Electronic Structure, Properties and Volatility of Chlorides and Oxychlorides of Group-4 Elements Zr, Hf, and Element 104, Rf

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Volatility of halides, oxyhalides and oxides of elements at the beginning of the 6d-series, i.e., of Rf through Hs has been studied using gas-phase separation techniques [1]. While the understanding of nature of molecule-surface interactions has been gained in group 6 through 8, such an understanding in group 4 and 5 has never been achieved. Neither have the experimentally observed trends in volatility of the halides, Zr < Hf > Rf and Nb < Ta > Db, been explained.

Recently, we have studied volatility of the group-5 bromides, MBr_5 (M = Nb, Ta, and Db), on the basis of calculated molecular properties and a model of dispersion interaction [2]. We have shown that the properties of these compounds change smoothly in the group, so that the volatility should also change smoothly. In this work, we undertake a similar study for the group-4 chlorides. With this aim in view, we have calculated the electronic structures and properties of MCl_4 (M = Zr, Hf, and Rf).

The calculations were performed with the use of the 2-component relativistic X2C DFT method implemented in the DIRAC12 program package [3]. The uncontracted triple-zeta relativistic basis sets of Dyall were used [4]. The obtained results, for the B88/P86 exchange-correlation potential (Table 1), show an increase in the bond lengths and a decrease in the ionizations potentials in the group, though the polarizabilities show a "zig-zag" behaviour. The latter are much reduced by relativity, with the effect increasing with Z. Using these properties and a model of dispersion interaction [5], adsorption enthalpies, $-\Delta H_{ads}$, of the chlorides on a quartz surface were determined (Table 1).

Table 1: Equilibrium bond lengths, R_e (in Å), dissociation energies, D_e (in eV, from Ref. [6]), ionization potentials, IP (in eV), polarizabilities, α (in a.u.), and adsorption enthalpies, ΔH_{ads} (in kJ/mol), of MCl_4 (M = Zr, Hf, and Rf) on quartz

	R_e	D_e	IP	α	ΔH_{ads}
$ZrCl_4$	2.336	20.34	11.00	103.6	106.5
$HfCl_4$	2.316	20.80	11.00	99.3	103.0
$RfCl_4$	2.370	19.40	10.96	101.2	102.7

The obtained $-\Delta H_{ads}$ are indicative of the following trend in the adsorption strength: Zr > Hf > Rf. Using a correlation of $-\Delta H_{ads}$ with the sublimation enthalpies, ΔH_{sub} of 104.2 kJ/mol was predicted for $RfCl_4$. Thus, according to the calculations, $RfCl_4$ should be the most volatile compound in its group, in agreement with previous

Table 2: Equilibrium bond lengths, R_e (in Å), dissociation energies, D_e (in eV), ionization potentials, IP (in eV), and dipole moments, μ (in D), of $MOCl_2$ (M = Zr, Hf, and Rf)

	R_e(M-Cl)	R_e(M=O)	D_e	IP	μ
$ZrOCl_2$	2.386	1.741	21.76	10.76	3.67
$HfOCl_2$	2.352	1.753	21.01	10.63	4.33
$RfOCl_2$	2.385	1.822	19.40	10.35	5.20

predictions [7]. The obtained trend is, however, in contradiction with the experimental observations [1].

To check the possible (at the presence of oxygen in the chromatography column) formation of the oxychlorides, as well as their volatility, we have also performed the electronic structure calculations for $MOCl_2$ (M = Zr, Hf, and Rf). The obtained total energy differences between $MOCl_2$ and MCl_4 are indicative of the following trend in the oxychloride formation: Zr > Hf > Rf. This means that the assumed earlier preference of Hf to form the oxychloride should not take place. The other properties of interest are summarized in Table 2. The $MOCl_2$ are shown to be stable as a bent structure, though the difference in the total energy with respect to the flat one is very small. The Rf compound should be less stable than those of Zr and Hf, similarly to MCl_4. The central atom - ligand separation increases from Hf to Rf, which also leads to an increase in the dipole moments. Such an increase in μ should result in a decrease in the volatility of $MOCl_2$ with Z as adsorption on a quartz surface due an increase in the dipole moment - surface charge interactions. Thus, volatility of the oxychlorides should change as Zr < Hf < Rf. This trend is, however, also in disagreement with the experimental observations [1]. Thus, the experimentally determined reversed trend in group 4 cannot find its theoretical explanation; neither can the one in group 5 be interpreted.

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