PNPI school 2006

On the chemical identification of E112: is E112 a relatively inert element? Precise calculations of E112 compounds.

Titov A.V., Mosyagin N.S., Petrov A.N., Isaev T.A.,
PNPI RAS, Gatchina
Zaitsevskii A.V., Rykova E.A.
Kinetics Technology Ltd., Moscow

1. Importance of chemical indentification of E112.
2. Historical review of calculations on E112 compounds.
3. Our calculations of E112H, $E112H^+$, $E112_2$, E112Au.

Synthesis of E112

1996, GSI (Darmstadt) [Hofmann:96]:

cold fusion $^{70}Zn + {}^{208}Pb \rightarrow {}^{278}E112^{*} \rightarrow {}^{277}E112 + 1n$

$^{277}E112(\alpha,0.7ms) \rightarrow {}^{273}E110(\alpha,0.2ms)$

JINR (Dubna) [Oganessian:99, Oganessian:04]:

hot fusion $^{48}Ca + {}^{238}U \rightarrow {}^{286}E112^{*} \rightarrow {}^{283}E112 + 3n$

$^{283}E112(\alpha,4s) \rightarrow {}^{279}E110(SF,0.2s)$

JINR result was not confirmed at LBNL (Berkeley) [Loveland:02,Gregorich:05].

Chemical identification is required [Yakushev:03,Soverna:05].

Semiempirical estimations for properties of E112

E112 has the closed shell $6d^{10}7s^2$ configuration in the ground state.

In [Pitzer:75], volatility and inertness of E112 was suggested.

Atom	Transition	Energy(HFD)
Hg	$5d^{10}6s^2 \rightarrow 5d^{10}6s^16p^1$	5.2 eV
E112	$6d^{10}7s^2 \rightarrow 6d^{10}7s^17p^1$	8.6 eV
Rn	$6s^26p^6 \rightarrow 6s^26p^57s^1$	9.2 eV

His prediction: *E112 will behave like Rn rather than Hg.*

First *ab initio* calculations

In [Eliav:95], relativistic correlation (DCB/RCCSD) calculations on Hg and E112 atoms were carried out.

The ground state of $E112^{+}$ ion will be $6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}$ unlike Hg^{+} $5d_{3/2}^{4}5d_{5/2}^{6}6s_{1/2}^{1}$.

In [Seth:97], correlation (CCSD(T), MRCI) calculations on the $E112H^{+}$, $E112F_2$ and $E112F_4$ molecules were carried out with the help of the pseudopotential (adjusted in the LS-coupling scheme) method.

However, the XeF_2, XeF_4 and XeF_6 molecules *also exist*.

Table 1. Transition Energies (TE) for E112 (in cm^{-1}).

	HFDB	GRECP	RECP Nash 1997	PP Seth 1997	PP Seth 2003
Configuration	TE	Absolute errors			
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{2} \rightarrow$					
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{1}7p_{1/2}^{1}$	46406	-17	3198	-14254	153
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{1}7p_{3/2}^{1}$	64559	-29	5480	-3754	27
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{1}$	93797	-18	5456	303	94
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}7p_{1/2}^{1}$	28701	305	-3723	-15073	380
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}7p_{3/2}^{1}$	52595	277	-1254	-2198	189
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}$	84449	322	-1531	1781	308
$6d_{3/2}^{3}6d_{5/2}^{6}7s_{1/2}^{2}7p_{1/2}^{1}$	53581	387	-3903	-15588	22
$6d_{3/2}^{3}6d_{5/2}^{6}7s_{1/2}^{2}7p_{3/2}^{1}$	75273	437	-1515	-2750	-126

Calculations of other groups

In [Nakajima:00], scalar-relativistic correlation (DK3/CCSD(T)) calculations on E112H, $E112H^+$ and $E112H^-$ were carried out.

However, they neglect the *large spin-orbit interactions*.

In [Nash:05], correlation (RCCSD(T)) calculations on $E112H^+$ and $E112_2$ with the help of the RECP method were carried out.

However, Hg_2, $E112_2$ and Xe_2 are *Van der Waals systems* with a small dissociation energy.

Semiempirical (RDFT) calculations on E112Pd, E112Cu, E112Ag, E112Au [Pershina:02] and $E112_2$ [Anton:04] were carried out.

Our calculations

Our correlation (RCCSD+HOCA) calculations on E112H and $E112H^+$ with the help of the GRECP method.

The ground state RnH and XeH molecules are not observed in the gas phase, whereas HgH can be obtained by *radiofrequency discharge* in hydrogen and metal vapor (see, e.g., Ref. [Dufayard:88]).

Our correlation (CCSD(T)) calculations on $E112_2$ and semiempirical (SODFT) calculations on E112H, E112Au with the help of the GRECP method.

Table 2. Spectroscopic constants for E112H and HgH.

Method	R_e(Å)	w_e(cm^{-1})	D_e(eV)
The HgH molecule			
GRECP/13e-RCCSD-1	1.709	1575	0.35
GRECP/13e-RCCSD(T)-1	1.738	1395	0.41
Experiment	1.738±0.003	1403±18	0.46
VGRECP/21e-SODFT	1.742	1353	0.45
The E112H molecule			
GRECP/13e-RCCSD-1	1.638	1859	0.36
GRECP/13e-RCCSD-1 + HOCA	1.662	1800	0.42
GRECP/13e-CCSD-1	1.746	1402	-0.03
DK3/19e-CCSD(T) [Nakajima:00]	1.829	1007	0.06
VGRECP/21e-SODFT	1.651	1766	0.62

Dispersion interactions between atoms

$$E_{disp} = -1.5\ \alpha_A\ \alpha_B\ I_A\ I_B / (I_A + I_B)\ R_{AB}^6 \qquad \text{for } R_{AB} \gg r_A + r_B$$

X	HFDB	Experiment. for H, Hg and Xe, [Seth:97] and [Eliav:95] for E112		For XH and $R_{AB} = r_A + r_B$
Hg	$\langle r \rangle_{6s}$ = 2.85 a.u.	α = 34. a.u.	I = 0.384 a.u.	E_{disp} = 0.20 eV
E112	$\langle r \rangle_{7s}$ = 2.50 a.u.	α = 26. a.u.	I = 0.440 a.u.	E_{disp} = 0.27 eV
Xe	$\langle r \rangle_{5p}$ = 2.35 a.u.	α = 27. a.u.	I = 0.446 a.u.	E_{disp} = 0.36 eV
H	$\langle r \rangle_{1s}$ = 1.50 a.u.	α = 4.5 a.u.	I = 0.500 a.u.	

Table 3. Spectroscopic constants for Hg_2 and $E112_2$.

Method	R_e(Å)	w_e(cm^{-1})	D_e(eV)
The Hg_2 molecule			
RDFT [Anton:05] (A)	3.63	14	0.009
GRECP/36e-CCSD(T)+SO	3.74	18.5	0.043
Experiment	3.66±0.03	19.65±0.05	0.045±0.002
RDFT [Anton:05] (B)	3.55	24	0.048
RECP/RCCSD(T) [Nash:05]	3.60		0.072
The $E112_2$ molecule			
RDFT [Anton:05] (A)	3.45	25	0.039
GRECP/36e-CCSD(T)+SO	3.65	23.5	0.053
RDFT [Anton:05] (B)	3.39	30	0.080
RECP/RCCSD(T) [Nash:05]	3.07		0.187

Table 4. Spectroscopic constants for HgAu and E112Au.

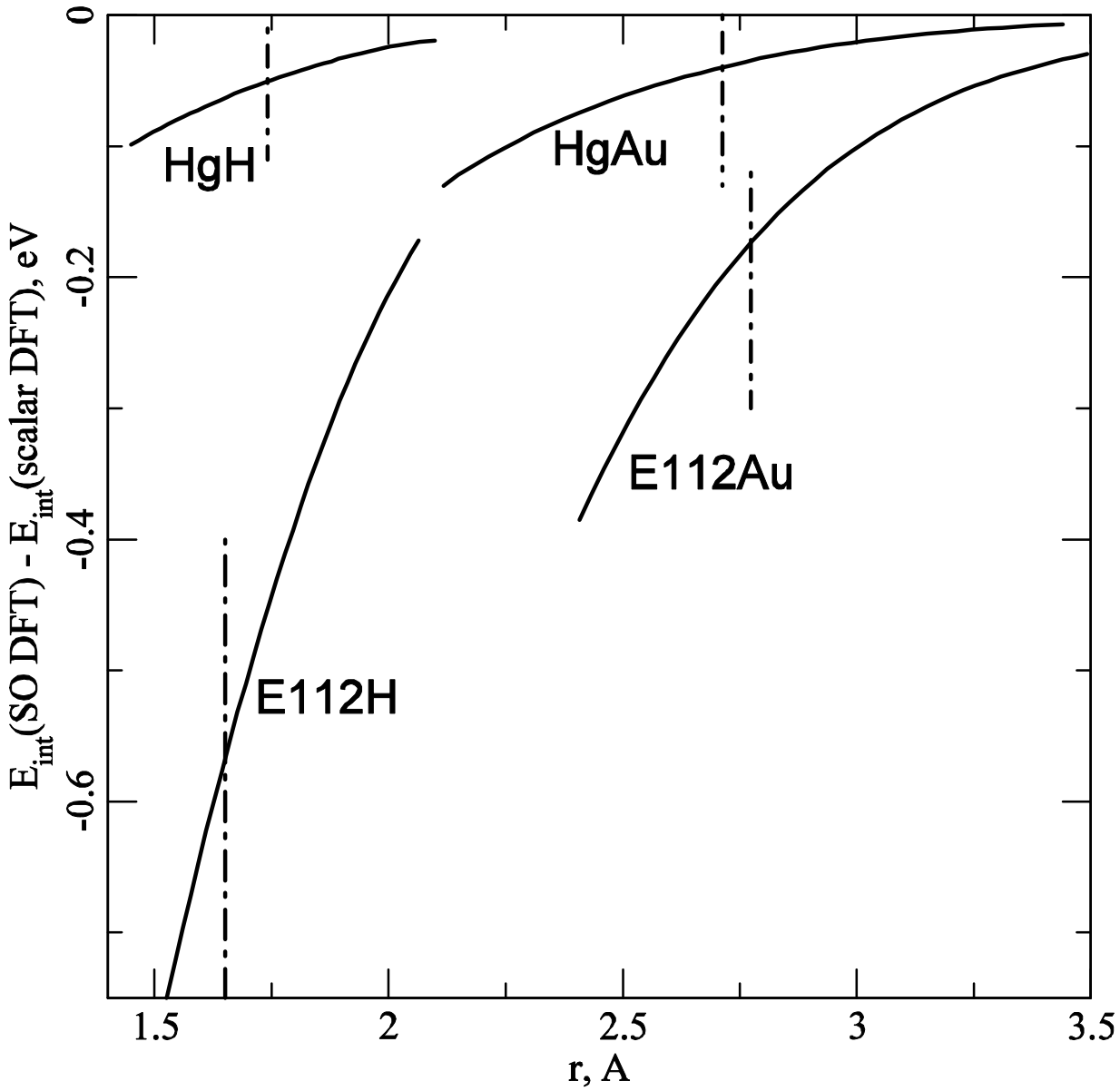
Method	R_e(Å)	w_e(cm^{-1})	D_e(eV)
The HgAu molecule			
VGRECP/21e-SODFT	2.71	104	0.51
RDFT [Pershina:02]	2.67	100	0.50
The E112Au molecule			
VGRECP/21e-SODFT	2.77	83	0.36
RDFT [Pershina:02]	2.73	74	0.27

Conclusions:

1. Accounting for both scalar-relativistic and spin-orbit effects is important in calculations of superheavy element compounds.
2. Our *ab initio* precise calculations on E112H and $E112H^{+}$ can be used to calibrate other semiempirical (DFT) methods.

The end.

Spin-orbit interaction curves



References:

[1] K.S.Pitzer, J.Chem.Phys. **63**, 1032 (1975).
[2] E.Eliav, U.Kaldor, Y.Ishikawa, Phys.Rev.A **52**, 2765 (1995).
[3] M.Seth, P.Schwerdtfeger, M.Dolg, J.Chem.Phys. **106**, 3623 (1997).
[4] T.Nakajima, K.Hirao, Chem.Phys.Lett. **329**, 511 (2000).
[5] C.S.Nash, J.Phys.Chem.A **109**, 3493 (2005).
[6] V.Pershina, *et al.*, Chem.Phys.Lett. **365**, 176 (2002).
[7] J.Anton, *et al.*, Chem.Phys. **311**, 97 (2005).
[8] G.Herzberg, *Spectra of Diatomic Molecules*, 1950.
[9] K.P.Huber, G.Herzberg, *Constants of Diatomic Molecules*, 1979.
[10] W.C.Stwalley, J.Chem.Phys. **63**, 3062 (1975).
[11] J.Dufayard, B.Majournat, O.Nedelec, Chem.Phys. **128**, 537 (1988).
[12] S.Hofmann, *et al.*, Z.Phys.A **354**, 229 (1996).
[13] Yu.Ts.Oganessian, *et al.*, Eur.Phys.J.A **5**, 63 (1999);
[13a] Yu.Ts.Oganessian, *et al.*, Phys.Rev.C **70**, 064609 (2004).
[14] W.Loveland, *et al.*, Phys.Rev.C **66**, 044617 (2002).
[15] A.B.Yakushev, *et al.*, Radiochim. Acta **91**, 433 (2003).
[16] C.S.Nash, *et al.*, J.Chem.Phys. **106**, 5133 (1997)
[17] M.Seth, *et al.*, to be published (P.Schwerdtfeger, private communication, 2003).

Transition Energies (TE) between states averaged over the relativistic configurations of E112 derived from all-electron HFDB calculations with Fermi nuclear model and the absolute errors of their reproducing in different all-electron and 20-electron RECP calculations (in cm^{-1}).

	HFDB[a] (Fermi)	HFD+B[b] (Fermi)	HFD[b] (Fermi)	HFD[a] (Point)	GRECP[c]	Ionic RECP[d]	Nash's RECP[e]	Seth's PP[f] (LS-coupling)	Seth's PP[g]
Configuration	TE				Absolute errors				
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{2} \rightarrow$									
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{1}7p_{1/2}^{1}$	46406	1	-27	1768	-17	588	3198	-14254	153
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{1}7p_{3/2}^{1}$	64559	-1	239	1964	-29	820	5480	-3754	27
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{1}8s_{1/2}^{1}$	72571	-1	257	1760	-25	719	5085	279	105
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{1}$	93797	-1	277	1875	-18	807	5456	303	94
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}7p_{1/2}^{1}$	28701	2	-576	-644	305	-422	-3723	-15073	380
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}7p_{3/2}^{1}$	52595	0	-267	-464	277	-181	-1254	-2198	189
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}8s_{1/2}^{1}$	62635	0	-252	-776	314	-315	-1879	1765	326
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}$	84449	0	-234	-672	322	-224	-1531	1781	308
$6d_{3/2}^{3}6d_{5/2}^{6}7s_{1/2}^{2}7p_{1/2}^{1}$	53581	2	-281	-765	387	-376	-3903	-15588	22
$6d_{3/2}^{3}6d_{5/2}^{6}7s_{1/2}^{2}7p_{3/2}^{1}$	75273	0	7	-600	437	-84	-1515	-2750	-126
$6d_{3/2}^{3}6d_{5/2}^{6}7s_{1/2}^{2}8s_{1/2}^{1}$	85677	-1	25	-915	477	-213	-2126	1228	22
$6d_{3/2}^{3}6d_{5/2}^{6}7s_{1/2}^{2}$	107531	-1	44	-811	484	-122	-1777	1245	1

[a]All-electron HFDB calculations with Fermi and point nuclear charge distributions, correspondingly.

[b]All-electron HFD calculation without and with accounting for Breit interaction in the framework of the first order of the perturbation theory, correspondingly.

[c]Generalized RECP (GRECP) generated from HFDB calculation.

[d]Semi-local RECP generated from HFDB calculation on the ionic closed-shell generator-state.

Spectroscopic constants of the ground states of the $E112H^+$ and HgH^+ ions.

Method	R_e(Å)	w_e(cm^{-1})	D_e(eV)	B_e(cm^{-1})	w_ex_e(cm^{-1})	α_e($10^{-3}cm^{-1}$)	$-Y_{02}$($10^{-6}cm^{-1}$)
The HgH^+ ion							
GRECP/12e-RCCSD-1	1.596	2037	2.67	6.60	39	200	279
GRECP/12e-RCCSD(T)-1	1.599	2013	2.68	6.58	41	208	282
Experiment (Ref. 8)	1.594	2034	(2.4)[a]	6.61	46	206	285
Experiment (Ref. 9)	1.594	2028	(3.11)[a]	6.61	41	206	285
The $E112H^+$ ion							
GRECP/20e-CCSD-1	1.537	2587	4.60	7.10	46	198	215
GRECP/20e-CCSD-2	1.531	2681	4.46	7.15	35	168	205
GRECP/18e-CCSD-1	1.537	2588	4.61	7.10	47	198	215
GRECP/18e-CCSD-2	1.531	2680	4.46	7.16	35	169	205
GRECP/12e-CCSD-1	1.535	2590	4.96	7.12	47	200	216
GRECP/12e-CCSD-2	1.527	2679	4.75	7.19	37	175	208
GRECP/12e-RCCSD-1	1.537	2569	3.96	7.11	47	201	218
GRECP/12e-RCCSD-2	1.519	2752	3.80	7.28	45	187	204
GRECP/12e-RCCSD-1 + HOCA	1.540	2547	4.35	7.08	45	195	220
DK3/18e-CCSD [4]	1.528	2621		7.18			
DK3/18e-CCSD(T) [4]	1.532	2595		7.15			
PP/CCSD(T) [3][b]	1.515	2640	5.15		51		
PP/MRCI+SO [3][b]	1.503	2620	3.86				
PP/CCSD(T)+SO [3][b]	1.517	2673	4.09		52		
RECP/RCCSD(T) [5] [b]	1.583		3.50				

Spectroscopic constants of the ground states of the E112H and HgH molecules.

Method	R_e(Å)	w_e(cm^{-1})	D_e(eV)	B_e(cm^{-1})	w_ex_e(cm^{-1})	α_e($10^{-3}cm^{-1}$)	$-Y_{02}$($10^{-6}cm^{-1}$)
The HgH molecule							
GRECP/13e-RCCSD-1	1.709	1575	0.35	5.76	56	262	312
GRECP/13e-RCCSD(T)-1	1.738	1395	0.41	5.56	83	348	363
Experiment (Ref. 9)	[1.766][c]	[1203][c]	0.46	[5.39][c]			[395][c]
Experiment (Ref. 11)	1.741	1385	0.46	5.55	75	271	
Experiment (Ref. 8)	1.740	1387	0.46	5.55	83	312	344
Experiment (Ref. 10)	1.735	1421	0.46	5.59	121	404	346
The E112H molecule							
GRECP/21e-CCSD-1	1.742	1438	-0.03	5.53	113	409	340
GRECP/21e-CCSD-2	1.801	1104	-0.02	5.15			
GRECP/19e-CCSD-1	1.741	1439	-0.03	5.53	113	409	340
GRECP/19e-CCSD-2	1.801	1102	-0.02	5.15			
GRECP/13e-CCSD-1	1.746	1402	-0.03	5.50	119	429	354
GRECP/13e-CCSD-2	1.808	1038	-0.05	5.10			
GRECP/13e-RCCSD-1	1.638	1859	0.36	6.25	95	338	288
GRECP/13e-RCCSD-2	1.663	1649	0.32	6.06	123	425	340
GRECP/13e-RCCSD-1 + HOCA	1.662	1800	0.42	6.07	152	385	287
VGRECP/21e-SODFT(B98)	1.651	1766	0.62				
DK3/19e-CCSD [4]	1.823	991	0.04	5.05			
DK3/19e-CCSD(T) [4]	1.829	1007	0.06	5.02			

Spectroscopic constants of the ground states of the Hg_2, $E112_2$, HgAu and E112Au molecules.

Method	R_e(Å)	w_e(cm^{-1})	D_e(eV)	$w_e x_e$(cm^{-1})
The Hg_2 molecule				
RDFT(B88/P86) [7]	3.63	14	0.009	
GRECP/36e-CCSD(T)+SO	3.74	18.5	0.043	0.239
Experiment	3.63	19.7	0.043	
Experiment	3.69	19.6	0.047	0.25
RDFT(PW91) [7]	3.55	24	0.048	
RECP/RCCSD(T) [5]	3.60		0.072	
The $E112_2$ molecule				
RDFT(B88/P86) [7]	3.45	25	0.039	
GRECP/36e-CCSD(T)+SO (preliminary)	3.65	23.5	0.053	0.343
RDFT(PW91) [7]	3.39	30	0.080	
RECP/RCCSD(T) [5]	3.07		0.187	
The HgAu molecule				
VGRECP/21e-SODFT(B98)	2.71	104	0.51	
RDFT(VWN,B88/P86) [6]	2.67	100	0.50	
The E112Au molecule				
VGRECP/21e-SODFT(B98)	2.77	83	0.36	
RDFT(VWN,B88/P86) [6]	2.73	74	0.27	