

Relativistic effects on the electronic structure and volatility of the group-8 tetroxides MO₄ (M=Ru, Os and Hs)

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Element 108 was identified chemically by studying volatility of its tetroxide HsO₄ along with that of the osmium tetroxide, OsO₄ [1]. The MO₄ molecules were adsorbed on/desorbed from a quartz surface of a chromatography column and the temperatures of the 50% of the chemical yield of the products that passed through the column, T_{50%}, provided an information about their volatilities in a comparative study. Theoretically, volatility, as the adsorption enthalpy, ΔH_{ads}, of the tetroxides on a quartz surface of the column, was predicted using a model of physisorption, with molecular spectroscopic properties being *ab initio* calculated using the fully relativistic (four-component) density functional theory (DFT) method [2]. On the basis of these predicted ΔH_{ads} with the use of thermodynamic models of adsorption, T_{50%} of HsO₄ was expected to be about 2 degrees lower than T_{50%} of OsO₄, which means that HsO₄ should be more volatile [3]. Experiments have, however, observed a larger T_{50%} for HsO₄, which was interpreted as HsO₄ having a lower volatility than that of OsO₄ [1]. The reasons for this disagreement will hopefully be found by the future research, while those from the theoretical point of view are analyzed in [3].

Theoretically, results of the DFT calculations [2] and the thermodynamic considerations [3] indicate that HsO₄ should be more volatile than OsO₄ due to its larger molecular size (i.e. large molecule-surface interaction distance) and a larger molecular weight. To investigate the influence of relativistic effects on the electronic structure and properties of MO₄ (M=Ru, Os and Hs), especially on volatility, non-relativistic calculations for these molecules have been performed by us in addition to our former relativistic calculations [2].

Comparison of the obtained non-relativistic with relativistic values shows that relativistic effects, as expected, increase binding energies and decrease bond lengths in those compounds, as they decrease molecular polarizabilities. Results of those recent investigations with respect to the influence of relativistic effects on molecular volatility and on the trend in Group-8 are discussed.

References

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