

Calculations of the adsorption energies of element 112 and its homolog Hg on the Au(100) surface with improved basis sets

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Within the framework of the theoretical study of the adsorption of element 112 and its homolog, Hg, on surfaces of transition-element metals [1-3], results of the improved calculations for ad-atom-gold cluster systems are reported here. The fully relativistic, 4-component Density Functional Theory (DFT) method [4] in its embedded cluster approximation was used for that purpose. For exchange-correlation effects, the Relativistic Local Density (RLDA) and General Gradient (BP88/P86), a higher level of theory, approximations were used. According to the embedding technique, the surface was simulated by a metal cluster embedded into an environment. This enables one to take effects of the environment explicitly into account and to achieve converged results with clusters of a moderate size.

In the calculations, inner clusters Au_m of $m=14, 16, 22$ and 29 atoms embedded in outer clusters of 112, 110, 92 and 156 atoms, respectively, were used to simulate the Au(100) surface. Hg and element 112 were considered in the on-top, bridge and hollow adsorption positions with respect to the surface atoms. The calculations were performed with two types of basis set: the set of type B includes the filled 1s through ns orbitals and virtual np and (n-1)f orbitals, while a more extended basis set of type B' includes the virtual nd, (n-2)g and nf orbitals in addition to those of the basis set B. Binding (adsorption) energies E_b of Hg and element 112 with clusters of various size and the different adsorption positions, calculated with the basis sets B and B', are shown in Fig. 1 and Table 1 (for the basis set B').

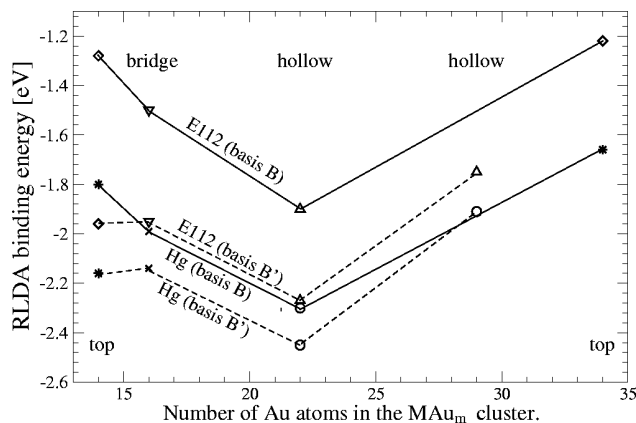


Fig. 1. The RLDA binding energies of element 112 and Hg with Au_m calculated for the basis set of types B and B'.

The results show that using the basis set B' improves E_b . Thus, $E_b(\text{B88/P86})$ for Hg in the preferential hollow position approaches the experimentally measured $\Delta H_{\text{ads}} = 101 \text{ kJ/mol}$ (1.04 eV) [5].

Table 1. The RLDA and GGA(B88/P86) binding energies E_b and bond lengths r of Hg and element 112 with Au_m calculated for the basis set of type B'

m posit.	Approx.	HgAu_m		112Au_m	
		E_b , eV	r , a.u.	E_b , eV	r , a.u.
14 top	RLDA	2.16	4.82	1.96	5.10
	B88/P86	1.64	4.97	1.47	5.32
16 bridge	RLDA	2.14	4.30	1.95	4.50
	B88/P86	1.26	4.30	1.07	4.50
22 hollow	RLDA	2.45	3.50	2.27	3.80
29 hollow	RLDA	1.91	3.51	1.75	3.80
	B88/P86	0.86	4.11	0.72	4.37

The difference in the binding energies between Hg and element 112, $E_b^{\text{Hg}} - E_b^{112}$, stays almost the same for the basis set of type B or B', independently of m and the adsorption position (Fig. 2). Using the extended basis set B' instead of B brings this difference from $\sim 0.4 \text{ eV}$ down to 0.15 eV. A slight decrease in ΔE_b is also observed with increasing m .

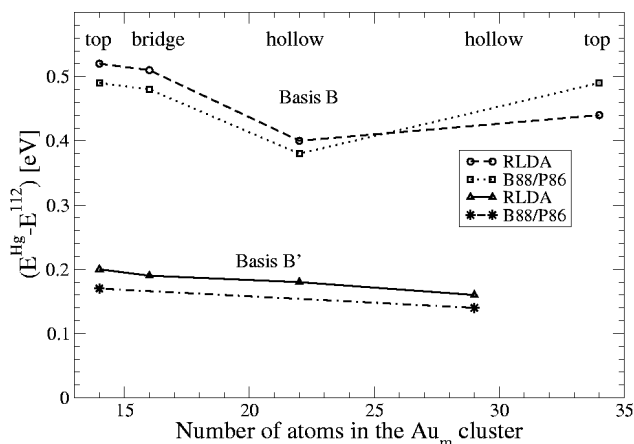


Fig. 2. The difference in the binding energies, $E_b^{\text{Hg}} - E_b^{112}$, between Hg and element 112 interacting with Au_m .

Thus, results of these calculations with the more extended basis set show that element 112 should be about 0.15 eV (15 kJ/mol) weaker adsorbed on the (100) Au surface than Hg, in agreement with our earlier conclusions made on the basis of the calculations for the Hg and 112 dimers [1,2].

References

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