Relativistic Effects on Volatility of Element 112

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Investigation of influence of relativistic (rel.) effects on properties of the heaviest elements, especially on volatility of element 112, is one of the most fundamental and interesting tasks. Volatility is usually measured as the adsorption temperature, T_{ads}, in a chromatography column from which the adsorption enthalpy, ΔH_{ads}, is deduced. The only way to "detect" rel. effects is to compare measurements with rel. *vs.* nonrelativistic (nr.) predictions. The aim of the present study is to show the influence of rel. effects on volatility of element 112 in comparison with that of Hg as adsorption on inert and metal surfaces.

Adsorption on inert surfaces. For adsorption on inert surfaces (a quartz column, or a metal column covered with ice), a trend in volatility of the group-12 elements could be predicted using the following equation for the dispersion interaction energy [2]

$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon-1}{\varepsilon+2}\right)\frac{\alpha_{at}}{\left(\frac{1}{IP_{slab}}+\frac{1}{IP_{at}}\right)x^3}, \quad (1)$$

where IP_{slab} is the ionization potential of the surface atom, ε is the dielectric constant of the surface (slab) substance and x is the interaction distance. Substituting calculated rel. and nr. values of α and IP of Hg and element 112 into eq. (1) gives results of Fig. 1.

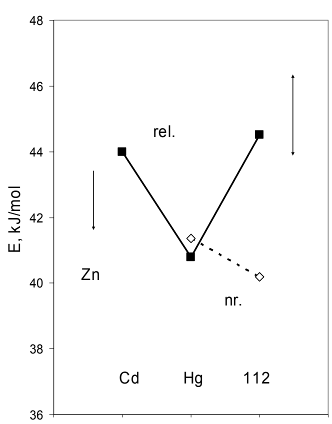

Fig. 1. Rel. and nr. dispersion interaction energies of the group-12 elements with quartz surface.

Thus, upon adsorption on an inert surface, element 112 will have the largest $E = -\Delta H_{ads}$ in group 12 and, hence, will be the least volatile. Non-relativistically, the trend is opposite.

Adsorption on metal surfaces. For the case of adsorption of element 112 and Hg on metal surfaces, e.g., Au(100), the influence of rel. effects on ΔH_{ads} could be different depending on the adsorption position – on-top, bridge or hollow – with respect to the surface atoms. In the on-top position, the main stereochemically active orbitals of Hg and element 112 are the ns and $np_{1/2}$, whose nr. and rel. R_{max} change in opposite ways in group 12. In the hollow position, the (n-1)d valence orbitals of these elements should be predominantly involved in bonding, whose rel. and nr. R_{max} change in the same way in the group. Present fully rel. and nr. 4c-DFT calculations for Hg and element 112 interacting with Au clusters of 14 and 9 atoms helped to elucidate this effect quantitatively. The results are summarized in Table 1 and Fig. 2.

Table 1. Rel. and nr. binding energies ($D_e = -\Delta H_{ads}$, eV) and optimized bond lengths (R_e, a.u.) for $M\text{-}Au_{14}$ in the on-top and for $M\text{-}Au_9$ in the hollow positions (M = Hg and element 112)

Case	top		hollow	
	R_e	D_e	R_e	D_e
		$Hg\text{-}Au_{14}$		$Hg\text{-}Au_9$
rel.	5.0	0.86	3.8	0.85
nr.	5.5	0.64	4.6	0.41
		$112\text{-}Au_{14}$		$112\text{-}Au_9$
rel.	5.2	0.71	4.2	0.79
nr.	5.8	0.70	4.9	0.52

Thus, upon adsorption on the Au (100) surface, element 112 will be more volatile than Hg. Rel. effects do not increase $-\Delta H_{ads}$ of element 112 when adsorbed in the on-top position, while for the hollow position, rel. effects strongly increase the interaction energy, so that, relativistically, element 112 will be less volatile than nonrelativistically. The rel. and nr. ΔH_{ads} show opposite trends from Hg to element 112.

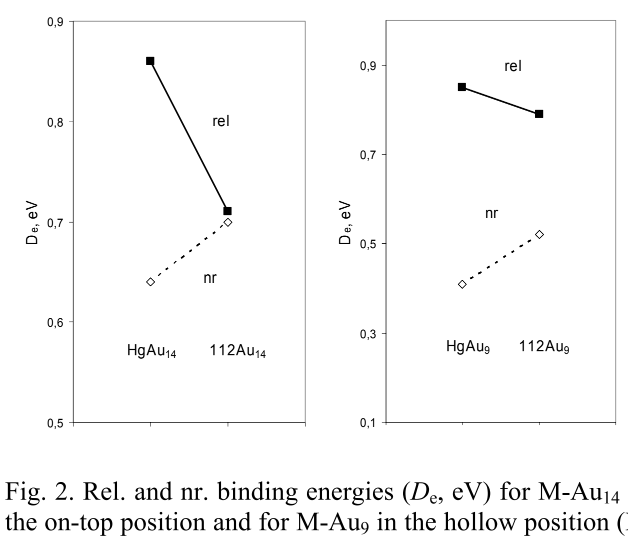

Fig. 2. Rel. and nr. binding energies (D_e, eV) for $M\text{-}Au_{14}$ in the on-top position and for $M\text{-}Au_9$ in the hollow position (M = Hg and element 112).