

Theoretical predictions of the adsorption energy of element 112 on a gold surface

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Recent discoveries of elements 112 through 116 have renewed the interest in the field of the superheavy elements (SHE). Element 112, first produced at the GSI, is of particular interest for chemical experiments: because of its closed electron shell and strongest relativistic effects it should exhibit properties similar to those of the noble gases. Thus, it was planned to study its volatility as adsorption on the gold surface of a chromatography column and compare it with the behaviour of the next nearest homologue Hg. To assist experimental investigations, adsorption of element 112 and Hg on gold is studied in the present work on the basis of fully relativistic density functional theory (DFT) electronic structure calculations.

From a theoretical point of view any surface can be considered as a huge molecule and the adsorption phenomenon as essentially local. We, therefore, approximate the surface by a gold cluster of moderate size. Taking into account the rest of the surface, this cluster is embedded in the potential produced by the atoms from the surrounding region.

In our DFT code [1], Vosko, Wilk and Nusair parameterization [2] is used for the exchange and correlation potentials. Nonlocal corrections are used perturbatively for exchange (with the relativistic form of RGGA of Becke's [3] approximation) and correlation (Perdew functional) [4] (B88/P86 in the tables), as well as the Perdew-Wang [5] for both exchange and correlation functionals (PW91/PW91 in the tables).

Calculations were performed for minimal and optimized atomic basis sets used previously in our calculations for the HgAu and 112Au dimers. The optimized basis includes additional functions $6p$ and $5f$ for Au and Hg, and $7p$ and $6f$ for element 112 on top of the minimal basis.

System	Binding energy E_b [eV]		
	RLDA	B88/P86	PW91/PW91
$HgAu_{14}$	-1.05	-0.45	-0.55
$112Au_{14}$	-0.58	0.03	-0.07
$HgAu_{34}$	-0.78	-0.18	-0.27
$112Au_{34}$	-0.37	0.23	0.13

Table 1: Binding energy of Hg and element 112 on the embedded Au clusters in the top position, when minimal neutral atomic basis sets are utilized.

First we performed computations for the top position, with the inner cluster simulated by 14 and 34 atoms using minimal basis sets. To estimate occupation number of the atoms of the surrounding cluster, we used the copy method described in [1]. An analysis of the results presented in Table 1 shows that the binding energy (E_b) decreases with increasing cluster size from 14 to 34 atoms (for the top position of the ad-atom relative to the surface). The difference in the binding energies ($\Delta E_b = E_b^{Hg} - E_b^{112}$) decreases from 0.47 eV to 0.41 eV, respectively. Results show

that Hg is weakly bound and element 112 is even unbound for the GGA values for $112Au_{34}$.

System	Binding energy E_b [eV]		
	RLDA	B88/P86	PW91/PW91
$HgAu_{14}$ (top)	-1.79	-1.14	-1.24
$112Au_{14}$ (top)	-1.23	-0.58	-0.68
$HgAu_{22}$ (hollow)	-2.57	-1.26	-1.44
$112Au_{22}$ (hollow)	-1.89	-0.67	-0.83

Table 2: Binding energy of Hg and element 112 on the embedded Au clusters, when optimized atomic basis sets are utilized.

For the optimized bases sets, the results in Table 2 show a significant increase of 0.69 eV and 0.61 eV in the binding energies of Hg and element 112 on the Au_{14} cluster, respectively. E_b^{Hg} is now much closer to the experimental value of 1.05 eV (101 kJ/mol [6]). This leads to an increase in ΔE_b from 0.47 eV to 0.56 eV. In the case of the hollow position of the ad-atom, this difference is about 0.6 eV. Thus, the influence of the potential created by the surrounding can be seen in the increased binding energies and in their enlarged difference between Hg and element 112. It may, however, happen that with the further increase of the Au-cluster size ΔE_b will be smaller, as is the case of MAu_{34} with respect to MAu_{14} for the neutral basis sets.

Comparison of the present data with our previous results [7] shows that obviously not a full convergence for the binding energies has previously been obtained due to the missing effects of the cluster surrounding.

On the basis of the present calculations, we can predict ΔH_{ads}^{112} on gold as ~ 0.5 eV with respect to the measured ΔH_{ads}^{Hg} of 1.05 eV [6].

References

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