

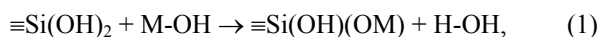
# First periodic relativistic calculations of adsorption of the superheavy elements on a quartz surface

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Gas-phase chromatography experiments provide information about volatility of superheavy elements (SHE) and their homologs as adsorption enthalpies,  $\Delta H_{\text{ads}}$ , on a surface of a chromatography column. Two main types of surfaces are used: gold and quartz. Straightforward theoretical predictions of  $\Delta H_{\text{ads}}$  were made in the past on the basis of cluster calculations for adsorption on metals (e.g., gold [1]), or physisorption models for adsorption on inert surfaces [2]. Periodic codes were until recently not suited for solid state, or adsorption calculations on the SHEs. With further developments of the relativistic quantum theory and computational algorithms, as well as creation of proper basis sets, treatment of those phenomena for  $Z \leq 120$  became now possible using the ADF BAND code [3]. Accordingly, we started the 2c-DFT calculations of  $\Delta H_{\text{ads}}$  of Hg, Cn, and Fl on a gold and of Tl and element 113 on a quartz surfaces using this program package. Here, preliminary results for the latter case are presented.

In the presence of oxygen in the chromatography column, element 113 should form 113OH by analogy with TlOH. A quartz surface is very probably fully hydroxylated forming *geminal silanols*,  $\equiv\text{Si}(\text{OH})_2$ , the most stable modification. The M atoms ( $M = \text{Tl}$  and element 113) may then react with such a surface in the following way



so that replacement of H of a surface OH group by M can take place. Accordingly, we have optimized a quartz (001) slab cut out of the  $\alpha$ -quartz bulk, where the surface O-bonds are saturated with H, i.e.,  $\equiv\text{Si}(\text{OH})_2$ . The scalar relativistic (SR) geometry optimization with fully relaxed upper 3 layers of the Si and surrounding O atoms have given the formation energy,  $E_f$ , of such a slab as -138.97 kJ/mol. The SR geometry optimization of a slab with Tl or element 113 atoms substituting one H (Fig. 1) have then given  $E_f$  of  $\equiv\text{Si}(\text{OH})(\text{OTl})$  of -137.06 eV and  $E_f$  of  $\equiv\text{Si}(\text{OH})(\text{O113})$  of -137.02 eV. Earlier, we have obtained 4c-DFT  $D_e(\text{Tl-OH}) = 3.68$  eV and  $D_e(\text{113-OH}) = 2.42$  eV [4]. Taking into account  $D_e(\text{H-OH})$  of 4.77 eV, as well as the differences in  $D_e$  between H-OH and Tl-OH and between H-OH and 113-OH, the energy balance of reaction (1) was predicted as 1.91 eV for Tl and -0.4 eV kJ/mol for element 113 using the obtained  $E_f$  of  $\equiv\text{Si}(\text{OH})(\text{OM})$  and  $\equiv\text{Si}(\text{OH})_2$ . The single-point SO calculations (i.e., with the SO interaction on top of the SR optimized geometry) have

given the reaction (1) energy as 2.32 eV for Tl and -0.47 eV for element 113. These values mean that the reaction will proceed to the right with the formation of the  $\equiv\text{Si}(\text{OH})(\text{OM})$  complex only for element 113. The Tl-OH bond is obviously too strong in the molecule to be replaced by the  $\equiv\text{Si}(\text{OH})(\text{O-Tl})$  one, while the 113-OH one is weak enough, so that the reaction can proceed to the right. Further calculations with the geometry optimization at the SO level and a supercell model treating single adsorbed atoms should be performed to confirm these preliminary conclusions.

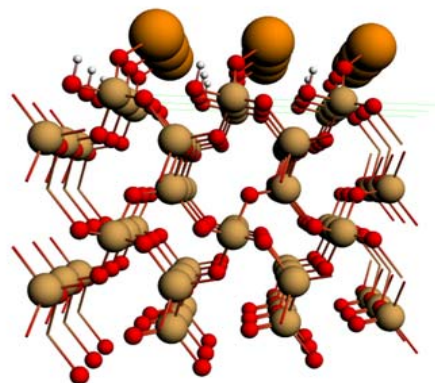


Fig. 1. Atom M ( $M = \text{Tl}$  and element 113), the largest circles, chemisorbed on the fully hydroxylated quartz surface (side view).

The obtained results are, however, in some contradiction with the measured  $-\Delta H_{\text{ads}}(\text{TlOH})$  of  $134 \pm 5$  kJ/mol on quartz similar to  $-\Delta H_{\text{ads}}(\text{TlOH})$  of  $146 \pm 3$  kJ/mol on gold [5]. Those like values are an indication that the mechanism of adsorption on quartz and gold is obviously the same, caused by long-range interactions. This scenario could be considered in the next study using BAND.

## References

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