

# Relativistic Effects on the Electronic Structure and Volatility of Group-8 Tetroxides $\text{MO}_4$ , where $M = \text{Ru}, \text{Os},$ and Element 108, $\text{Hs}$

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Recently, first chemical experiments were conducted with the heaviest element Hs by studying volatility of its tetroxide,  $\text{HsO}_4$  [1].  $\text{HsO}_4$  was shown to behave similarly to  $\text{OsO}_4$ , though being adsorbed at somewhat larger temperatures. Earlier, fully relativistic DFT calculations [2] were performed indicating similarity of properties between  $\text{OsO}_4$  and  $\text{HsO}_4$ . To show the influence of relativistic effects on the electronic structures and volatility of the group-8 tetroxides, non-relativistic calculations for  $\text{MO}_4$  ( $M = \text{Ru}, \text{Os}, \text{Hs}$ ) were performed in addition to our previous relativistic ones [2]. Non-relativistic adsorption enthalpies of  $\text{MO}_4$  on the quartz surface of the chromatography column have been predicted on their basis. Results are visualized in Figs. 1-3.

Relativistic effects on the d-orbitals only enhance orbital effects. As expected, relativistic effects increase the binding energy ( $D_e$ ) in  $\text{HsO}_4$  essentially, so that the trends in  $D_e$  for group-8 tetroxides become opposite for relativistic and non-relativistic values. Relativistic and non-relativistic polarizabilities show similar trends, since molecular bonding is determined by the d orbitals. Non-relativistically, polarizability of  $\text{HsO}_4$  is the largest. Since  $\alpha \sim 1/\text{IP}^2$ , ionization potentials show trends opposite to those of  $\alpha$ . The trends are similar for the relativistic and non-relativistic values, though relativistic effects dramatically increase IP of  $\text{HsO}_4$ .

The energy of the dispersion interaction of  $\text{MO}_4$  with the quartz surface is defined via the following equation

$$E(x) = -\frac{3}{16} \left( \frac{\epsilon - 1}{\epsilon + 2} \right) \frac{\alpha_{mol}}{\left( \frac{1}{\text{IP}_{slab}} + \frac{1}{\text{IP}_{mol}} \right) x^3} \quad (1)$$

Using the calculated relativistic and non-relativistic values, trends in relativistic and nonrelativistic  $E(x)$  are defined as those shown in Fig. 3. They are similar for both relativistic and non-relativistic values.

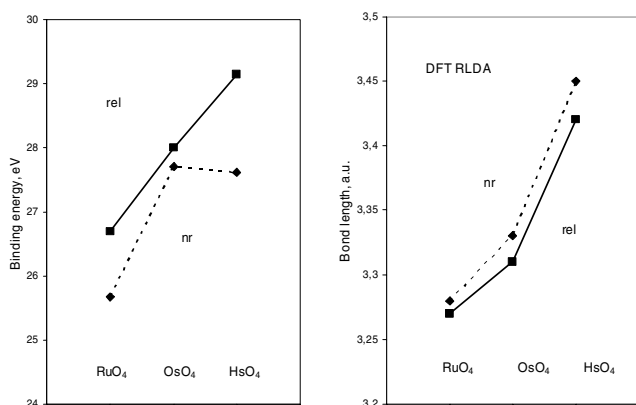


Fig. 1 Relativistic and non-relativistic binding energies ( $D_e$ ) and bond lengths ( $R_e$ ) in  $\text{MO}_4$  ( $M = \text{Ru}, \text{Os}$  and  $\text{Hs}$ ).

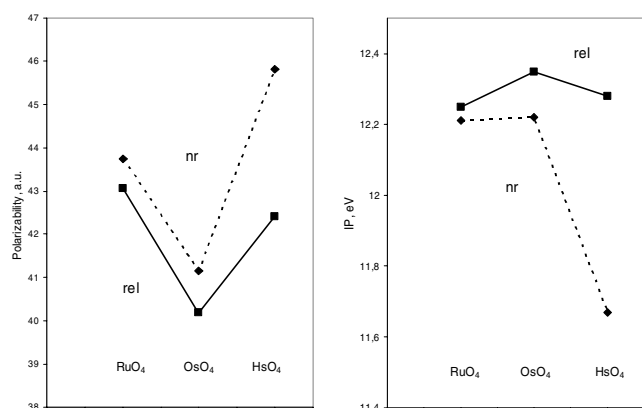


Fig. 2. Relativistic and non-relativistic polarizabilities ( $\alpha$ ) and ionization potentials (IP) in  $\text{MO}_4$  ( $M = \text{Ru}, \text{Os}$  and  $\text{Hs}$ ).

Trends for both relativistic and non-relativistic bond lengths ( $R_e$ ) were shown to be the same. This is due to the fact that trends in the spatial distribution of the relativistic and non-relativistic d orbitals are similar from Ru to Os and to Hs:

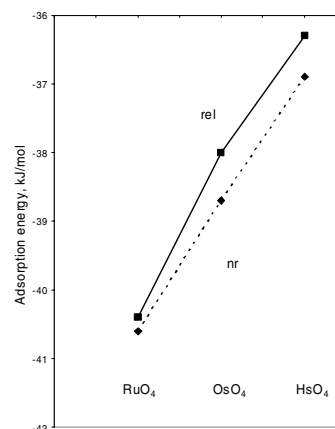


Fig. 3. Relativistic and non-relativistic adsorption energies of  $\text{MO}_4$  ( $M = \text{Ru}, \text{Os}$  and  $\text{Hs}$ ) on quartz surface.

This is due to the fact that relativistic effects on  $\alpha$  and IP cancel each other in eq. (1) and the trends are determined by  $x$ , the distance of  $\text{MO}_4$  to the surface. It is taken proportional to the size of the molecules changing similarly for relativistic and non-relativistic values from Ru to Hs. Thus, relativistic effects increase volatility of each compound by about a couple of kJ/mol, but do not influence the trend for group-8 tetroxides.

## References

- [1] C. Düllman *et al.* Nature (Letters), **418**, 859 (2002).
- [2] V. Pershina *et al.* J. Chem. Phys. **115**, 792 (2001).