, and PbF<sub>4</sub> molecules with closed-shell configurations.<sup>39,42</sup> The PbO and PbO<sub>2</sub> molecules with closed-shell configurations are also contracted by 0.004 Å and 0.002 Å, respectively, at the CCSD(T) level of theory.<sup>41</sup> Recently, van Lenthe *et al.* showed that the bond length contractions for PbH<sub>2</sub> (Ref. 43) and PbO (Ref. 17) molecules are 0.014 Å and 0.002 Å, respectively, at the all-electron SRZORA/ZORA level of theory.

Figure 1 shows that spin-orbit effects on the bond lengths for seventh-row hydrides are qualitatively similar to those for corresponding sixth-row cases, but substantial due to the enormous spin-orbit splitting of 7p orbitals. In spite of the larger principal quantum number, the calculated bond lengths of seventh-row hydrides are not so different from those of the corresponding sixth-row ones at the scalar relativistic level (AREP in Fig. 1) because of the significant relativistic contraction of 7s and 7p orbitals. This similarity disappears once spin-orbit interactions are taken into account (REP in Fig. 1). For (113)H, a heavier homologue of TIH, adding spin-orbit terms leads to the bond length contraction of 0.206 Å and the REP bond length (1.759 Å) lies between those of the fourth-row homolog GaH (1.696 Å)<sup>44</sup> and the fifth-row homolog InH (1.838 Å).<sup>45</sup> The relativistic bond length contraction in (113)H may be rationalized by the spin-orbit contraction of the 7p<sub>1/2</sub> spinor ( $\langle r \rangle_{7p} - \langle r \rangle_{7p_{1/2}} = 0.51$  Å).<sup>4</sup> All the seventh-row hydrides except (113)H have longer bond lengths than the corresponding

TABLE III. The AREP and REP dissociation energies ( $D_e$  in eV) and spin-orbit effects ( $\Delta D_e(\text{SO})$ ) at the CCSD(T) level of theory.<sup>a</sup>

	AREP	REP	$\Delta D_e$ (SO)	DiLabio <i>et al.</i> <sup>b</sup>	Seijo <sup>c</sup>	Dolg <i>et al.</i> <sup>d</sup>
				spin-orbit CI	spin-orbit CI	CIPSI/ CIPSO
TIH	2.45	1.98	-0.47	-0.51	-0.09	-0.41
	2.52	2.00	-0.52			
PbH	2.32	1.61	-0.71	-0.77	-0.94	-0.71
	2.41	1.69	-0.72			
BiH	2.16	2.24	0.08	0.02	-0.01	0.13
PoH	2.56	2.27	-0.29	-0.29	-0.47	-0.21
AtH	2.99	2.31	-0.68	-0.66	-0.90	-0.67 <sup>e</sup>

<sup>a</sup>The second rows for TIH and PbH are results of calculations with 21VE and 22VE RECPs for Tl and Pb, respectively.

<sup>b</sup>The REP dissociation energies at the MR-SOCISD level of theory are 1.91, 1.54, 2.18, 2.26, and 2.25 eV for TIH, PbH, BiH, PoH, and AtH, respectively, Ref. 16. Available experimental values for dissociation energies are TIH, 2.06 eV; PbH, <1.69 eV; BiH, <3.00 eV, Ref. 45.

<sup>c</sup>Reference 15.

<sup>d</sup>Reference 9.

<sup>e</sup>Two-component Kramers' restricted CISD result, Ref. 10.

sixth-row hydrides, probably due to the participation of the 7p<sub>3/2</sub> spinor in the bonding. The 7p<sub>3/2</sub>-valence molecules, such as (115)H, (116)H, and (117)H, are elongated reflecting the radial expansion of the 7p<sub>3/2</sub> spinors and additional screening effects of inner 7p<sub>1/2</sub> closed-shell spinors. The maximum elongation is predicted for the (115)H molecule where the element 115 has a (p<sub>1/2</sub>)<sup>2</sup>(p<sub>3/2</sub>)<sup>1</sup>-valence configuration. A qualitative argument for the spin-orbit effects seems to be in order. If p<sub>1/2</sub> spinors dominate in bonding, the spin-orbit coupling would shorten the bond. If the p<sub>3/2</sub> spinors mainly contribute to the chemical bonding, the spin-orbit coupling would elongate the bond. In this regard, relatively small changes due to the spin-orbit interactions for PbH and (114)H may be interpreted as the participation of both p<sub>1/2</sub> and p<sub>3/2</sub> spinors in bonding.

Tables III and IV show the dissociation energies ( $D_e$ ) of sixth- and seventh-row p-block element monohydrides, which are also depicted in Fig. 2. A reasonable description of  $D_e$  for the sixth- and seventh-row hydrides requires inclusion of molecular spin-orbit effects. For example, spin-orbit induced molecular stabilization energies amount to 30% and 65% of the atomic energy lowerings for AtH and (117)H, respectively, at the HF level of theory.<sup>25</sup> The  $D_e$  values at the CCSD(T) level are in very good agreement with the MR-

TABLE IV. The AREP and REP dissociation energies ( $D_e$  in eV) and spin-orbit effects [ $\Delta D_e(\text{SO})$ ] at the CCSD(T) level of theory.

	AREP	REP	$\Delta D_e(\text{SO})$	Spin-orbit CI	
(113)H	2.39	1.46	-0.93	-0.98 <sup>a</sup>	-0.96 <sup>b</sup>
(114)H	2.39	0.21	-2.18	-2.07 <sup>c</sup>	
(115)H	2.05	1.82	-0.23		
(116)H	2.44	1.81	-0.63		
(117)H	2.83	1.79	-1.04	-0.57 <sup>d</sup>	

<sup>a</sup>References 21, 22.

<sup>b</sup>DK/DHF-CCSD(T) result, Refs. 21, 22.

<sup>c</sup>Reference 6.

<sup>d</sup>Reference 19.

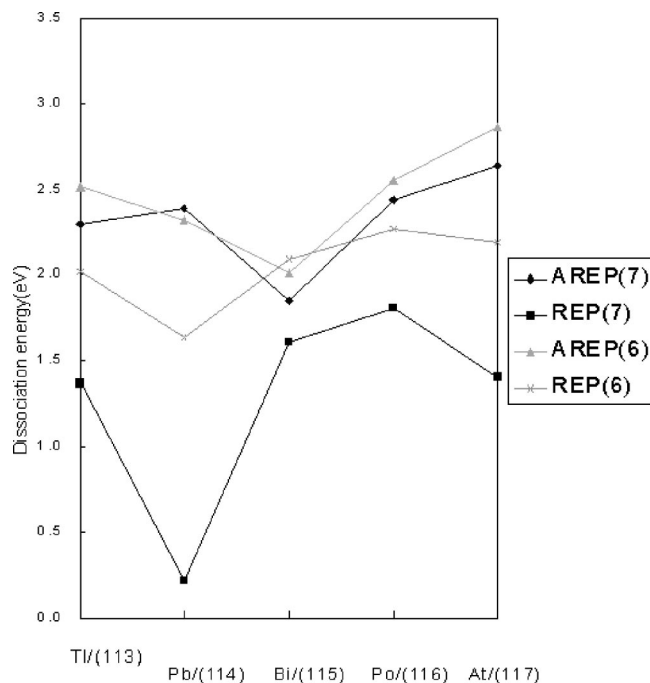


FIG. 2. Dissociation energies of sixth- and seventh-row element monohydrides MH (M=TI-At and element 113-117).

CISD ones for the sixth-row hydrides. The MRCISD dissociation energies are given as footnotes in Table III. Experimental dissociation energies are uncertain except for TIH, but usually in good accord with calculated ones. Alekseyev *et al.*<sup>46</sup> suggested the  $D_e$  value (2.28 eV) for BiH on the basis of the experimental data and their CI calculations, which is also in good agreement with calculated ones. The spin-orbit effects ( $\Delta_e(\text{SO})$ ) at the MRCISD level are very similar to the present results for the sixth-row hydrides. The CIPSI/CIPSO calculations also provide similar spin-orbit effects, but the spin-orbit CI results using the AIMP somewhat differ from other data. In particular, the  $\Delta D_e(\text{SO})$  value for TIH is difficult to rationalize given the large spin-orbit splitting (0.97 eV) (Ref. 47) in the ground-state TI atom as noted already by van Lenthe *et al.*<sup>17</sup>

The spin-orbit interaction weakens the bond between the heavy element and the hydrogen atom with the exception of BiH.<sup>16</sup> In the diatomic molecules of  $p$  valence electrons,  $p\sigma$  and  $p\pi$  bonds could be weakened by the admixture of  $p\pi^*$  and  $p\sigma^*$  orbitals, respectively, in the presence of the spin-orbit interactions. In the spinor picture,  $p_{1/2}$  and  $p_{3/2}$  spinors might mix to form spinors which are purely or mostly bonding in a scheme known as the relativistic hybridization.<sup>48-50</sup> In either interpretation, the energy cost will be a fraction of the spin-orbit splitting energy of the atomic  $p$  orbital and reflected as a reduced bond energy. As in the case of bond lengths, the dissociation energies of seventh-row hydrides are not so different from those of corresponding sixth-row ones at the scalar relativistic level of theory (Fig. 2). The pattern of spin-orbit effects for the seventh-row hydrides appear very similar to that for the sixth-row homologs, but the effects are significantly larger for the seventh-row cases. Significant destabilization effects due to spin-orbit interactions make the seventh-row ele-

ments difficult to form bonds. In particular, the element 114 with a closed-shell structure in the  $jj$ -coupling scheme has a very weak bond with hydrogen ( $D_e=0.21$  eV). Nash *et al.*<sup>6</sup> reported somewhat larger  $D_e$  values of 0.5-0.6 eV for (114)H at the various spin-orbit CI levels of theory than ours but essentially in agreement that the (114)-H bond is very weakened. Their spin-orbit effects on the  $D_e$  value ( $< -2.07$  eV) is also similar to our value  $-2.18$  eV. In order to assess the basis set effects for (114)H, we tested the  $9p7sd3f$  basis set for the element 114 and the  $(6s3p1d)/[3s3p1d]$  for hydrogen and obtained the  $D_e$  values of 2.61 and 0.39 eV for the AREP and REP calculations, respectively. We also tried Seth's one- and two-component energy-adjusted RECPs and corresponding basis sets<sup>21</sup> and found the  $D_e$  values for (114)H to be 2.65 and 0.40 eV for AREP and REP, respectively. The inertness of the element 114 seems to be a combined result of both the spin-orbit effect and the double occupancy of the  $7p_{1/2}$  spinor. The next two excited states for (114)H connected with the open  $7s^2 7p_{1/2}^1 7p_{3/2}^1$  configuration of the element 114 are substantially separated from the ground state.<sup>6</sup>

In the case of (117)H, the relativistic hybridization energy will make the formation of pure  $\sigma$  or  $\pi$  bonds less favorable, which means that the atomic  $p_{1/2}$  spinor remains nonbonding.<sup>51,21</sup> The bonding orbital is then formed solely from the halogen  $p_{3/2}$  and the hydrogen  $s_{1/2}$ . Since the halogen  $p_{3/2,1/2}$  is two-thirds  $\sigma$  in character, the (117)-H bond calculated with spin-orbit interaction is expected to be roughly two thirds as strong as that in the absence of spin-orbit coupling, which is in line with the present results (2.83 eV without SO and 1.79 eV with SO in Table IV). Nash *et al.*<sup>19</sup> calculated (117)H using the AREP-CCSD(T) with spin-orbit CI corrections and reported the larger  $D_e$  value (2.21 eV) than our value (1.79 eV). The discrepancy occurs because their spin-orbit induced change in the dissociation energy of (117)H,  $-0.57$  eV, is smaller than that in AtH,  $-0.61$  eV. However, the unusual moderation in the effect of spin-orbit coupling on the dissociation energy is not observed for (117)H in the present calculation. We also tested the 39VE shape-consistent RECPs (Ref. 29) including  $5f$  electrons in the valence space for the spin-orbit effects on the dissociation energy of (117)H at the HF level of theory. The spin-orbit interactions reduce the dissociation energy by 1.00 eV, which is very similar to the case of 25VE (1.04 eV) at the same level of theory. Nash *et al.*<sup>19</sup> used a contracted basis set  $(6p6sd1pf)/[4p6sd1pf]$  for the element 117, but the contraction changes  $D_e$  by no more than 0.02 eV in our CCSD(T) calculations. Spin-orbit coupling increases the  $D_e$  value for (117)F by 0.16 eV at the CCSD(T) level of theory<sup>41</sup> in contrast to the case of (117)H, which can be explained by the increased ionic interaction between the element 117 having spin-orbit lowered ionization potential and the highly electronegative fluorine.

Since several RECP studies reported problematic behaviors of  $dsp$ -type RECPs such as the underestimation for the  $^2P$  spin-orbit splittings of the TI atom,<sup>52,53</sup> calculations using  $spdsp$ -type RECPs were also performed here for TIH and PbH using 21VE and 22VE RECPs published for TI and Pb, respectively, to assess the accuracy of the  $dsp$ -type

RECPs for the sixth-row elements. The REP bond lengths are closer to the experimental values and the REP dissociation energies are little changed in comparison to the results with the *dsp*-type RECPs. As shown in Tables I and III, using the *spdsp*-type RECPs little change spin-orbit effects on the bond lengths and dissociation energies, indicating that the *dsp*-type RECPs probably provide reliable spin-orbit effects in the sixth-row hydrides.

The bond lengths and dissociation energies of RnH and (118)H molecules were also calculated. Since it is widely known that the binding energy between a noble gas atom and hydrogen is merely meV order,<sup>54</sup> the correction for the basis set superposition error (BSSE) (Ref. 55) is necessary to obtain a reasonable result with basis sets of moderate sizes. The counterpoise correction<sup>56</sup> is employed in this work. The bond lengths for RnH using AREP and REP are 4.412 and 4.387 Å, respectively, and the dissociation energies are 1.79 and 1.84 meV, respectively. These spin-orbit effects are qualitatively similar to the Rn<sub>2</sub> case, where the spin-orbit effects are  $-0.019$  Å for the bond length and  $+2.0$  meV for the dissociation energy at the CCSD(T) level of theory.<sup>57</sup> The bond lengths for (118)H are 4.264 and 3.857 Å and the dissociation energies are 3.56 and 5.50 meV for the AREP and REP calculations, respectively, implying that the spin-orbit effects are qualitatively similar to the RnH and Rn<sub>2</sub> cases. When there is no spin-orbit splittings in the valence shell of an atom due to the vanishing angular momentum, the higher-order effect of the spin-orbit coupling in a molecule may result in bond strengthening, as in the case of Hg<sub>2</sub>, Au<sub>2</sub>, AuH, CsHg, and rare gas dimers.<sup>58</sup> It is noted that the quality of the present basis sets is not adequate to describe van der Waals interactions, resulting in significant underestimation for the dissociation energy. The spin-orbit effect is also underestimated for the dissociation energy in this case.<sup>57</sup> In the absence of additional calculations using an extended basis set, dissociation energies for RnH and (118)H are expected to be more than 6.20 meV considering that experimental dissociation energies<sup>54,59</sup> for NeH, ArH, KrH, and XeH are 1.49, 4.67, 5.82, and 6.20 meV, respectively. But we confirmed that the (118)-H bond is a typical van der Waals bond between rare gas atom and hydrogen.

The element 118 may readily form stable molecules with highly electronegative atoms such as fluorines due to the radial expansion and the energetic destabilization of the  $p_{3/2}$ -valence spinors. The increase of the F<sub>2</sub> elimination energy due to the spin-orbit interactions for the (118)F<sub>2</sub> molecule is calculated as 46.1 kcal/mol.<sup>8</sup> The F<sub>2</sub> elimination energy calculated with extended basis sets, a *9p7sd3f* basis set for (118) and the aug-cc-pVTZ basis set for F, is 59.9 kcal/mol at the scalar relativistic level. The F<sub>2</sub> elimination energy for (118)F<sub>2</sub> is estimated as 106.0 kcal/mol assuming that spin-orbit effects are little altered by the extension of the basis set. The F<sub>2</sub> elimination energy of (114)F<sub>2</sub> obtained from the procedure similar to the one used for (118)F<sub>2</sub> is 73.4 kcal/mol, where the spin-orbit destabilization energy is  $-107.5$  kcal/mol. Seth *et al.*<sup>21,23</sup> reported the F<sub>2</sub> elimination energy for (114)F<sub>2</sub> molecule as 68.6 kcal/mol with the spin-orbit destabilization energy of  $-104.2$  kcal/mol. Somewhat larger F<sub>2</sub> elimination energy in the present calculations is

attributed to the larger basis set used here. The F<sub>2</sub> elimination energy calculated by Seth *et al.*<sup>66</sup> is 59.8 kcal/mol for the (112)F<sub>2</sub> molecule without spin-orbit interaction. Liu *et al.*<sup>60</sup> also reported the F<sub>2</sub> elimination energy for (112)F<sub>2</sub> as 59.3 kcal/mol at the four-component Dirac-Kohn-Sham (DKS) density functional theory (DFT) (Ref. 61) and the  $D_e$  value as 0.75 eV for (112)H. For corresponding sixth-row molecules, Liu *et al.*<sup>62</sup> calculated the F<sub>2</sub> elimination energy for HgF<sub>2</sub> as 86.5 kcal/mol with the spin-orbit stabilization energy of  $+0.3$  kcal/mol. Son *et al.*<sup>42</sup> calculated the F<sub>2</sub> elimination energy for PbF<sub>2</sub> as 150.4 kcal/mol including spin-orbit energy change of  $-29.2$  kcal/mol at the CCSD(T) level of theory. We calculated the F<sub>2</sub> elimination energy value for RnF<sub>2</sub> using extended basis sets, (*9s9p6d6f*)/[*7s7p6d6f*] for Rn (Ref. 63) and aug-cc-pVTZ for F, at the scalar relativistic level using energy-adjusted 8VE RECPs.<sup>64</sup> The final value is estimated as 48.7 kcal/mol including spin-orbit energy change<sup>8</sup> of  $+9.9$  kcal/mol.

From the above calculations, the molecular stabilities are summarized as RnH $\ll$ HgH $<$ PbH and (118)H $\ll$ (114)H  $<$ (112)H for the hydrides, but as RnF<sub>2</sub> $<$ HgF<sub>2</sub> $<$ PbF<sub>2</sub> and (112)F<sub>2</sub> $<$ (114)F<sub>2</sub> $<$ (118)F<sub>2</sub> for the difluorides. The unreactive element 114 and the reactive element 118 can be rationalized by the larger spin-orbit splitting of *7p* orbitals than *6p* ones. Spin-orbit splittings for Pb<sup>+</sup>, Rn<sup>+</sup>, (114)<sup>+</sup>, and (118)<sup>+</sup> are 1.75 eV, 3.83 eV,<sup>65</sup> 4.77 eV,<sup>21</sup> and 11.40 eV,<sup>6</sup> respectively. More stable (118)F<sub>2</sub> than (114)F<sub>2</sub> can be explained by the lower first ionization potential of the element 118(7.32 eV) than that of the element 114(8.56 eV), whereas the first ionization potential of Rn(10.21 eV) is much higher than that of Pb(7.04 eV).<sup>6</sup> The (112)F<sub>2</sub> is less stable than HgF<sub>2</sub> since the ionization potential of the element 112(11.97 eV) is higher than that of Hg(10.43 eV) (Ref. 66) due to the enormous relativistic stabilization of the *7s* orbitals.

#### IV. CONCLUSIONS

We evaluated spin-orbit effects on the bond lengths and dissociation energies of sixth- and seventh-row *p*-block element monohydrides using RECPs at the CCSD(T) level of theory. It is difficult to overstate the impact of spin-orbit coupling on the electronic structures of the transactinide *p*-block element monohydrides, implying that the *jj*-coupling scheme is more appropriate than the *ls*-coupling. Spin-orbit effects on the bond lengths and dissociation energies of seventh-row hydrides are qualitatively similar to, but substantially larger than those of the corresponding sixth-row ones due to the enormous spin-orbit splitting of *7p* orbitals. Spin-orbit interactions change the bond lengths of sixth- and seventh-row hydrides by  $-0.02\sim+0.03$  Å and  $-0.21\sim+0.21$  Å, respectively. Spin-orbit interactions usually elongate the bond lengths except for the molecules of the ( $p_{1/2}$ )<sup>1</sup>-valence atoms. The maximum elongation is predicted for (115)H where the element 115 has the ( $7p_{3/2}$ )<sup>1</sup> configuration outside the ( $7p_{1/2}$ )<sup>2</sup> closed shell. If  $p_{1/2}(p_{3/2})$  spinors dominate in bonding, the spin-orbit coupling would shorten(elongate) the bond. Relatively small changes due to

the spin-orbit interactions for PbH and (114)H may be interpreted as the participation of both  $p_{1/2}$  and  $p_{3/2}$  spinors in bonding.

Spin-orbit coupling weakens the bond between the heavy element and the hydrogen except for BiH and changes the dissociation energies by  $-0.71 \sim +0.08$  eV and  $-2.18 \sim -0.23$  eV for sixth- and seventh-row hydrides, respectively. The decrease due to spin-orbit coupling is maximized in the (114)H molecule, because the element 114 has a closed-shell electronic configuration in the  $jj$ -coupling scheme. The resulting dissociation energy is merely 0.39 eV. The bonding between another closed-shell element 118 and hydrogen is found to be very weak being in meV order, but the element 118 forms stronger bonds with highly electronegative elements such as fluorine than other closed-shell elements 112 and 114, which can be explained by relativistic variations of  $7s_{1/2}$ ,  $7p_{1/2}$ , and  $7p_{3/2}$  spinors.

## ACKNOWLEDGMENTS

This research is supported by the Korea Research Foundation and the MOST-FOTD Grant. Thanks are due to Professor P. Schwerdtfeger for the reprints and Dr. M. Seth's Ph.D. thesis. We thank Dr. C. S. Nash for the preprint and helpful discussion and Dr. W. Liu for the DKS-DFT results for the molecules containing element 112 and comments. Thanks are also due to Dr. E. van Lenthe for the SRZORA/ZORA results for PbH<sub>2</sub> and Professor P. A. Christiansen for the 21VE RECP for the Tl atom. We acknowledge the use of CRAY C90 at the ETRI supercomputer center.

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