Theoretical predictions of properties and volatility of chlorides and oxychlorides of group-4 elements. II. Adsorption of tetrachlorides and oxydichlorides of Zr, Hf, and Rf on neutral and modified surfaces

V. Pershina,^{1,a)} A. Borschevsky,² M. Iliaš,³ and A. Türler⁴

¹GSI Helmholtzzentrum für Schwerionenforschung, Planckstr. 1, Darmstadt D-64291, Germany

²Helmholtz Institute Mainz, Mainz D-55128, Germany and Centre for Theoretical Chemistry and Physics, New Zealand Institute for Advanced Study, Massey University, Private Bag 102904, 0745 North Shore MSC, Auckland, New Zealand

³Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, SK-974 00 Banská Bystrica, Slovakia

⁴Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland and Laboratory for Radiochemistry and Environmental Chemistry, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

(Received 8 April 2014; accepted 16 July 2014; published online 14 August 2014)

With the aim to interpret results of gas-phase chromatography experiments on volatility of group-4 tetrachlorides and oxychlorides including those of Rf, adsorption enthalpies of these species on neutral, and modified quartz surfaces were estimated on the basis of relativistic, two-component Density Functional Theory calculations of MCl_4 , MOCl_2 , MCl_6^- , and MOCl_4^{2-} with the use of adsorption models. Several mechanisms of adsorption were considered. In the case of physisorption of MCl_4 , the trend in the adsorption energy in the group should be $\text{Zr} > \text{Hf} > \text{Rf}$, so that the volatility should change in the opposite direction. The latter trend complies with the one in the sublimation enthalpies, ΔH_{sub} , of the Zr and Hf tetrachlorides, i.e., $\text{Zr} < \text{Hf}$. On the basis of a correlation between these quantities, $\Delta H_{\text{sub}}(\text{RfCl}_4)$ was predicted as 104.2 kJ/mol. The energy of physisorption of MOCl_2 on quartz should increase in the group, $\text{Zr} < \text{Hf} < \text{Rf}$, as defined by increasing dipole moments of these molecules along the series. In the case of adsorption of MCl_4 on quartz by chemical forces, formation of the MOCl_2 or MOCl_4^{2-} complexes on the surface can take place, so that the sequence in the adsorption energy should be $\text{Zr} > \text{Hf} > \text{Rf}$, as defined by the complex formation energies. In the case of adsorption of MCl_4 on a chlorinated quartz surface, formation of the MCl_6^{2-} surface complexes can occur, so that the trend in the adsorption strength should be $\text{Zr} \leq \text{Hf} < \text{Rf}$. All the predicted sequences, showing a smooth change of the adsorption energy in the group, are in disagreement with the reversed trend $\text{Zr} \approx \text{Rf} < \text{Hf}$, observed in the “one-atom-at-a-time” gas-phase chromatography experiments. Thus, currently no theoretical explanation can be found for the experimental observations. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4891531>]

I. INTRODUCTION

The ability of group-4 elements to form volatile halides was exploited in the 1960 and 1970 of the last century at the JINR, Dubna, for their chemical separation from the actinides and other non-volatile by-products of nuclear reactions.^{1–4} The experiments were conducted using gas-phase thermochromatography, one of the fast-chemistry separation techniques.^{5,6} According to this technique, single volatile species pass through a chromatography column, usually made of quartz, to which a longitudinal negative temperature gradient is applied, undergoing numerous adsorption-desorption steps. The deposition temperature, T_{ads} , on the column is measured and used to deduce the adsorption enthalpy, ΔH_{ads} , with the help of thermodynamic models and Monte Carlo simulations.⁴ The obtained ΔH_{ads} are then used to deduce the sublimation enthalpy, ΔH_{sub} , of a compound via an empirical

correlation between these quantities. The ΔH_{sub} is considered to be a measure of volatility.

It was shown^{1–4} that the volatile halides of Rf were deposited in the area of T_{ads} of the Hf chlorides. In this way, it was demonstrated that the new element, Rf, has properties similar to those of Hf and is the first element of the new, 6d series. The Rf halides (chlorides and bromides) turned out to be slightly more volatile than the Hf ones.

Other experiments followed at the PSI, Switzerland,^{7,8} and LBNL, USA,^{9,10} using isothermal gas-phase chromatography, another fast gas-phase separation technique.^{5,6} According to this technique, single volatile species pass through the length of an isothermal chromatography column whereby their retention time is indicative of their volatility at a given temperature. A series of temperatures is run and the temperature, $T_{50\%}$, at which 50% of the species pass through the column, i.e., 50% of the chemical yield, is determined. These later experiments conducted with more sophisticated chemical set ups and detection techniques allowed for the unambiguous identification of the separated Rf nuclides and for

^{a)} Author to whom correspondence should be addressed. Electronic mail: V.Pershina@gsi.de.

providing more accurate values of $T_{50\%}$ and, therefore, more reliable ΔH_{ads} . (One should note, however, that ΔH_{ads} in both types of the measurements are deduced from T_{ads} or $T_{50\%}$ using thermodynamic models based on some assumptions, so that their absolute values should be used with caution. Also, the surface of a quartz column might be modified with some aerosol or carrier gas particles, such as MoO_3 or KCl , see Ref. 4.)

Even though the absolute values of ΔH_{ads} in those measurements differ, all of them came to a conclusion that the volatility should change as $\text{ZrCl}_4 \approx \text{RfCl}_4 > \text{HfCl}_4$, and $\text{ZrBr}_4 \approx \text{RfBr}_4 > \text{HfBr}_4$. A summary of the results and their critical analysis are given in Ref. 11 (see also Table 2 and Fig. 37 there).

Theoretically, there were several attempts to predict volatility of group-4 halides. The quality of predictions depended clearly on the status of the chemical theory at the time of the investigations. Thus, in early works,^{12,13} based on results of fully relativistic Dirac-Slater Discrete-Variational (DS-DV) calculations of effective charges and overlap populations (OP) of the group-4 through group-6 halides, it was established that the larger covalence (larger OP) of the high symmetry molecules of the 6d elements should result in their higher volatility in comparison with the lighter homologs. A more covalent RfCl_4 was, therefore, expected to be more volatile than ZrCl_4 and HfCl_4 . Such an increase in the covalence and volatility was shown to be a relativistic effect caused by the stabilization and contraction of the 7s atomic orbitals (AOs), as well as expansion of the 6d AOs of the metal atoms.¹³ This was in contrast to simple extrapolation procedures using a radius-volatility correlation that predicted that RfCl_4 should be less volatile than ZrCl_4 and HfCl_4 .^{14,15} Also, non-relativistically, RfCl_4 should have been less volatile than ZrCl_4 and HfCl_4 (see Fig. 30 in Ref. 11). Thus, experimentally measuring the volatility of RfCl_4 in comparison with its lighter homologs ZrCl_4 and HfCl_4 provided an ideal test case for studying relativistic effects.

It was also suggested^{16,17} to use vapor pressure curves of macroamounts of the substances as a measure of volatility for the “one-atom-at-a time” experiments. Such a “hypothetical” vapor pressure was predicted for RfCl_4 in the relativistic¹³ and non-relativistic cases.¹⁵ Using results of the DS-DV calculations for MBr_5 ($M = \text{Nb}$, Ta , and Db) and models of intermolecular interactions, a higher vapor pressure was also predicted for DbBr_5 in comparison with that of NbBr_5 and TaBr_5 .¹⁶

With the development of more accurate methods, such as, e.g., the 4c-DFT¹⁸ or the RECP CCSD(T),¹⁹ it became possible to optimize geometries and to give accurate values of dissociation energies of species of interest (e.g., of RfCl_4 ^{19,20}). Some other properties, needed to predict adsorption energy of the species of interest on various surfaces with the help of physisorption models, were also calculated for group-5 through group-8 compounds. Thus, e.g., accurate 4c-DFT calculations²¹ of properties of group-8 tetroxides MO_4 ($M = \text{Ru}$, Os , and Hs) allowed for predicting ΔH_{ads} of these molecules on quartz, in excellent agreement with the experiment.²² Very recently, similar predictions were made for adsorption of group-5 bromides, MBr_5 ($M = \text{Nb}$, Ta , and

Db), on quartz.²³ In that work, not only physisorption was considered but also the complex formation on a quartz surface modified with aerosol materials (e.g., KCl). For the latter case, two independent experiments (see Ref. 11) have shown different trends in volatility of the pentabromides, so that the last word is with the experimentalists. Group-6 and group-7 oxyhalides were also treated theoretically on their volatility, with results being in excellent agreement with an experimental outcome (see Ref. 11 for a review).

Historically, group-4 halides and oxyhalides (including those of Rf) were not treated theoretically on their volatility in such a detailed way. To fill this gap, we have performed calculations of properties of MCl_4 and MOCl_2 ($M = \text{Zr}$, Hf , and Rf) needed to predict their volatility with the use of adsorption models (Paper I).²⁴ In addition, to treat adsorption of these species on a quartz surface modified with some aerosol (e.g., KCl) materials, calculations were performed in this work for group-4 halide and oxyhalide complexes, such as MCl_6^{2-} and MOCl_4^{2-} , that might be formed on the surface upon chemisorption.

One should note here that all those considerations are based on various assumptions and semi-empirical models, rather than on *ab initio* calculations. This is due to the fact that advanced calculations with the use of the first principle methods and periodic boundary conditions are not possible at the time being for the heaviest elements, because available computer codes are mostly scalar-relativistic and – with the exception of the ADF/BAND²⁵ – not developed (having no basis sets and suitable pseudo-potentials) for the transactinide elements, neither all of them can treat weak interactions for these systems due to the absence of dispersion DFT corrections. In addition, the real surface of the column in those complex experiments has never been studied or determined, so that the mechanisms of adsorption are not at all known. Therefore, various plausible mechanisms are considered in this work with the hope to find an explanation to the experimental observations.

In Sec. II, the method of the calculations and a model of adsorption are described. The results of the calculations and the discussion are given in Sec. III, followed by a summary and conclusions in Sec. IV.

II. COMPUTATIONAL DETAILS

A. Method of calculations

The calculations were performed using the DIRAC12 program package.²⁶ We used the infinite order exact two-component (X2C) relativistic Hamiltonian.^{27,28} The X2C Hamiltonian was shown to nicely reproduce results obtained using the standard 4c-Dirac-Coulomb (DC) Hamiltonian for a variety of systems and different electronic properties.^{29,30}

The calculations were performed in the framework of the relativistic Density Functional Theory (RDFT) implemented in the DIRAC12 program.^{31,32} We used the Becke 1988 exchange GGA functional (B88)³³ and a combination of the non-local correlation functional of Perdew (PW86),³⁴ as well as the 1981 local correlation functional of Perdew and Zunger.³⁵

TABLE I. Equilibrium bond lengths, R_e (in Å), atomization energies, D_e (in eV), ionization potentials, IP (in eV), polarizabilities, α (in a.u.), molecule-surface interaction distances, x (in Å), adsorption enthalpies, $-\Delta H_{\text{ads}}$ (in kJ/mol), and sublimation enthalpies, ΔH_{sub} (in kJ/mol), of MCl_4 ($\text{M} = \text{Zr}, \text{Hf}, \text{ and Rf}$).

	R_e^a	D_e^b	IP ^a	α^a	x	$-\Delta H_{\text{ads}}$	ΔH_{sub}^c	$-\Delta H_{\text{ads}} (\text{exp})^d$	$-\Delta H_{\text{ads}} (\text{exp})^e$
ZrCl_4	2.336	20.34	11.00	103.6	2.68	106.5	110.5	79 ± 5	97
HfCl_4	2.316	20.80	11.00	99.3	2.67	103	104.7	103 ± 5^f	103^f
RfCl_4	2.370	19.4 ± 0.2	10.96	101.2	2.69	102.7	(104.2)	82 ± 5	87

^aSee Paper I in this issue.²⁴

^bRecommended values.²⁰

^cReference 44 for Zr and Hf and the present estimate for Rf.

^dReference 9.

^eReference 8, the recommended values used for comparison (for other values, see Ref. 11).

^fValues taken as a reference point.

Extended basis sets were employed: the aug-cc-pvtz ones^{36,37} in their uncontracted form for Cl and O, while the uncontracted triple-zeta relativistic basis sets of Dyall *et al.*^{38–40} were used for Zr, Hf, and Rf. Convergence with respect to the basis set was verified. A more detailed description of the used methods and details of the calculations is given in Paper I.²⁴

B. Adsorption model

For calculations of the dispersion interaction energy of molecules with a neutral surface, the following model for a molecule-slab interaction was used:⁴¹

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

Here, ε is the dielectric constant of the surface material, IP is the ionization potential of the molecule and surface material, α is the molecular polarizability, and x is the molecule-surface interaction distance.

The relation between the adsorption energy and enthalpy is given by the following equation coming from the model of mobile adsorption:⁴²

$$-\Delta H_{\text{ads}} = E(x) + 0.5RT. \quad (2)$$

III. RESULTS OF THE CALCULATIONS AND DISCUSSION

A. Adsorption of MCl_4 on quartz

The MCl_4 species could be adsorbed on a quartz surface by long-range forces. In this case, the energy of the van der Waals molecule-surface interaction can be obtained using Eq. (1). The calculated molecular properties required by Eq. (1) are given in Table I. The ε for quartz is taken as 3.81.⁴³

As in our previous works,^{21,42} we tried to estimate $-\Delta H_{\text{ads}}$ of a species of interest with respect to a measured $-\Delta H_{\text{ads}}$ of one of the homologs. For this purpose, $-\Delta H_{\text{ads}}(\text{HfCl}_4)$ of 103 kJ/mol from two independent experiments^{8,9} is a good reference point. We also assumed that the MCl_4 molecules approach the surface by a facet. The molecule-surface distance x is then the one from the center of the molecule to the surface through this facet plane (Fig. 1). Using the experimental $\Delta H_{\text{ads}}(\text{HfCl}_4)$ and Eq. (1), x equal to

2.67 Å was deduced. The corresponding x values for ZrCl_4 and RfCl_4 were obtained then taking into account the difference between $R_e(\text{MCl}_4)$ ($\text{M} = \text{Zr}$ and Rf) and $R_e(\text{HfCl}_4)$ (see Table I). For those x , ΔH_{ads} of ZrCl_4 and RfCl_4 were calculated as given in Table I. According to these values, the sequence in the van der Waals adsorption energy should be $\text{Zr} > \text{Hf} > \text{Rf}$, with a very small difference between the homologs. The volatility of the tetrachlorides should change then as $\text{Zr} < \text{Hf} < \text{Rf}$.

The obtained sequence in the volatility is in agreement with the trend in ΔH_{sub} of macroamounts of ZrCl_4 and HfCl_4 (Table I).⁴⁴ These data are indicative of a slightly higher volatility of HfCl_4 than ZrCl_4 . (Also, P_{mm} of HfCl_4 over the solid is higher than that of ZrCl_4 .⁴⁴) This nice correlation might be due to the fact that bonding in the $(\text{MCl}_4)_2$ dimer, being a structural unit of the solid MCl_4 ($\text{M} = \text{Zr}$ and Hf),^{45–47} is obviously of van der Waals nature. Using a linear correlation between the calculated $-\Delta H_{\text{ads}}(\text{MCl}_4)$ and experimental $\Delta H_{\text{sub}}(\text{MCl}_4)$ in the row of the homologs, $\Delta H_{\text{sub}}(\text{RfCl}_4)$ was then estimated as 104.2 kJ/mol (Fig. 2). The obtained $\Delta H_{\text{sub}}(\text{RfCl}_4)$ is smaller than ΔH_{sub} of the Zr and Hf counterparts (Table I), which means that the trend in the volatility of the tetrachlorides should be $\text{Zr} < \text{Hf} < \text{Rf}$. This sequence is in agreement with our earlier predictions,¹³ though the difference between the homologs turns out to be very small.

The measurements,^{8,9} however, indicate HfCl_4 to be stronger attracted to the surface than ZrCl_4 and RfCl_4 , so that the trend in volatility is $\text{Zr} \approx \text{Rf} > \text{Hf}$. This means that the predicted sequence in the adsorption of MCl_4 by

FIG. 1. A scheme of adsorption of the MCl_4 molecule on an inert surface.

FIG. 2. Correlation between $-\Delta H_{\text{ads}}(\text{MCl}_4)$, where $M = \text{Zr}$, Hf , and Rf , on an inert surface and ΔH_{sub} of the corresponding substances.⁴⁴

van der Waals forces does not describe the experimental observations, though it correlates with the trend in ΔH_{sub} . The experimental^{8,9} $-\Delta H_{\text{ads}}(\text{MCl}_4)$ do, however, *not* correlate with the ΔH_{sub} of macroamounts of MCl_4 , so that the $\Delta H_{\text{sub}}(\text{RfCl}_4)$ cannot be determined from the measured $\Delta H_{\text{ads}}(\text{RfCl}_4)$, even though this is the aim of the investigations.

B. Formation of MCl_6^{2-} on the surface of KCl or a chlorinated quartz surface

At temperatures below $\sim 250^\circ\text{C}$, the quartz surface of the chromatography column is usually coated with the materials used to generate the transporting aerosol particles (e.g., KCl), or the surface is chlorinated by a reactive gas (e.g., chlorine) used to form volatile species.⁴ Adsorption of MCl_4 on such a modified surface takes probably place with the formation of the MCl_6^{2-} surface complexes, because the group-4 elements prefer a coordination number 6 (Fig. 4 in Ref. 23). The reaction that governs the chemisorption process is then

The energy of the $\text{MCl}_4 \rightarrow \text{MCl}_6^{2-}$ complex formation reaction will, therefore, define the adsorption energy of the MCl_4 molecules on a chlorinated surface and the trend in the row of homologs. With this aim in view, total energy, E_t , calculations with optimization of geometry were performed for MCl_6^{2-} ($M = \text{Zr}$, Hf , and Rf). (Total energies of MCl_4 were calculated in the previous work.²⁴) The equilibrium bond lengths (R_e) of the MCl_6^{2-} complexes calculated at the DFT (B88/P86) level of theory are shown in Table II. As in MCl_4 , $R_e(\text{RfCl}_6^{2-})$ is 0.05 Å larger than $R_e(\text{HfCl}_6^{2-})$ at the B88/P86 level of theory.

The E^t , as well as the reaction energies $\Delta E(\text{MCl}_4 \rightarrow \text{MCl}_6^{2-})$, also with respect to those of Zr , $\Delta \Delta E$, are given

TABLE II. Bond lengths (in Å) of the MCl_6^{2-} ($M = \text{Zr}$, Hf , and Rf) complexes at the DFT (B88/P86) level of theory.

	ZrCl_6^{2-}	HfCl_6^{2-}	RfCl_6^{2-}
R_e	2.516	2.497	2.550

TABLE III. Total X2C DFT (B88/P86) energies, E (in a.u.), of the MCl_4 and MCl_6^{2-} molecules and the energies of the $\Delta(\text{MCl}_4 \rightarrow \text{MCl}_6^{2-})$ ($M = \text{Zr}$, Hf , and Rf) reaction, also with respect to that of Zr , $\Delta \Delta/\text{Zr}$.

	Zr	Hf	Rf
MCl_4	-5446.213839	-16937.963885	-40533.858955
MCl_6^{2-}	-6369.786578	-17861.536905	-41457.437239
$\Delta(\text{MCl}_6^{2-} - \text{MCl}_4)$	-923.572739	-923.573020	-923.578284
$\Delta \Delta/\text{Zr}$	0	-0.000281	-0.005545
$\Delta \Delta/\text{Zr}$, kJ/mol	0	-0.8	-14.6
$-\Delta \Delta H_{\text{ads}}/\text{Zr}$, kJ/mol	0	6	-10
(expt. ^a)			

^aReference 18 (see also Ref. 11).

in Table III. According to these data, the trend in the complex formation and, hence, in the adsorption strength should be $\text{Zr} \leq \text{Hf} < \text{Rf}$. Experimental values,^{8,9} also listed in Table III, are, however, indicative of the following trend in the adsorption energy: $\text{Zr} \approx \text{Rf} < \text{Hf}$. Obviously, the mechanism of the MCl_6^{2-} complex formation does not describe the experimentally observed trend either.

C. Formation of oxychlorides on the surface

This adsorption scenario is also plausible provided a reaction of MCl_4 with a silica surface takes place (see Fig. 5.19 B in Ref. 4). Upon the interaction of the halides with a non-chlorinated quartz surface, the substitution of the hydroxyl surface groups can take place according to the following reaction:

We can therefore try to estimate a trend in the formation of $\equiv(\text{SiO})_2\text{MCl}_2$ in the row Zr , Hf , and Rf from the energy of the following reaction $\text{MCl}_4 \rightarrow \text{MOCl}_2$. The required total energies of the components of this reaction were calculated in Paper I.²⁴ The resulting reaction energies are given in Table IV. They are indicative of the following trend in the surface oxyhalide formation: $\text{Zr} \gg \text{Hf} \gg \text{Rf}$. This trend, as well as the very large differences in the reaction energies between the homologs, are, however, again in disagreement with the experimental observations,^{8,9} so that this adsorption mechanism does not correspond to the reality.

TABLE IV. Total energies, E (in a.u.), of the MCl_4 and MOCl_2 molecules and the energies of the reaction $\Delta(\text{MCl}_4 \rightarrow \text{MOCl}_2)$ ($M = \text{Zr}$, Hf , and Rf), also with respect to that of Zr , $\Delta \Delta/\text{Zr}$.

	Zr	Hf	Rf
MCl_4	-5446.213839	-16937.96388	-40533.85896
MOCl_2	-4598.006867	-16089.73827	-39685.621802
$\Delta(\text{MOCl}_2 - \text{MCl}_4)$	848.206972	848.22561	848.237158
$\Delta \Delta(\text{MOCl}_2 - \text{MCl}_4)/\text{Zr}$	0	0.018638	0.030186
$\Delta \Delta(\text{MOCl}_2 - \text{MCl}_4)/\text{Zr}$ (kJ/mol)	0	48.9	79.3
$-\Delta \Delta H_{\text{ads}}/\text{Zr}$, kJ/mol	0	6	-10
(expt. ^a)			

^aReference 8 (see also Ref. 11).

TABLE V. Bond lengths, R_e (in Å), and Cl-M-Cl angles (in degrees) of the MOCl_4^{2-} (M = Zr, Hf, and Rf) complexes at the DFT levels of theory.

	$R_e(\text{M-Cl})$	$R_e(\text{M-O})$	$\angle\text{Cl-M-Cl}$
ZrOCl_4^{2-}	2.586	1.779	150.6
HfOCl_4^{2-}	2.553	1.790	150.0
RfOCl_4^{2-}	2.595	1.859	151.4

D. Adsorption of MOCl_2 on a quartz surface

Another possible scenario is physisorption of the MOCl_2 species on the surface, if those by any circumstances are formed under experimental conditions. It was observed that the addition of O_2 to the chemical set up led to a significant shift of the $T_{50\%}$ of both Hf and Rf to higher temperatures by about 100–200 °C.⁸ This behavior was interpreted as being due to a transport reaction mechanism, since, in contrast to the group-5 oxychlorides, the oxychlorides of group-4 elements are expected to be less stable than the pure tetrachlorides and it is uncertain whether compounds such as ZrOCl_2 or HfOCl_2 exist in the gas phase.⁸ Also, the affinity of Rf towards oxygen is lower than that of Zr and Hf, as is shown in Paper I (see Table VI in Ref. 24).

Some qualitative considerations can be made in this case using Eqs. (6)–(11) of Ref. 48. Due to the availability of dipole moments, μ , of MOCl_2 (M = Zr, Hf, and Rf) (see Table VI in Paper I²⁴), the adsorption of these species on a (chlorinated) quartz surface can take place via the μ -surface charge, μ - α (surface) and α - α (surface) long range interactions. Increasing dipole moments in the row (in D): 3.67 (ZrOCl_2) < 4.33 (HfOCl_2) < 5.2 (RfOCl_2) should result then in an increase in the adsorption energy in this direction, so that the trend in volatility should be: $\text{ZrOCl}_2 > \text{HfOCl}_2 > \text{RfOCl}_2$. The increasing trend in $-\Delta H_{\text{ads}}$ was also predicted for the group-5 through group-7 oxyhalides (due to the same reason) in agreement with experimental observations.^{11,47–50} The trend for group-4 species is, however, in disagreement with the experimental observations, showing the strongest adsorption of Hf.^{8,9} So, the physisorption of MOCl_2 on quartz does, obviously, not take place.

E. Formation of oxychloride complexes on a quartz surface

The last possible scenario is the formation of oxychloride complexes on a quartz surface that might take place according

TABLE VII. Summary of the trends in adsorption and volatility of group-4 chlorides and oxychlorides predicted using various adsorption scenarios in comparison with experiment.

Mechanism of adsorption	Trend in adsorption	Trend in volatility
Van der Waals of MCl_4	$\text{Zr} > \text{Hf} > \text{Rf}$	$\text{Zr} < \text{Hf} < \text{Rf}$
$\Delta H_{\text{sub}}(\text{MCl}_4)$	$\text{Zr} > \text{Hf} > \text{Rf}$	$\text{Zr} < \text{Hf} < \text{Rf}$
MCl_6^- formation	$\text{Zr} \leq \text{Hf} < \text{Rf}$	$\text{Zr} \geq \text{Hf} > \text{Rf}$
MOCl_2 formation ^a	$\text{Zr} >> \text{Hf} >> \text{Rf}$	$\text{Zr} << \text{Hf} << \text{Rf}$
Long-range MOCl_2	$\text{Zr} < \text{Hf} < \text{Rf}$	$\text{Zr} > \text{Hf} > \text{Rf}$
MOCl_4^{2-} formation	$\text{Zr} > \text{Hf} > \text{Rf}$	$\text{Zr} < \text{Hf} < \text{Rf}$
Experiment ^b	$\text{Zr} < \text{Hf} > \text{Rf}$	$\text{Zr} > \text{Hf} < \text{Rf}$

^aLess probable, since the oxychlorides are obviously not formed.

^bReferences 8, 9, and 11.

to the following reaction (see Fig. 5.19 D in Ref. 4):

In this case, the MCl_4 molecule is attached to the surface via two oxygen bridge atoms. The energy of reaction (5) can be estimated by calculating the energy of the following complex formation reaction $\text{MCl}_4 \rightarrow \text{MOCl}_4^{2-}$. (The latter complexes are also structural units in the solid ZrOCl_2 .⁴⁷) For that purpose, geometry optimization and total energy calculations were performed for the MOCl_4^{2-} complexes. The results are given in Table V. Similarly to MCl_4 , there is an increase in $R_e(\text{Rf-L})$ (L = Cl, O) with respect to $R_e(\text{Hf-L})$: the obtained $R_e(\text{Rf} = \text{O})$ is 0.042 Å larger than $R_e(\text{Hf} = \text{O})$, and $R_e(\text{Rf-Cl})$ is 0.069 Å larger than $R_e(\text{Hf-Cl})$.

The E^t , as well as the reaction energies, $\Delta E(\text{MCl}_4 \rightarrow \text{MOCl}_4^{2-})$, also with respect to those of Zr, $\Delta\Delta E$, are given in Table VI. They show the same trend in the formation of the oxychloride complexes as that in the formation of the oxychlorides: $\text{Zr} > \text{Hf} > \text{Rf}$. Experimental values, also listed in Table VI, are indicative, however, of the following trend in the adsorption strength of MCl_4 on quartz: $\text{Zr} \approx \text{Rf} < \text{Hf}$. In addition, the difference between the elements is much smaller than the predicted one according to this scenario. Thus, the mechanism of the complex formation does not describe the experimentally observed trend either.

A summary of all possible cases in comparison with experiment is given in Table VII and Fig. 3.

TABLE VI. Total X2C DFT (B88/P86) energies, E (in a.u.), of the MCl_4 and MOCl_4^{2-} molecules and the energies of the reaction $\Delta(\text{MCl}_4 \rightarrow \text{MOCl}_4^{2-})$ (M = Zr, Hf, and Rf), also with respect to that of Zr, $\Delta\Delta/\text{Zr}$.

	Zr	Hf	Rf
MCl_4	− 5446.213839	− 16937.963885	− 40533.858955
MOCl_4^{2-}	− 5521.619003	− 17013.35968	− 40609.247712
$\Delta(\text{MOCl}_4^{2-} - \text{MCl}_4)$	− 75.405164	− 75.395795	− 75.388757
$\Delta\Delta/\text{Zr}$	0	0.009369	0.016407
$\Delta\Delta/\text{Zr}$ (kJ/mol)	0	24.6	43.1
$-\Delta\Delta H_{\text{ads}}$ (kJ/mol) (expt. ^a)	0	6	− 10

^aReference 8 (see also Ref. 11).

FIG. 3. A summary of the predicted trends in volatility (energies, E , as a function of the atomic number, Z) of group-4 halides and oxyhalides according to the various scenarios: van der Waals interaction of MCl_4 ($M = \text{Zr}$, Hf , and Rf) (open circles connected by the dotted line); the MCl_6 formation (open triangles connected by the dashed line); the MOCl_2 formation on the surface (open squares connected by the long dashed line); the MOCl_4^{2-} formation (stars connected by the dashed-dotted line), in comparison with experiment on adsorption of MCl_4 on a (modified) quartz surface^{8,9,11} (filled rhomboids connected by the solid line).

IV. SUMMARY AND CONCLUSIONS

Present 2c-DFT calculations of the electronic structures of the chlorides, oxychlorides, as well as chloride- and oxychloride complexes of group-4 elements have allowed for estimating adsorption enthalpies of chlorides and oxychlorides of Zr and Rf on a (modified) quartz surface with respect to the measured $\Delta H_{\text{ads}}(\text{HfCl}_4)$ with the use of adsorption models.

The obtained results show that when adsorbed by dispersion forces, the trend in the adsorption energy of MCl_4 should be $\text{Zr} > \text{Hf} > \text{Rf}$. This correlates with $\Delta H_{\text{sub}}(\text{MCl}_4)$ decreasing from ZrCl_4 to HfCl_4 , so that $\Delta H_{\text{sub}}(\text{RfCl}_4)$ obtained via this correlation is 104.2 kJ/mol, less than ΔH_{sub} of the homologs. This means that, in agreement with the earlier predictions, RfCl_4 should be slightly more volatile than ZrCl_4 and HfCl_4 . If the oxychlorides, MOCl_2 , were formed in the gas-phase, their interaction with the surface due to long-range forces would give the opposite trend in volatility, $\text{Zr} > \text{Hf} > \text{Rf}$. If the oxychlorides, or oxychloride complexes are formed from MCl_4 upon the interaction with the surface, the volatility should follow the trend: $\text{Zr} < \text{Hf} < \text{Rf}$. The formation of the pure chloro-complexes on the surface should give an opposite trend in volatility, $\text{Zr} \geq \text{Hf} > \text{Rf}$.

All those trends are, however, in disagreement with the one observed in the “one-atom-at-a-time” experiments on the adsorption of the group-4 chlorides on quartz (Fig. 3). The calculations show a smooth change in properties of MCl_4 and MOCl_2 in the group, even though the effect of the lanthanide contraction is seen in R_c and α from ZrCl_4 to HfCl_4 . Accordingly, the predicted adsorption energies also reveal a smooth trend – either to an increase or to a decrease in the group – depending on the adsorption scenarios. Due to this simple logic,

we find, therefore, no explanation of the reversed trend in the behaviour of the group-4 chlorides, $\text{Zr} < \text{Hf} > \text{Rf}$, observed experimentally.

At the end, it is worth comparing group 4 and 5 on the volatility of their halides. The trends predicted in this work according to the different scenarios are the same as those predicted in our work²³ on the volatility of group-5 MBr_5 ($M = \text{Nb}$, Ta , and Db). Thus, a large number of calculations show a consistent picture and the similarity between group 4 and 5. Experimentally, however, a reversed trend in the volatility was observed in both groups.^{8,9,51–53}

The existing difference between the theoretical considerations and experimental observations might come from the fact that the studied processes and phenomena are very complex and have not been investigated experimentally in detail. The chemical composition and structure of both the adsorbent and the adsorbate are not really known, so that various assumptions had to be made. This work might therefore be prolonged, provided a detailed information comes from the experimental side, as well as theoretical methods receive further development. At the time being, we hope that the outlined considerations are helpful in better understanding the complex adsorption phenomena involving the heaviest elements.

ACKNOWLEDGMENTS

The authors appreciate fruitful discussions of the gas-phase chemistry with Dr. A. Yakushev. M.I. thanks for the financial support from the Slovak Research and Development Agency (Grant No. APVV-0059-10) and from the Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic for the Structural Funds of EU (ITMS 26110230082).

¹I. Zvara, Y. T. Chuburkov, R. Tsaletka, T. S. Zvarova, M. R. Shalaevski, and B. V. Shilov, *Sov. At. Energy* **21**, 709 (1966).

²I. Zvara, Y. T. Chuburkov, V. Z. Belov, G. V. Buklanov, B. B. Zakhvataev, T. S. Zvarova, O. D. Maslov, R. Caletka, and M. R. Shalaevski, *J. Inorg. Nucl. Chem.* **32**, 1885 (1970).

³I. Zvara, V. Z. Belov, V. P. Domanov, and M. R. Shalaevski, *Sov. Radiochem.* **18**, 328 (1976).

⁴I. Zvara, *The Inorganic Radiochemistry of Heavy Elements* (Springer, 2008).

⁵H. W. Gäggeler and A. Türlér, “Gas-phase chemistry,” in *The Chemistry of Superheavy Elements*, edited by M. Schädel (Kluwer Academic, Dordrecht, 2003), pp. 237–285.

⁶A. Türlér and K. E. Gregorich, “Experimental techniques,” in *The Chemistry of Superheavy Elements*, edited by M. Schädel (Kluwer Academic, Dordrecht, 2003), pp. 117–158.

⁷A. Türlér, H. W. Gäggeler, K. E. Gregorich, H. Barth, W. Brüchle, K. R. Czerwinski, M. K. Guber, N. J. Hannink, R. A. Henderson, D. C. Hoffman, D. T. Jost, C. D. Kacher, B. Kadkhodayan, J. Kovacs, J. V. Kratz, S. A. Kreek, D. M. Lee, J. D. Leyba, M. J. Nurmia, M. Schädel, U. Scherer, E. Schimpf, D. Vermeulen, A. Weber, H. P. Zimmerman, and I. Zvara, *J. Radioanal. Nucl. Chem. Art.* **160**, 327 (1992).

⁸A. Türlér, G. V. Buklanov, B. Eichler, H. W. Gäggeler, M. Grantz, S. Hübener, D. T. Jost, V. Y. Lebedev, D. Piguet, S. N. Timokhin, A. Yakushev, and I. Zvara, *J. Alloys Compd.* **271–273**, 287 (1998).

⁹B. Kadkhodayan, A. Türlér, K. E. Gregorich, P. A. Baisden, K. R. Czerwinski, B. Eichler, H. W. Gäggeler, T. M. Hamilton, D. T. Jost, C. D. Kacher, A. Kovacs, S. A. Kreek, M. R. Lane, F. Mohar, M. P. Neu, N. J. Stoyer, E. R. Sylwester, D. M. Lee, M. J. Nurmia, G. T. Seaborg, and D. C. Hoffman, *Radiochim. Acta* **72**, 169 (1996).

¹⁰E. R. Sylwester, K. E. Gregorich, D. M. Lee, B. Kadkhodayan, A. Türlér, J. L. Adams, C. D. Kacher, M. R. Lane, C. A. Laue, C. A. McGrath, D. A.

- Shaughnessy, D. A. Strellis, P. A. Wilk, and D. C. Hoffman, *Radiochim. Acta* **88**, 837 (2000).
- ¹¹A. Türler and V. Pershina, *Chem. Rev.* **113**, 1237 (2013).
- ¹²V. Pershina and B. Fricke, *J. Phys. Chem.* **98**, 6468 (1994).
- ¹³V. Pershina and B. Fricke, in *Heavy Elements and Related New Phenomena*, edited by W. Greiner and R. K. Gupta (World Scientific, Singapore, 1999), Vol. 1, p. 194.
- ¹⁴I. Zvara, *J. Radioanal. Nucl. Chem.* **204**, 123 (1996).
- ¹⁵A. Türler, *Radiochim. Acta* **72**, 7 (1996); *Habilitationsschrift* (Universität Bern, 1999).
- ¹⁶V. Pershina, W.-D. Sepp, B. Fricke, D. Kolb, M. Schädel, and G. V. Ionova, *J. Chem. Phys.* **97**, 1116 (1992).
- ¹⁷V. Pershina, W.-D. Sepp, T. Bastug, B. Fricke, and G. V. Ionova, *J. Chem. Phys.* **97**, 1123 (1992).
- ¹⁸J. Anton, B. Fricke, and E. Engel, *Phys. Rev. A* **69**, 012505 (2004).
- ¹⁹Y.-K. Han, S.-K. Son, Y. J. Choi, and Y. S. Lee, *J. Phys. Chem. A* **103**, 9109 (1999).
- ²⁰J. Anton, M. Hirata, B. Fricke, and V. Pershina, *Chem. Phys. Lett.* **380**, 95 (2003).
- ²¹V. Pershina, J. Anton, and T. Jacob, *Phys. Rev. A* **78**, 032518 (2008).
- ²²C. E. Düllmann, W. Brühl, R. Dressler, K. Eberhardt, B. Eichler, R. Eichler, H. W. Gäggeler, T. N. Ginter, F. Glaus, K. E. Gregorich, D. C. Hoffman, E. Jäger, D. T. Jost, U. W. Kirbach, D. M. Lee, H. Nitsche, J. B. Patin, V. Pershina, D. Piguet, Z. Qin, M. Schädel, B. Schausten, E. Schimpf, H. J. Schött, S. Sovner, R. Sudowe, P. Thörle, S. N. Timokhin, N. Trautmann, A. Türler, A. Vahle, G. Wirth, A. B. Yakushev, and P. M. Zielinski, *Nature (London)* **418**, 859 (2002).
- ²³V. Pershina and J. Anton, *J. Chem. Phys.* **136**, 034308 (2012).
- ²⁴V. Pershina, A. Borschevsky, and M. Ilias, *J. Chem. Phys.* **141**, 064314 (2014).
- ²⁵BAND2013, SCM, *Theoretical Chemistry* (Vrije Universiteit, Amsterdam, The Netherlands, 2013), see <http://www.scm.com>.
- ²⁶DIRAC package, Dirac, a relativistic *ab initio* electronic structure program, Release DIRAC12.0 (2012), written by H. J. Aa. Jensen, T. Saue, and L. Visscher with contributions from V. Bakken, E. Eliav, T. Enevoldsen, T. Fleig, O. Fossgaard, T. Helgaker, J. Laerdahl, C. V. Larsen, P. Norman, J. Olsen, M. Pernpointner, J. K. Pedersen, K. Ruud, P. Salek, J. N. P. van Stralen, J. Thyssen, O. Visser, and T. Winther, see <http://dirac.chem.sdu.dk>.
- ²⁷M. Barysz and A. J. Sadlej, *J. Chem. Phys.* **116**, 2696 (2002).
- ²⁸M. Iliáš and T. Saue, *J. Chem. Phys.* **126**, 064102 (2007).
- ²⁹R. Bast, A. Koers, A. S. P. Gomes, M. Iliáš, L. Visscher, P. Schwerdtfeger, and T. Saue, *Phys. Chem. Chem. Phys.* **13**, 864 (2011).
- ³⁰J. Sikkema, L. Visscher, T. Saue, and M. Iliáš, *J. Chem. Phys.* **131**, 124116 (2009).
- ³¹T. Saue and T. Helgaker, *J. Comput. Chem.* **23**, 814 (2002).
- ³²O. Fossgaard, O. Gropen, M. C. Valero, and T. Saue, *J. Chem. Phys.* **118**, 10418 (2003).
- ³³A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ³⁴J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).
- ³⁵J. P. Perdew, *Phys. Rev. B* **23**, 5048 (1981).
- ³⁶D. E. Woon and T. H. Dunning, *J. Chem. Phys.* **98**, 1358 (1993).
- ³⁷N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.* **123**, 064107 (2005).
- ³⁸K. G. Dyall, *Theor. Chem. Acc.* **117**, 483 (2007).
- ³⁹K. G. Dyall and A. S. P. Gomes, *Theor. Chem. Acc.* **125**, 97 (2010).
- ⁴⁰K. G. Dyall, *Theor. Chem. Acc.* **129**, 603 (2011).
- ⁴¹V. Pershina and T. Bastug, *Chem. Phys.* **311**, 139 (2005).
- ⁴²V. Pershina and J. Anton, *J. Chem. Phys.* **138**, 174301 (2013).
- ⁴³*CRC Handbook of Chemistry and Physics*, 93rd ed., edited by W. M. Haynes (Taylor & Francis Ltd., 2012).
- ⁴⁴*Thermochemical Properties of Inorganic Substances*, edited by O. Knacke, O. Kubaschewski, and K. Hesselmann (Springer-Verlag, Berlin, 1991).
- ⁴⁵D. C. Bradley and P. Thornton, "Zirconium and hafnium," in *Comprehensive Inorganic Chemistry*, edited by J. C. Bailar, H. J. Emeleus, Sir R. Nyholm, and A. F. Trotman-Dickenson (Pergamon Press, Oxford, 1973), Vol. 3, pp. 419–490.
- ⁴⁶J. Weidlein, V. Müller, and K. Dehnicke, *Spectrochim. Acta, Part A* **24**, 253 (1968).
- ⁴⁷J. Hala, *Halides, Oxyhalides, and Salts of Halogen: Complexes of Titanium, Zirconium, Hafnium, Vanadium, Niobium and Tantalum: 040 (IUPAC Solubility Data)* (Pergamon, 1989).
- ⁴⁸V. Pershina and T. Bastug, *J. Chem. Phys.* **113**, 1441 (2000).
- ⁴⁹V. Pershina, in *Theoretical and Computational Chemistry. Relativistic Electronic Structure Theory, Part 2. Applications*, edited by P. Schwerdtfeger (Elsevier, Amsterdam, 2004), Vol. 14, p. 1.
- ⁵⁰V. Pershina, in *Relativistic Methods for Chemists*, edited by M. Barysz and Y. Ishikawa (Springer Science+Business Media B.V., Dordrecht, 2010), Vol. 10, p. 451.
- ⁵¹H. W. Gäggeler, D. T. Jost, J. Kovacs, U. W. Scherer, A. Weber, D. Vermeulen, A. Türler, K. E. Gregorich, R. A. Czerwinski, B. Kadkhodayan, D. M. Lee, M. Nurmia, D. C. Hoffman, J. V. Kratz, M. K. Guber, H. P. Zimmermann, M. Schädel, W. Brühl, E. Schimpf, and I. Zvara, *Radiochim. Acta* **57**, 93 (1992).
- ⁵²A. Türler, B. Eichler, D. T. Jost, D. Piguet, H. W. Gäggeler, K. E. Gregorich, B. Kadkhodayan, S. A. Kreek, D. M. Lee, M. Mohar, E. Sylwester, D. C. Hoffman, and S. Hübener, *Radiochim. Acta* **73**, 55 (1996).
- ⁵³Z. Qin, M. S. Lin, F. L. Fan, W. X. Huang, X. L. Yan, J. Bai, X. L. Wu, F. A. Lei, H. J. Ding, F. Ma, G. S. Li, H. B. Zhou, and J. S. Guo, *Radiochim. Acta* **100**, 285 (2012).