

물리 및 무기화학 석사세미나

Ab initio calculations of
SuperHeavy elements and
their compounds

“정말 무거운 원소에서는
어떤 현상들이 나타날 것인지
계산화학으로 밝혀 보자.”

KAIST 양자화학연구실
손상길

Superheavy Element



1 H	Elements 113–118 have yet to be observed												2 He				
3 Li	4 Be																
11 Na	12 Mg																
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57– La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89– Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	(113)	(114)	(115)	(116)	(117)	(118)

Lanthanide series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Transfermium WARS

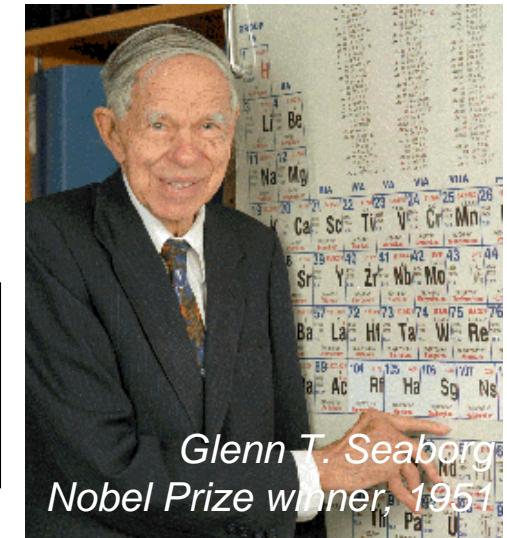
1997 IUPAC

101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt
------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------

- Rf : 1964, Nuclear Institute at Dubna, and U. C. Berkeley
- Db : 1967, Nuclear Institute at Dubna, and U. C. Berkeley
- Sg : 1974, Lawrence Berkeley Laboratory, and Livermore National Laboratory

101 Md	102 No	103 Lr
------------------	------------------	------------------

104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt
------------------	------------------	------------------	------------------	------------------	------------------



Glenn T. Seaborg
Nobel Prize winner, 1951

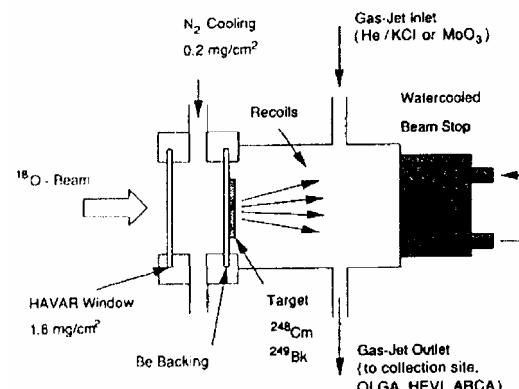
- Bh : 1981, GSI in Darmstadt
- Hs : 1984, GSI in Darmstadt
- Mt : 1982, GSI in Darmstadt
- 110 : 1994, GSI in Darmstadt
- 111 : 1994, GSI in Darmstadt
- 112 : 1996, GSI in Darmstadt

recommended
by ACS

Experimental procedure

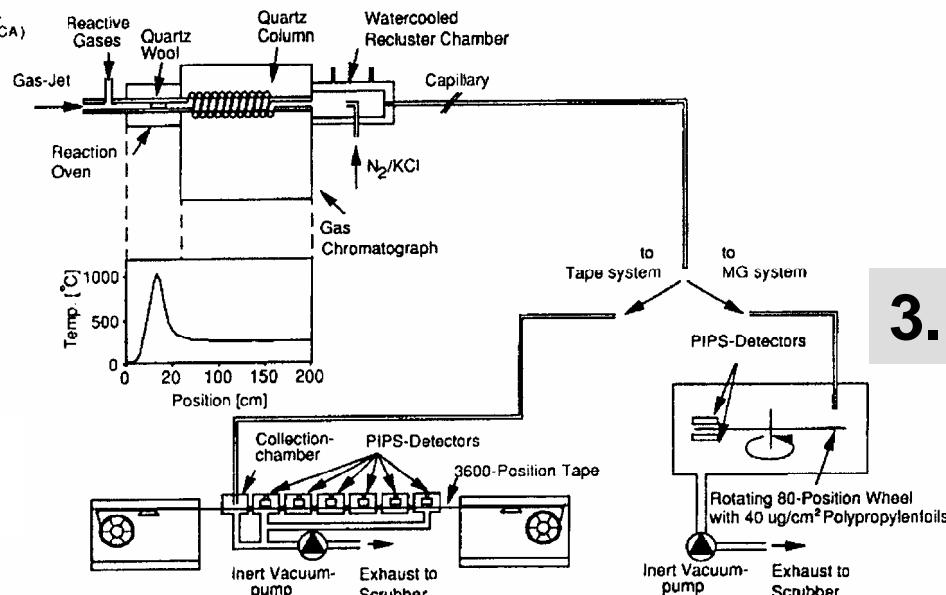
1. Synthesis

- Nuclear fusion



2. Separation

- Gas-phase chromatography
- Liquid chromatography
- Liquid-liquid extraction



3. Detection

Schädel, M. *Radiochimica Acta*,
1995, 70/71, 207-223

112번 원소까지 합성
반감기는 수 sec에서 수 msec정도
수십 sec정도면 화학적인 실험가능
106번 Sg까지 화합물 합성

실험에서의 어려운 점

- one-atom-at-a-time
- 너무 짧은 반감기



이론적인 예측이 반드시 필요

Half-lives

104	105	106	107	108	109
Rf	Db	Sg	Bh	Hs	Mt

^{255}Rf : 1.7 s

^{256}Rf : 0.007 s

^{257}Rf : 4.7 s

^{258}Rf : 0.012 s

^{259}Rf : 3.4 s

^{260}Rf : 0.020 s

^{261}Rf : 1.1 m

^{262}Rf : 1.2 s

^{255}Db : 1.6 s

^{256}Db : 2.6 s?

^{257}Db : 1.5 s

^{258}Db : 4.2 s

^{259}Db : 1.2 s

^{260}Db : 1.5 s

^{261}Db : 1.8 s

^{262}Db : 34 s

^{263}Db : 30 s

^{259}Sg : 0.9 s

^{260}Sg : 0.0036 s

^{261}Sg : 0.23 s

^{263}Sg : 0.8 s

^{265}Sg : 16 s

^{266}Sg : 20 s

^{260}Bh :

^{261}Bh : 0.0118 s

^{262}Bh : 0.102 s

^{263}Hs : 1 s

^{264}Hs : 0.00008 s

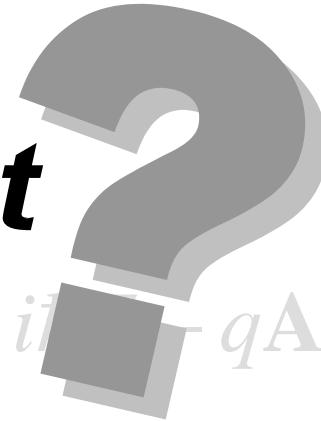
^{265}Hs : 0.0018 s

^{267}Hs : 0.0033 s

^{266}Mt : 0.0034 s

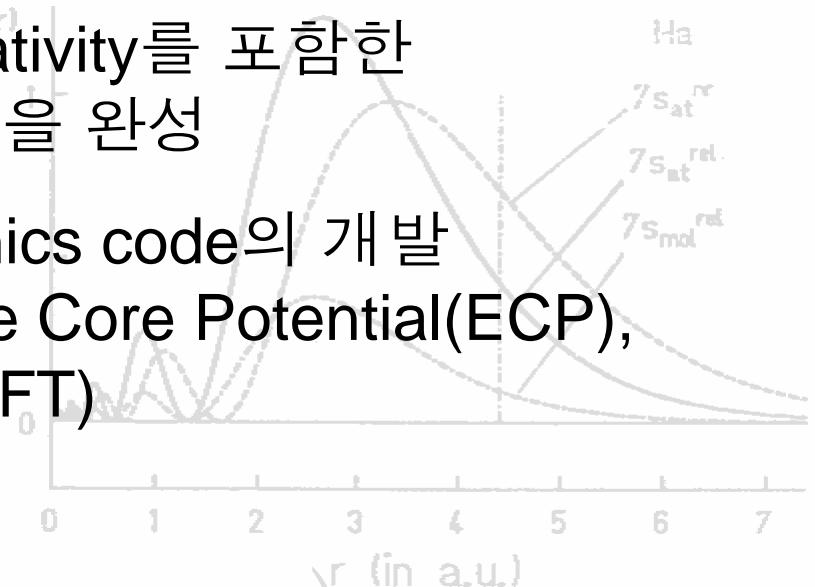
^{267}Mt : 0.070 s

Relativistic Effect ?



$$\left(i\hbar \frac{\partial}{\partial t} - q\phi \right) \Psi = c\alpha \cdot (-i\hbar \partial_{rr} - qA_r) \Psi + \beta mc^2 \Psi$$

- Hg의 경우 1s 전자의 속도는 빛의 속도의 60%정도
- 1928년, P. A. M. Dirac이 relativity를 포함한 파동방정식인 Dirac equation을 완성
- Relativistic quantum mechanics code의 개발
all-electron *ab initio*, Effective Core Potential(ECP),
Density Functional Theory(DFT)



$$H - q\phi = c\alpha \cdot (\mathbf{p} - q\mathbf{A}) + \beta mc^2$$

$$c\alpha^\mu \left(-i\hbar \partial_{rr} - q A_{rr} \right) \Psi = \beta mc^2 \Psi$$

Lanthanide contractions

diffuse f-orbital :

핵전하를 효과적으로
screen하지 못함.

바깥쪽의 orbital은 더
큰 effective charge를
받게됨.

contraction 일어남.
5주기와 6주기의
전이금속 성질이 비슷.

Actinide contractions

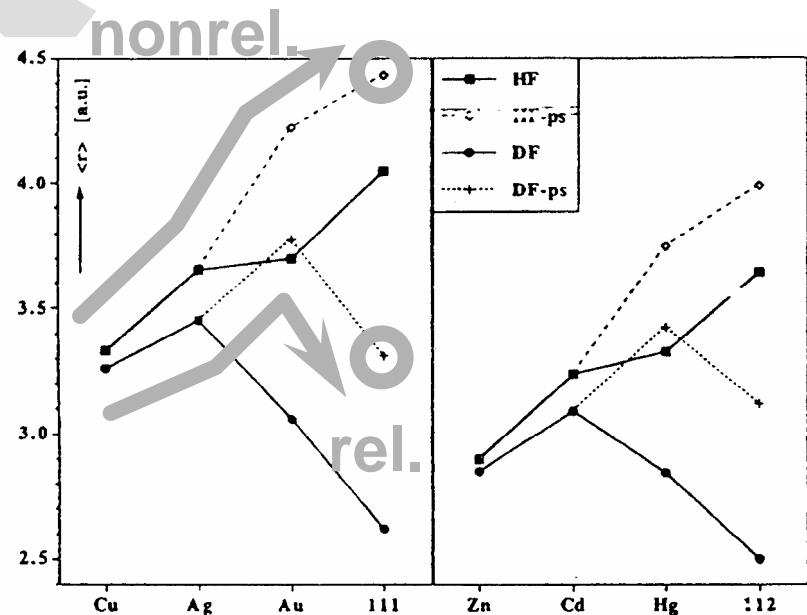


Figure 2. $\langle r \rangle$ -expectation value of the valence ns orbitals ($n = 4-7$). HF-ps and DF-ps indicate nonrelativistic and relativistic calculations for the pseudoatoms, respectively.

Seth, M.; Dolg, M.; Fulde, P.; Schwerdtfeger, P. *J. Am. Chem. Soc.* **1995**, 117, 6597-6598

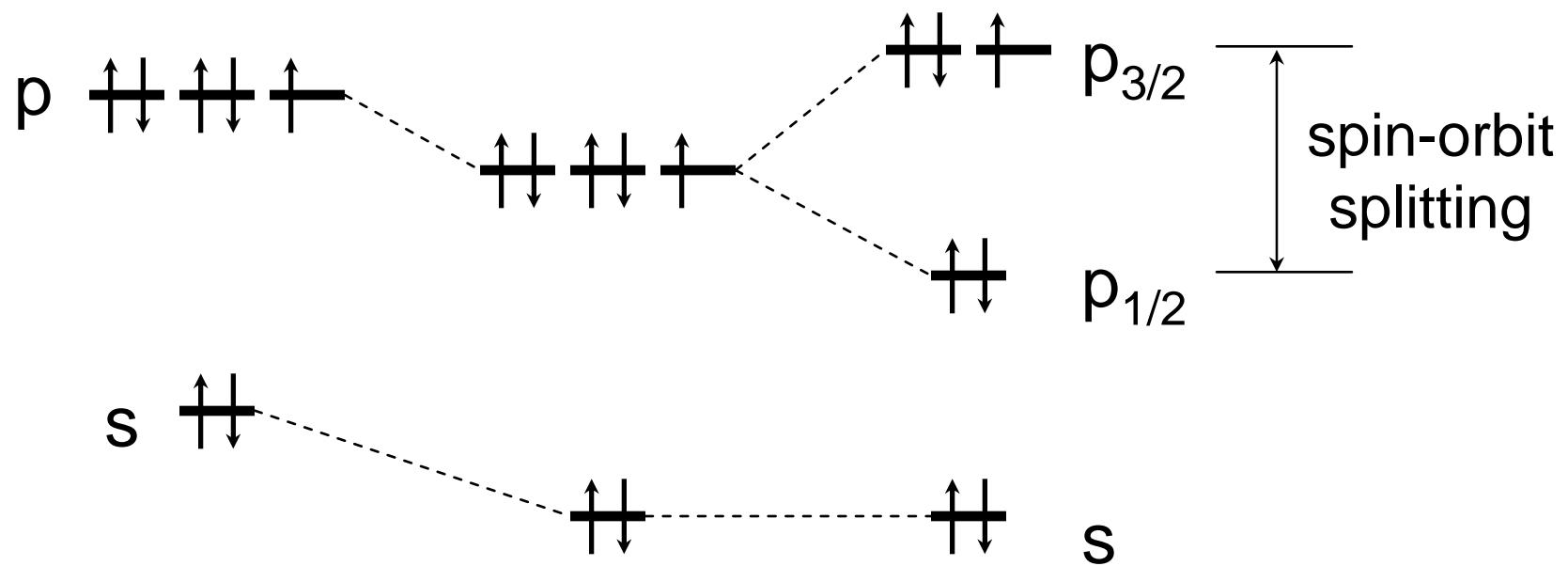
Relativistic Effects

Scalar relativistic effect

- direct effect : s, p stabilized(contraction)
- secondary effect : d, f destabilized(dilatation)

핵전하를 효과적으로
screen하게됨

Spin-orbit effect : $p_{1/2}$, $p_{3/2}$ splitting



9	F
17	Cl
35	Br
53	I
85	At
117	117

Bond length of H(117)

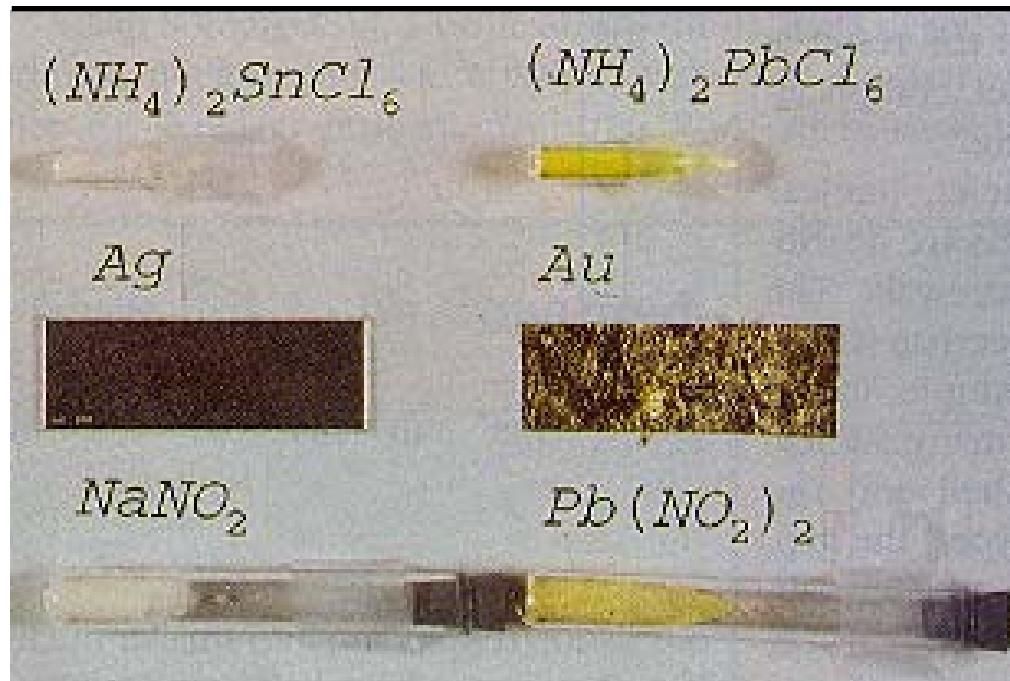


Units are in Å.

	NR-HF	DHF	AREP-HF	REP-KRHF
Hl	1.608	1.602	1.595	1.598
HAt	1.709	1.712	1.689	1.717
H(117)	1.849	1.978	1.784	1.973

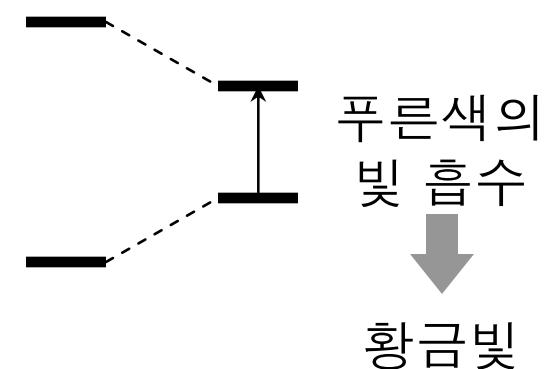
p contraction p_{3/2} dilatation

Relativistic effects can be seen with the naked eye.



March 23, 1998, Chem. & Eng. News

Au : 5d¹⁰ 6s



6주기 원소들의 특징적인 색깔은 s-d transition에서 오는 것이다.

Electronic configurations

Lr : $7s^2\ 7p_{1/2}$, not $7s^2\ 6d$

Rf : $6d\ 7s^2\ 7p_{1/2}$

Db : $6d^3\ 7s^2$

Sg : $6d^4\ 7s^2$

111 : $6d^9\ 7s^2$

112 : $6d^{10}\ 7s^2$

Pershina, V. G.
Chem. Rev. **1996**, 96, 1977-2010

		M	M ⁺
group 4	Zr	$4d^2\ 5s^2$	$4d^2\ 5s$
	Hf	$5d^2\ 6s^2$	$5d\ 6s^2$
	Rf	$6d^2\ 7s^2$	$6d\ 7s^2$
group 5	Nb	$4d^4\ 5s$	$4d^4$
	Ta	$5d^3\ 6s^2$	$5d^3\ 6s$
	Db	$6d^3\ 7s^2$	$6d^2\ 7s^2$
group 6	Mo	$4d^5\ 5s$	$4d^5$
	W	$5d^4\ 6s^2$	$5d^4\ 6s$
	Sg	$6d^4\ 7s^2$	$6d^3\ 7s^2$

Molecular Orbital Energies

relativistic HOMO is stabilized

→ increase IP

relativistic LUMO is destabilized

→ decrease EA

increase ΔE



explain the stability of
 $\text{DbCl}_5(\text{HaCl}_5)$

Pershina, V.; Fricke, B.
J. Chem. Phys. **1993**, 99, 9720

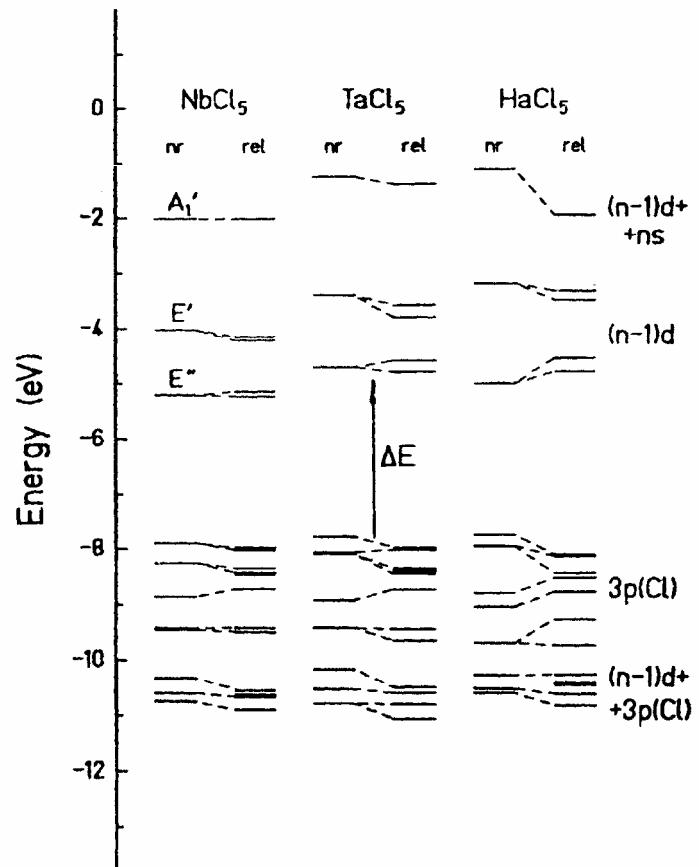


Figure 9. Energy level diagrams for NbCl_5 , TaCl_5 , and HaCl_5 as a result of the HFS nonrelativistic (nr) and DS DVM relativistic (rel) calculations. (Reproduced from ref 57. Copyright 1993 American Institute of Physics.)

실험 결과의 예측 Volatility

- adsorption enthalpy ΔH_a
measured in gas-phase chromatography
- more covalent, more volatile

Overlap Population

$HfCl_4$	0.55
$RfCl_4$	0.57

6d 7s² 7p_{1/2}

Pershina, V.; Fricke, B.
J. Phys. Chem. **1994**, 98, 6468

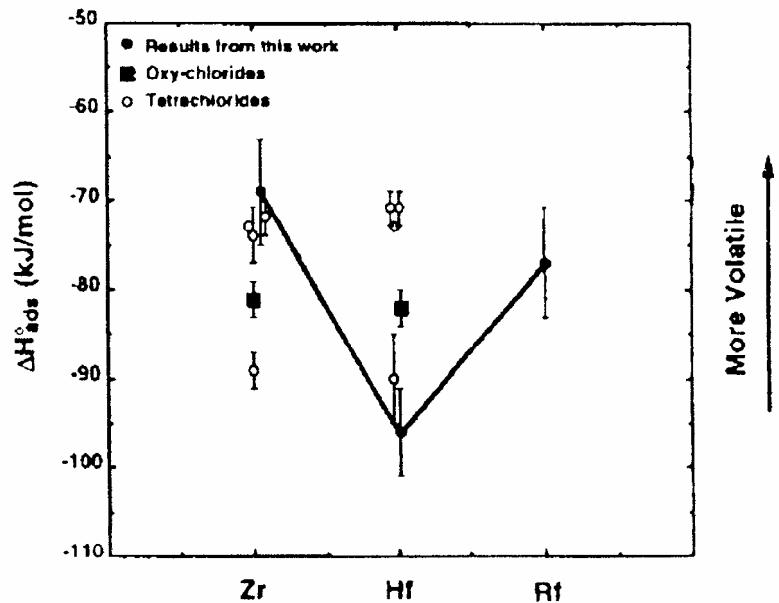
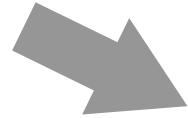


Fig. 10. Adsorption enthalpy values for group 4 chlorides and oxy-chlorides.

Kadkhodayan, B.
Radiochimica Acta, **1996**, 72, 169

실험 결과의 예측

양자계산으로 얻어진 전자구조,
effective charge, overlap population,
HOMO-LUMO energy level, dipole
moment, ...



- Adsorption enthalpy
- Sublimation enthalpy
- Extraction coefficient

Gas-phase chromatography의 실험대상인
Halides, Oxyhalides에 대한 연구가 진행중 :

MoCl_6 , WCl_6 , SgCl_6 , MoOCl_4 , WOCl_4 , SgOCl_4 ,
 MoO_2Cl_2 , WO_2Cl_2 , SgO_2Cl_2 , ...

6	7
B	C
14	15
Al	Si
32	33
Ga	Ge
49	50
In	Sn
81	82
Tl	Pb
113	114
113	114

Bond Energies of $^{113}\text{X}_n$, $^{114}\text{X}_n$ ($\text{X}=\text{H,F}$)

M-X bond energies(kcal/mol)

	AREP-HF	REP-HF
$^{114}\text{H}_2$	29.5	-11.4
$^{114}\text{H}_4$	20.1	-3.9
$^{114}\text{F}_2$	50.7	-7.0
$^{114}\text{F}_4$	-3.0	-32.1

Son, S. K.; Han, Y. K.; Lee, Y. S. *in preparation*

Summary

- Superheavy element는 112번까지 합성되었고 104~106번의 원소에 대해서 화학적 실험이 가능하다.
- Superheavy element에서는 relativistic effect가 반드시 고려되어야 한다.
- Relativistic effect에 의해 s와 p orbital이 contraction되고 spin-orbit splitting이 나타나므로 전자구조에 많은 영향을 끼친다.