Two-component calculations for polyatomic hydrides and fluorides containing superheavy elements 113 and 114

손 상 길 · 한 영 규 · 이 윤 섭

한국과학기술원 화학과

KAIST

Korea Advanced Institute of Science & Technology

한국과학기술원

Abstract

Superheavy elements have become the center of interest in theoretical chemistry for their unusual trends on the periodic table. Element 113 and 114 which have not been synthesized yet have $7s^2\ 7p_{1/2}^1$ and $7s^2\ 7p_{1/2}^2$ valence configurations, respectively. Considerable changes of molecular structures, vibrations, and stabilities are expected from spin–orbit interactions for molecules containing these superheavy elements since the $p_{1/2}$ valence is stabilized by enormous 7p spin–orbit splitting. For MX, MX_3 (M=Tl, 113, X=H, F), MX_2, MX_4 (M=Pb, 114, X=H, F), we performed geometry optimizations and normal mode analysis at the HF level of theory, and evaluated the stabilities at the CCSD(T) level using relativistic effective core potential with and without spin–orbit interactions. Spin–orbit coupling contracts the bond lengths for all cases and the bond contraction is more significant for the hydrides than the fluorides. Normal mode analysis reveal that molecular shapes of 113 and 114 molecules are analogous to Tl and Pb ones except for $113H_3$ and $113F_3$, and changes for vibrational frequencies of the hydrides are substantial. Spin–orbit interactions reduce bond energies by about 10~50 kcal/mol. The bonds become very weak and, in particular, element 114 seems to be chemically inert. These results can be explained by the stabilization and the relativistic radial contractions of the $p_{1/2}$ valence spinor by spin–orbit splitting.

Introduction

12	13	14	15
48 Cd	49 In	50 Sn	51 Sb
80 Hg	81 Tl	82 Pb	83 Bi
112 112	113 113	114 114	115 115

- Superheavy element는 112번까지 합성되었으며 113, 114번 원소를 합성하기 위한 노력이 진행중이다.
- 상대성효과는 원자번호가 커질수록 증가하므로 5주기 이상 무거운 원소에 대해서는 상대론적 효과가 반드시 포함되어야 한다.
- 113, 114는 p–valence를 가지고 있으며 P state는 spin–orbit coupling에 의해서 $P_{1/2}$과 $P_{3/2}$로 2.79, 4.77 eV정도 각각 splitting되므로 전자구조에 많은 변화를 가져온다.
- Electronic configuration
  113 : [core] $7s^2\ 7p_{1/2}^1$
  114 : [core] $7s^2\ 7p_{1/2}^2$
- 114번의 경우는 closed shell 형태가 되므로 inert한 성질을 가질 것으로 예측된다.

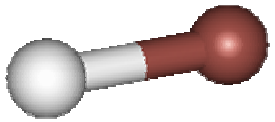
Computational Details

- Basis & RECP
  - Tl : Christiansen *et al.*, [4s5p5d]
  - Pb : Christiansen *et al.*, [5s5p6d]
  - 113 : Nash *et al.*, [6sd6p]
  - 114 : Nash *et al.*, [6sd6p]
  - H : (5s1p) / [3s1p]
  - F : (9s5p1d) / [4s2p1d]
- RECP(Relativistic Effective Core Potential)는 Dirac–Fock valence spinor와 spinor energy에서 유도된 REP와 spin–weighted potential average scheme을 이용한 AREP를 사용하였다.
- HF수준에서 AREP, REP 각각 geometry optimization과 normal mode analysis를 수행하였고 CCSD(T)수준으로 single point 계산을 수행하였다.
- AREP계산은 Gaussian 94, ACES II를 이용하였고, REP계산은 KRHF와 KRCC program을 이용하였다.

Molecular geometries of the Tl and Pb compounds.

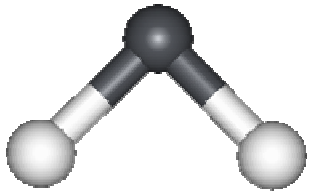
All bond lengths are in Å and all angles are in degrees.

TlX



	AREP	REP	Δ_{so}
Tl-H	1.894	1.867	-0.027
Tl-F	2.096	2.090	-0.006

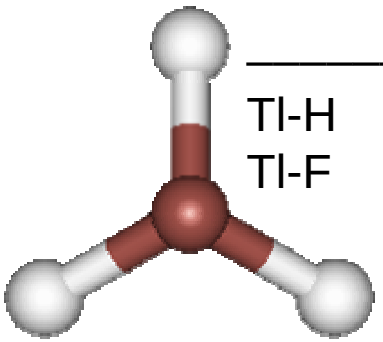
PbX_2



	AREP	REP	Δ_{so}
Pb-H	1.833	1.820	-0.013
Pb-F	2.037	2.033	-0.004

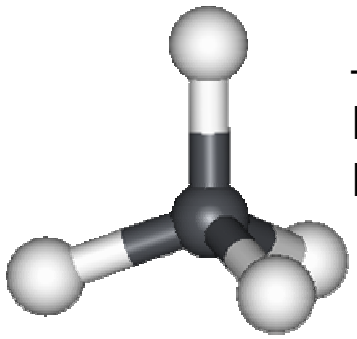
	AREP	REP	Δ_{so}
H-Pb-H	91.6	92.4	+0.8
F-Pb-F	95.1	94.7	-0.4

TlX_3



	AREP	REP	Δ_{so}
Tl-H	1.732	1.726	-0.006
Tl-F	1.972	1.970	-0.002

PbX_4

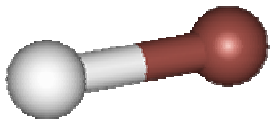


	AREP	REP	Δ_{so}
Pb-H	1.740	1.737	-0.003
Pb-F	1.951	1.950	-0.001

Molecular geometries of the 113 & 114 compounds.

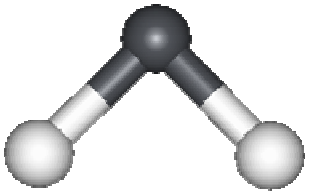
All bond lengths are in Å and all angles are in degrees.

113X



	AREP	REP	Δ_{so}
113-H	2.013	1.713	-0.300
113-F	2.265	2.221	-0.043

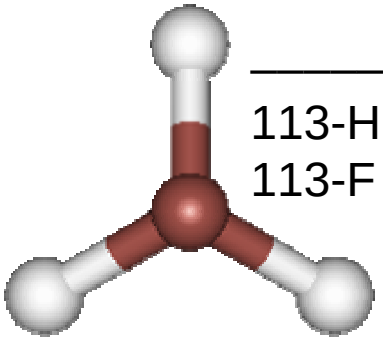
$114X_2$



	AREP	REP	Δ_{so}
114-H	1.909	1.851	-0.058
114-F	2.199	2.178	-0.021

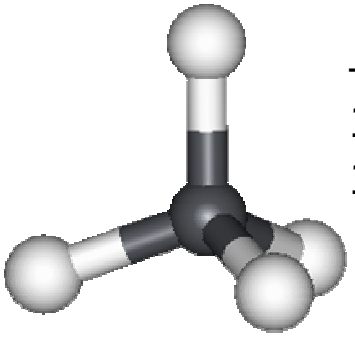
	AREP	REP	Δ_{so}
H-114-H	88.9	90.8	+1.9
F-114-F	100.7	97.8	-2.9

$113X_3$



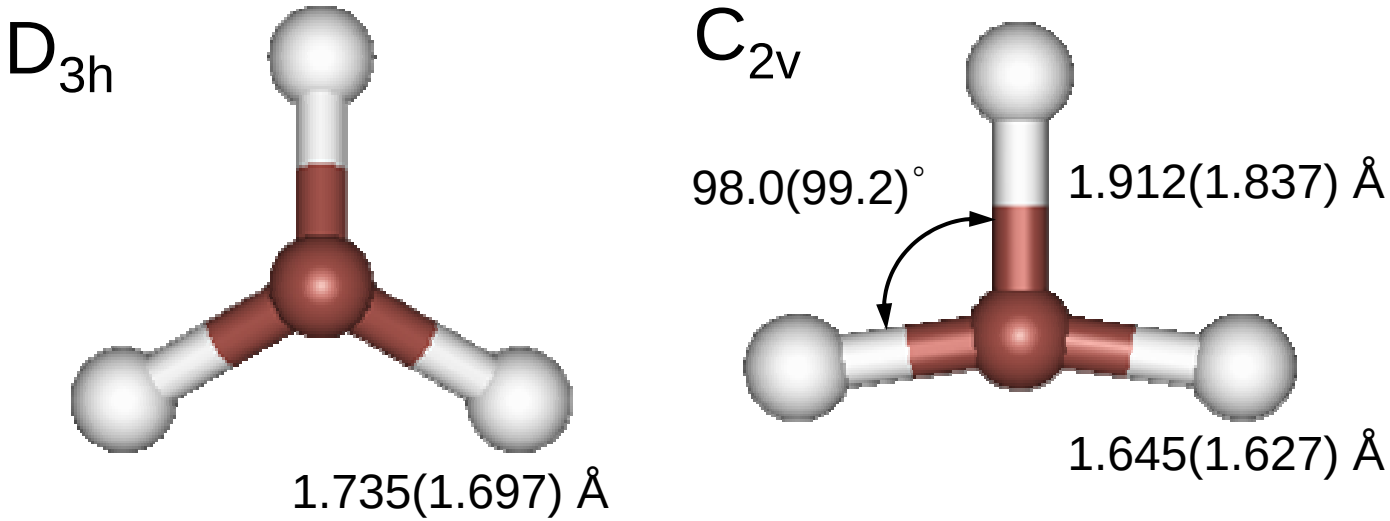
	AREP	REP	Δ_{so}
113-H	1.735	1.697	-0.038
113-F	2.075	2.062	-0.013

$114X_4$



	AREP	REP	Δ_{so}
114-H	1.780	1.769	-0.011
114-F	2.104	2.099	-0.005

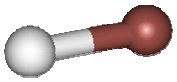
AREP(REP) optimized geometries of $113H_3$



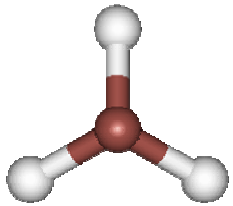
$113H_3$, $113F_3$인 경우 AREP, REP에서 모두 optimized geometry가 D_{3h}가 아닌 C_{2v}였으며, 에너지 차이는 각각 1.09, 0.82 eV로 근소한 차이를 보였다.

Vibrational frequencies of Tl and Pb compounds.

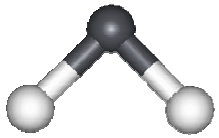
All frequencies are in cm^{-1}.



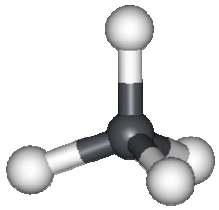
		AREP	REP	Δ_{so}
TlH	$\sum_g$	1410	1442	32
TlF	$\sum_g$	480	483	3



		AREP	REP	Δ_{so}
TlH_3	E'	584	586	2
	A_2''	687	688	1
	E'	1865	1874	9
	A_1'	1911	1923	12
TlF_3	E'	92	92	0
	A_2''	142	142	0
	E'	612	613	1
	A_1'	616	618	2



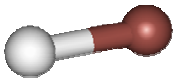
		AREP	REP	Δ_{so}
PbH_2	A_1	805	794	-11
	B_2	1679	1682	3
	A_1	1681	1695	14
PbF_2	A_1	177	178	1
	B_2	542	547	5
	A_1	562	565	3



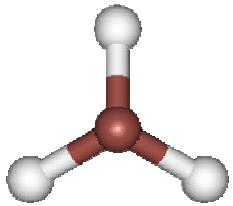
		AREP	REP	Δ_{so}
PbH_4	T_2	690	690	0
	E	769	771	2
	T_2	1958	1957	-1
	A_1	1974	1981	7
PbF_4	T_2	157	158	1
	E	122	123	1
	T_2	656	657	1
	A_1	656	657	1

Vibrational frequencies of 113 and 114 compounds.

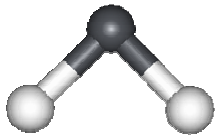
All frequencies are in cm^{-1}.



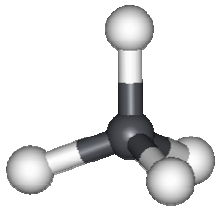
		AREP	REP	Δ_{so}
113H	$\sum_g$	1187	1618	431
113F	$\sum_g$	431	443	12



		AREP	REP	Δ_{so}
$113H_3$	E'	-164	-158	6
	A_2''	815	820	5
	E'	1864	1883	19
	A_1'	1936	2049	113
$113F_3$	E'	-149	-156	-7
	A_2''	152	158	6
	E'	521	527	6
	A_1'	559	569	10



		AREP	REP	Δ_{so}
$114H_2$	A_1	743	670	-73
	B_2	1469	1250	-219
	A_1	1552	1588	36
$114F_2$	A_1	131	139	8
	B_2	494	486	-8
	A_1	516	522	6



		AREP	REP	Δ_{so}
$114H_4$	T_2	508	492	-16
	E	645	633	-12
	T_2	1849	1762	-87
	A_1	1826	1854	28
$114F_4$	T_2	86	81	-5
	E	17	18	1
	T_2	549	543	-6
	A_1	531	536	5

M-X bond energies of Tl and Pb compounds.

All energies are in kcal/mol.

	HF			CCSD(T)		
	AREP	REP	Δ_{so}	AREP	REP	Δ_{so}
TlH	38.4	26.3	-12.1	54.7	43.7	-11.0
TlH_3	34.8	31.0	-3.8	46.8	43.4	-3.4
TlF	74.1	59.6	-14.5	109.9	96.8	-13.1
TlF_3	37.0	32.5	-4.5	67.4		
PbH_2	36.7	27.1	-9.6	54.3	41.8	-12.5
PbH_4	37.9	32.7	-5.2	52.1	45.5	-6.6
PbF_2	64.8	52.8	-12.0	102.3	87.7	-14.6
PbF_4	39.9	34.0	-5.9	73.5		

M-X bond energies of 113 and 114 compounds.

All energies are in kcal/mol.

	HF			CCSD(T)		
	AREP	REP	Δ_{so}	AREP	REP	Δ_{so}
113H	31.6	7.4	-24.2	50.7	30.8	-19.9
$113H_3$	18.1	9.5	-8.6	37.6	30.4	-7.2
113F	64.1	14.1	-50.0	99.7	56.1	-43.6
$113F_3$	-6.9	-22.5	-15.6	36.6		
$114H_2$	31.0	-11.4	-42.4	51.1	11.4	-39.7
$114H_4$	20.8	-3.9	-24.7	40.8	17.3	-23.5
$114F_2$	54.5	-4.8	-59.3	90.8	37.0	-53.8
$114F_4$	0.1	-29.8	-29.9	45.5		

Summary

- 113, 114 화합물의 bond length는 spin–orbit 효과에 의해 0.30 Å이내로 감소하였다. 예측되는 bond length는 Tl, Pb화합물에 비해 비슷하거나 약간 크게 나타났지만, 113H과 $113H_3$의 경우는 오히려 줄어들었다.
- Bond length와 vibrational frequency의 spin–orbit 효과에 의한 변화는 hydride의 경우에서 크게 나타났다. Fluoride의 경우 electronegative fluorine이 $p_{1/2}$전자를 더 많이 끌어당기므로 분자상태에서의 spin–orbit 효과가 감소하기 때문이다.
- Spin–orbit 효과가 bond energy에 미치는 영향(Δ_{so})은 fluoride의 경우 크게 나타난다. bond energy의 Δ_{so}는 원자상태의 spin–orbit 효과와 분자상태의 spin–orbit 효과의 차이에 의해 나타나는데, fluoride는 분자상태의 spin–orbit 효과가 감소하여 Δ_{so}가 크게 나타난다.
- 113, 114의 화합물이 합성된다면 ligand와 매우 약한 결합을 하고 있을 것으로 예상되며, 이러한 경향성에는 spin–orbit 효과가 중요한 역할을 하고 있음을 확인할 수 있다.