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

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1. Importance of chemical identification 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 $^{70}Zn + {}^{208}Pb \rightarrow {}^{278}112^{*} \rightarrow {}^{277}112 + 1\,n$

$^{277}112(\alpha,0.7ms) \rightarrow {}^{273}110(\alpha,0.2ms)$

It was confirmed at RIKEN (Japan) [Morita:04].

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

hot fusion $^{48}Ca + {}^{238}U \rightarrow {}^{286}112^{*} \rightarrow {}^{283}112 + 3\,n$

$^{283}112(\alpha,4s) \rightarrow {}^{279}110(SF,0.2s)$

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 (Hg: $5d^{10}6s^2$, Rn: $6s^26p^6$).

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

Atom	Transition	Promotion 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

Discussion was initiated on the question: *will E112 behave like noble gas Rn rather than Hg.*

First *ab initio* calculations

In [Eliav:95], accurate relativistic correlation (DCB/RCCSD) calculations on Hg and E112 atoms were first 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*, so these calculations do not answer the question about Hg- or Rn-like behaviour.

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
$6d_{3/2}^{4}6d_{5/2}^{6}7s_{1/2}^{2} \rightarrow$					
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}7p_{1/2}^{1}$	28701	*305*[a]	-3723	-15073	380
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}7p_{1/2}^{1} \rightarrow$					
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}7p_{3/2}^{1}$	23894	-28	2469	12876	-192
$6d_{3/2}^{4}6d_{5/2}^{5}7s_{1/2}^{2}$	55747	17	2192	16855	-73

[a]*This error can be removed by self-consistent GRECP correction*.

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 E112X (X=Au,Ag,Cu,Pd) [Pershina:02], E112Au [Tudoran:03] and $E112_2$ [Anton:05] were carried out. However, the point nuclear model was used in [Tudoran:03] and [Anton:05]. The errors of using the point nuclear model and neglecting Breit interactions attain several tenths and several hundredths of eV for the transition energies of E112.

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 *ab initio correlation* (CCSD(T)) calculations on $E112_2$ and *semiempirical* (SO-DFT) 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-SO-DFT (becke98)	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-SO-DFT (becke98)	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 (B88/P86) [Anton:05]	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 (PW91) [Anton:05]	3.55	24	0.048
RECP/RCCSD(T) [Nash:05]	3.60		0.072
The $E112_2$ molecule			
RDFT (B88/P86) [Anton:05]	3.45	25	0.039
GRECP/36e-CCSD(T)+SO	3.65	23.5	0.053
RDFT (PW91) [Anton:05]	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/39e-SO-DFT (becke98)	2.71	104	0.51
RDFT (RLDA/RGGA) [Pershina:02]	2.67	100	0.50
RDFT (RLDA) [Tudoran:03]	2.6		1.03
RDFT (GGA) [Tudoran:03]			0.55
The E112Au molecule			
VGRECP/39e-SO-DFT (becke98)	2.77	83	0.36
RDFT (RLDA/RGGA) [Pershina:02]	2.73	74	0.27
RDFT (RLDA) [Tudoran:03]	2.6		0.93
RDFT (GGA) [Tudoran:03]			0.41

Conclusions:

1. Accounting not only for scalar-relativistic but also for spin-dependent effects is mandatory in calculations of SHE compounds even for Σ-states (where the spin-orbit contribution is supressed in the leading order).

2. Our *ab initio* precise GRECP calculations on E112H and $E112H^+$ can be used for calibration of other more approximate methods (DFT, semiempirical, etc.) to study more complicated systems (interactions with surfaces, etc.).

3. **E112 demonstrate *more complicated behaviour* than just Hg-like or Rn-like one in opposite to that suggested earlier.**

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