Theoretical Predictions of Properties and Gas-Phase Behaviour of Carbonyl Complexes of Group-6 Elements Cr, Mo, W, and Element 106, Sg

V. Pershina[1] and J. Anton[2]
[1]GSI, Darmstadt, Germany; [2]Institut für Elektrochemie, Universität Ulm, Germany.

Up to now, experimental gas-phase chemical studies were performed for elements 104 (Rf) through 108 (Hs), 112 (Cn) and 114 (Fl) [1]. A search for a new class of volatile species suitable for gas-phase chromatography studies resulted in the idea to synthesize carbonyl complexes of the heaviest elements. Accordingly, carbonyl complexes of Mo, W and Os, homologs of Sg and Hs, respectively, were synthesized and studied on their volatility by using both the isothermal (IC) and thermochromatography (TC) techniques [2].

Theoretical predictions of gas-phase properties and chromatography behaviour of the heaviest elements and their homologs has been a subject of our long-term research [3]. In the present work, we predict properties of group-6 $M(CO)_6$ (M = Cr, Mo, W, and Sg) and their adsorption behaviour on quartz for future gas-phase chromatography experiments. For calculations, we used our 4-component, fully relativistic, Density Functional Theory method developed within the non-collinear spin-polarized formalism [4]. For calculations of the adsorption energy of the molecules on a neutral (quartz) surface, the following model for a molecule-slab interaction was used [5]:

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

Here, ε is the dielectric constant of the surface material, IP_{mol} and IP_{slab} are ionization potentials of the molecule and surface material, respectively, α_{mol} is molecular polarizability and x is the molecule - surface interaction distance estimated using molecular bond lengths.

Results of the calculations of molecular properties (also in comparison with other calculations [6]) needed for predictions of adsorption are given in Tables 1 and 2.

Table 1. Calculated and experimental bond lengths, R_e (in Å), of $M(CO)_6$ (M = Cr, Mo, W, and Sg)

	Method	R_e(M-C)	R_e(C-O)
$Cr(CO)_6$	4*c*-DFT	1.913	1.152
	exp.	1.918	1.141
$Mo(CO)_6$	4*c*-DFT	2.067	1.152
	RECP CCSD(T)[a]	2.076	1.147
	exp.	2.063	1.145
$W(CO)_6$	4*c*-DFT	2.062	1.153
	RECP CCSD(T)[a]	2.065	1.148
	exp.	2.058	1.148
$Sg(CO)_6$	4*c*-DFT	2.123	1.154
	RECP CCSD(T)[a]	2.112	1.150

[a] Ref. [6].

Table 2. Ionization potentials, IP (in eV), average polarizabilities, α (in a.u.), molecule-surface adsorption distances, x (in Å), and adsorption enthalpies, $-\Delta H_{ads}$ (in kJ/mol), of $M(CO)_6$ (M = Cr, Mo, W, and Sg) on quartz

	IP	$<\alpha>$	x	$-\Delta H_{ads}$
$Cr(CO)_6$	9.07	133.24	2.695	45.4 ± 2.5
$Mo(CO)_6$	9.003	156.41	2.784	48.1 ± 2.5
				42.5 ± 2.5[a]
$W(CO)_6$	8.925	151.54	2.781	46.5 ± 2.5[b]
$Sg(CO)_6$	8.631	159.43	2.82	46.2 ± 2.5

[a] IC experiment [2]; [b] TC experiment [2].

The data show that the electronic structure of $Sg(CO)_6$ is very similar to those of the Mo and W homologs. Accordingly, its volatility should also be very similar to those of the lighter homologs (Table 2). Fig. 1 shows that, indeed, all the homologs will have similar, within the error bars, ΔH_{ads}(M) on quartz.

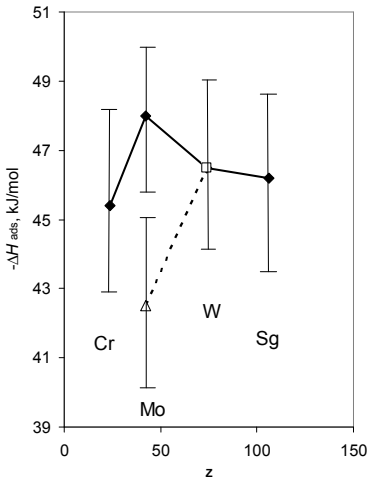

Fig. 1. Predicted (solid line) and measured (dashed line: the open rhomboid is the IC measurements; the open square is the TC ones [2]) adsorption enthalpies of $M(CO)_6$ (M = Cr, Mo, W, and Sg) on quartz.

References

[1] A. Türler and V. Pershina, Chem. Rev., in print
[2] J. Even, et al. Inorg. Chem. **51**, 6431 (2012).
[3] V. Pershina, Radiochim. Acta **99**, 459 (2011).
[4] J. Anton, et al., Phys. Rev. A **69**, 012505 (2004).
[5] V. Pershina and T. Bastug, Chem. Phys. **311**, 139 (2005)
[6] C. N. Nash, B. E. Bursten, J. Am. Chem. Soc., **121**, 10830 (1999).