

Intermetallic Compounds of Element 112: the Electronic Structure and Bonding of HgX and 112X (X = Pd, Ag and Au)

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The next heaviest element which is to be studied chemically at the JINR, Dubna, [1] and GSI [2] is element 112. Its properties are expected to be unique: high volatility and inertness due to the very strong relativistic stabilization of the 7s electrons and the closed-shell configuration, $7s^26d^{10}$ [3]. The surface of the chromatography column in the gas-phase chromatography experiments is to be made out of gold and palladium, since the interaction of Hg, the nearest homolog of element 112, with those metals was found to be rather strong [4].

To detect element 112 on those surfaces, the knowledge of its adsorption enthalpy is highly desirable. As a first step in the study of the metal-surface interaction, we have calculated here the electronic structure and bonding of the dimers, HgX and 112X (X = Pd, Ag and Au). The calculations were performed using the fully relativistic density-functional method (DFT) with the relativistic general gradient approximation (RGGA) for the exchange-correlation potential [5]. The Mulliken population analysis was applied additionally to study bonding in these systems. The calculated RGGA binding energies, D_e , optimized bond lengths, R_e , and harmonic frequencies, ω , are shown in Table 1. The obtained D_e are probably too large by about 0.2 eV, which is an average error of the DFT method [5].

Table 1. Calculated RGGA binding energies, D_e , bond lengths, R_e , and harmonic frequencies, ω , for HgX and 112X (X = Pd, Ag and Au)

Molecule	R_e , Å	D_e , kJ/mol	ω , cm ⁻¹
HgPd	2.56	61.2	125.62
HgAg	2.72	29.4	90.20
HgAu	2.66	52.7	101.95
112Pd	2.62	45.3	115.00
112Ag	2.76	19.0	75.41
112Au	2.73	31.7	79.17

Table 2. Overlap populations of the valence AO in HgAu and 112Au

Orbitals	HgAu	112Au
ns-ns	0.01	-0.02
ns-np _{1/2}	0.04	0.05
ns-np _{3/2}	0.06	0.03
np(tot)-ns	0.06	0.04
(n-1)d-np	0.01	0.00
(n-1)d-(n-1)d	-0.01	-0.01
OP(tot)	0.34	0.24

The calculations revealed an increase in R_e and a decrease in D_e of about 15 – 20 kJ/mol from HgX to 112X. The decrease in D_e is explained by a drastic relativistic stabilization and therefore

inertness of the 7s² shell. This results in a large decrease in the 7s(112)-Au overlap compared to the 6s(Hg)-Au one, as the data of Table 2 show. The contribution of the other orbitals is almost unchanged.

In Fig. 1, the calculated D_e are shown together with experimental adsorption enthalpies, ΔH_{ads} , of Hg on the corresponding metal surfaces [4]. One can see nice agreement for the trends between the two types of data, with the interaction of Hg and element 112 with Pd being the strongest.

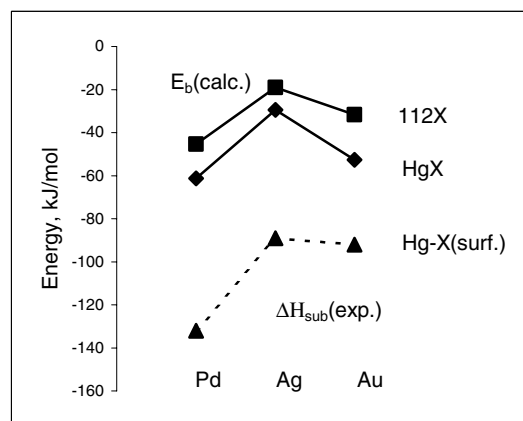


Fig. 2. Calculated binding energies for HgX and 112X (X = Pd, Ag and Au) and measured ΔH_{ads} on the corresponding metal surfaces [4,6]

Thus, the calculations describe the bonding in the right way, so that the difference in D_e between HgX and 112X could be related to the difference in ΔH_{ads} of Hg and element 112 on the metal surfaces. Thus, element 112 is expected to be weaker adsorbed than Hg, though not as weak as was expected earlier.

In the future calculations of adsorption on a cluster, one can foresee even a smaller difference between Hg and element 112, since the 6d orbitals of the latter will be more involved in the coordinated bonding due to their relativistic destabilization and expansion [3].

References

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