

## Relativistic coupled cluster study of the MAu and M<sub>2</sub> dimers of Hg, Cn, and Fl

A. Borschevsky<sup>1</sup>, V. Pershina<sup>2</sup>, E. Eliav<sup>3</sup>, and U. Kaldor<sup>3</sup>

<sup>1</sup>HIM, Mainz, Germany; <sup>2</sup>GSI, Darmstadt, Germany; <sup>3</sup>Tel Aviv University, Tel Aviv, Israel

The electronic structure of Cn (Z=112) and Fl (Z=114) experiences strong relativistic effects due to the relativistic stabilization and contraction of their valence orbitals, the 7s orbital in case of Cn, and the 7p<sub>1/2</sub> orbital in case of Fl. Thus, their molecular and chemical properties are expected to be determined by relativity.

These two elements are the heaviest atoms studied in chemical experiments. Their relative inertness makes them good candidates for studies of volatility through their adsorption on metal surfaces (such as gold) using the gas-phase thermochromatography technique [1, 2]. By performing calculations of the binding energy of the MAu dimers, the trends in the adsorption enthalpies of the atoms on a gold surface,  $-\Delta H_{\text{ads}}^{\text{Au}}(\text{M})$ , can be estimated. Bonding of an element in the solid state in the first approximation can be described by the bonding in its M<sub>2</sub> dimer. Thus, in order to obtain a theoretical insight into the trends in the binding of Hg, Cn, and Fl to a gold surface, and their binding in a solid, *ab initio* study of the molecular properties of their MAu and M<sub>2</sub> dimers was performed.

The calculations were carried out within the infinite-order two-component relativistic Hamiltonian obtained after the Barysz-Sadlej-Snijders (BSS) transformation of the Dirac Hamiltonian in a finite basis set [3]. This method treats scalar and spin-orbit relativistic effects simultaneously, and for valence molecular properties achieves similar accuracy to that of the 4-component Dirac Hamiltonian, while significantly reducing the computational effort. Electron correlation was treated in the framework of the single reference coupled cluster approach with single, double, and perturbative triple excitations (CCSD(T)). Faegri's dual family basis sets [4] were used; the basis sets were extended to convergence of the calculated molecular properties. All the calculations were performed using the DIRAC08 computational program package [5].

Table I contains the calculated bond lengths,  $R_e$ , and dissociation energies,  $D_e$ , of the MAu and M<sub>2</sub> molecules. Hg<sub>2</sub> is the only system for which experimental parameters are available [6]. The excellent agreement of the calculated binding energy with the experiment in case of Hg<sub>2</sub> lends credence to our predictions for the rest of the systems.

The calculated trend in the bond length of the MAu molecules is  $R_e(\text{FlAu}) > R_e(\text{CnAu}) > R_e(\text{HgAu})$ . The increase in  $R_e$  from HgAu to CnAu corresponds to the weakening of the bond in CnAu, and the  $R_e$  of FlAu is larger than that of CnAu due to the participation of the more diffuse 7p<sub>1/2</sub> and 7p<sub>3/2</sub> orbitals of Fl in the bond [7]. The present calculations predict the HgAu molecule to be the most stable of the three, followed by FlAu, and CnAu as

Table 1: Equilibrium bond lengths,  $R_e$  (in Å), and dissociation energies,  $D_e$  (in eV), of the MAu and M<sub>2</sub> molecules. The values in parenthesis are experimental for Hg<sub>2</sub> [6].

	HgAu	CnAu	FlAu
$R_e$	2.640	2.720	2.791
$D_e$	0.563	0.368	0.446
	Hg <sub>2</sub>	Cn <sub>2</sub>	Fl <sub>2</sub>
$R_e$	3.744 (3.69)	3.461	3.547
$D_e$	0.050 (0.046)	0.084	0.117

the least stable. Bonding in CnAu is weaker than in HgAu due to the strong relativistic stabilization of the 7s orbital in Cn compared to the 6s in Hg. FlAu should be stronger bound than CnAu due to the 7p<sub>1/2</sub> orbital in Fl being more accessible than the 7s of Cn for the bonding with the 6s orbital of gold [7]. Assuming that the trends in the binding energies of the gold containing diatomic molecules are a good indication of the trends in the adsorption enthalpies of the atoms on a gold surface, according to the current calculations Fl should be stronger adsorbed on gold than Cn.

Comparing the results for the three M<sub>2</sub> dimers, we observe that Hg<sub>2</sub> has the longest and Cn<sub>2</sub> the shortest bond. The trend in the dissociation energy is  $D_e(\text{Fl}_2) > D_e(\text{Cn}_2) > D_e(\text{Hg}_2)$ . Cn<sub>2</sub> and Hg<sub>2</sub> dimers behave as van der Waals systems; thus Cn<sub>2</sub> has a higher dissociation energy of the two, due to the strong relativistic contraction of the 7s orbital, which causes a decrease of  $R_{\text{vdW}}(\text{Cn})$  and a subsequent increase in the binding energy of the dimer. Group-14 elements, including Fl, behave like chemically bound systems, where  $D_e$  decreases with Z due to the spin-orbit splitting and the relativistic stabilization of the np<sub>1/2</sub> orbital. Thus, Fl<sub>2</sub> is the least bound dimer in group 14 [7]; however, due to the different type of interaction, it is stronger bound than both Hg<sub>2</sub> and Cn<sub>2</sub>.

### References

- [1] R. Eichler *et al.*, Nature **447**, 72 (2007)
- [2] A. Yakushev *et al.*, Inorg. Chem. **53**, 1624 (2014)
- [3] M. Iliaš and T. Saue, J. Chem. Phys. **126**, 064102 (2007)
- [4] K. Faegri, Theor. Chim. Acta **105**, 252 (2001)
- [5] DIRAC08 program package (<http://diracprogram.org/>)
- [6] J. Koperski, J.B. Atkinson, and L. Krause, J. Mol. Spectrosc. **184**, 300 (1997); Can. J. Phys. **72**, 1070 (1994)
- [7] V. Pershina *et al.*, J. Chem. Phys. **131**, 084713 (2009)

