

Relativistic *ab initio* Study of HgAu, Homologue of the Superheavy 112Au

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Predictions of the interaction of the superheavy elements with various surfaces are essential for their identification and separation. Recently, we have predicted the adsorption properties of the superheavy element 112 on inert surfaces [1]. The calculations were performed using the fully relativistic Dirac-Coulomb Hamiltonian combined with the coupled cluster method. The accuracy of the results was verified by performing the same calculations on mercury, which is a lighter homologue of element 112, and for which experimental data exist. For Hg, the results obtained were in excellent agreement with the experimental values, and we expect the same accuracy for its superheavy homologue. Similar investigations were performed on element 114 and Pb.

In this work we investigate the adsorption of superheavy element 112 and Hg on gold through the fully relativistic *ab initio* electronic structure calculations for the dimers 112Au and HgAu. The calculations have been completed for HgAu. Those for 112Au are under way.

The electronic structure calculations are performed using the DIRAC package [2]. In order to take relativity into account, we employ the 4-component Dirac-Coulomb Hamiltonian,

$$H_{DC} = \sum_i h_D + \sum_{i<j} 1/r_{ij}, \quad (1)$$

where

$$h_D = c\vec{\alpha} \cdot \vec{p} + \beta c^2 + V_{nuc}. \quad (2)$$

V_{nuc} is the nuclear attraction operator, and α and β are the four-dimensional Dirac matrices. In order to obtain computational efficiency, the interatomic SS-integral contributions were modeled by classical repulsion of small component atomic charges [3]. This is one of the most economical and accurate approximation to the full Dirac-Coulomb Hamiltonian. Electron correlation is taken into account using the Fock space coupled cluster (FS CC) method, which is considered to be one of the most powerful tools in quantum chemistry.

The basis set of Saue *et al* [4], consisting of 23s, 18p, 14d, and 8f orbitals, was used for the gold atom. For the mercury atom the basis set of Visscher [5] was used, with 20s, 18p, 12d, and 10f orbitals.

HgAu is an open shell system; hence we start our calculation with the closed shell reference state, HgAu⁻. After solving the Dirac-Fock equations and correlating the closed shell reference state, one electron is removed, to give the neutral system. After recorrelation, an additional electron is removed, and the positive ion HgAu⁺ is reached. Thus, in a single calculation we obtain the energies of HgAu, HgAu⁺ and HgAu⁻. The calculations were

repeated for different values of the interatomic distance, to obtain the potential curves of the systems under study. The spectroscopic properties of interest were obtained from the potential energy curves, using the LEVEL program package [6].

To our knowledge, no experimental spectroscopic data exist for the HgAu molecule. However, this system has been extensively studied theoretically [7-11], mostly using relativistic DFT methods. A relativistic coupled cluster single doubles (triples) (RCCSD(T)) investigation was also performed [10]. A comparison with the other calculations is given in Table 1. One can see very good agreement with the 4c-DFT result for HgAu [11].

Table 1. Spectroscopic properties of HgAu, HgAu⁺, and HgAu⁻: equilibrium bond lengths R_e (in Å), dissociation energies, D_e (in eV), adiabatic ionization potentials, IP_{ad} (in eV), and vibrational frequencies, ω_e (in cm⁻¹)

Property	AuHg	AuHg ⁺	AuHg ⁻	Method, Ref.
R_e	2.657	2.553	2.854	DC FSCC, this
	2.711	2.581	2.967	RCCSD(T) [10]
	2.67	-	-	4c-DFT [11]
D_e	0.478	1.712	0.520	DC FSCC, this
	0.389	1.856	0.381	RCCSD(T) [10]
	0.495	-	-	4c-DFT [11]
IP_{ad}	7.374	-	1.995	DC FSCC, this
ω_e	116	156	79	DC FSCC, this
	103	139	64	RCCSD(T) [10]

Our results are expected to be more accurate than the RCCSD(T) ones due to the larger basis set employed. The same degree of reliability may be expected for the heaviest homolog of HgAu, the 112Au molecule.

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