Gas-phase chemistry of $Sg(CO)_6$ – Measurements of the stability of novel superheavy element compounds

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Abstract

Experiments aimed at studying the chemical stability of the novel $Sg(CO)_6$ molecule, first synthesized in 2013, have been performed. Comparison studies with the stabilities of the lighter homolog molecules $Mo(CO)_6$ and $W(CO)_6$ were also performed. In separate experiments, exploratory studies with the goal to identify chemical synthesis routes for these compounds that feature higher chemical yields than previous approaches were carried out.

1. Research Objectives

Studying fundamental chemical properties of such heaviest elements at the extremes of the periodic table is an exciting perspective for the chemistry community. These elements' electronic shell structure is strongly influenced by relativistic effects induced by the high nuclear charge. Therefore, the prediction of chemical properties of new elements at the very edge of the periodic table is not straightforward. Highly sensitive chemical investigations are required at the single-atom-at-a-time level to benchmark our theoretical understanding of

those effects. The low production rates and short half-lives complicate and limit the applicability of standard chemical procedures and the selection of accessible chemical systems. Gas phase chemical studies on single atomic or single molecular species and their adsorption interaction with stationary surfaces have proven very successful [1,2]. Increasing relativistic effects seem to govern the chemistry of Cn [3,4] and Fl [5,6]. Such effects can also be probed in low oxidation state compounds of lighter transition metal transactinides, Rf, Db, Sg, Bh, Hs, Mt, and Ds, but such compounds were previously out of reach. Only in 2014, our observed formation and high volatility of group 6 hexacarbonyls including $Sg(CO)_6$ [7] opened the door for such studies. As a next step, the study of the compounds thermal stability appears uniquely possible based on our preparatory work with lighter homologs [8].

2. Research Contents

Relativistic density functional theory indicates the hexacarbonyl species of Mo, W, and Sg as the most stable ones and suggests an increase in stability (as expressed in the first bond dissociation energy, FBDE) towards the heavier elements [9,10]. Model experiments with isotopes of Mo and W revealed [8,11] that thermal decomposition studies on a silver surface assess the FBDE on a molecular level. A typical decomposition setup used for this purpose comprised a tubular flow reactor of 1 m length and 4 mm inner diameter entirely covered inside with thin silver foils. The reactor could be heated to defined temperatures between room temperature and 600°C. The amount of hexacarbonyl species able to pass this reactor in dependence of the selected isothermal temperature is measured in comparison to the total amount produced. A first experimental study on $Sg(CO)_6$ stability was carried out at the RILAC-GARIS facility at the RIKEN Nishina Center in FY16. The unique combination of the production of ^{265}Sg at the RIKEN RILAC accelerator, its efficient isolation in the RIKEN GARIS separator, together with our thermal stability experimental setup [8] was used. The aim of the experiment was to directly determine a chemical bond stability within a transactinide molecule.

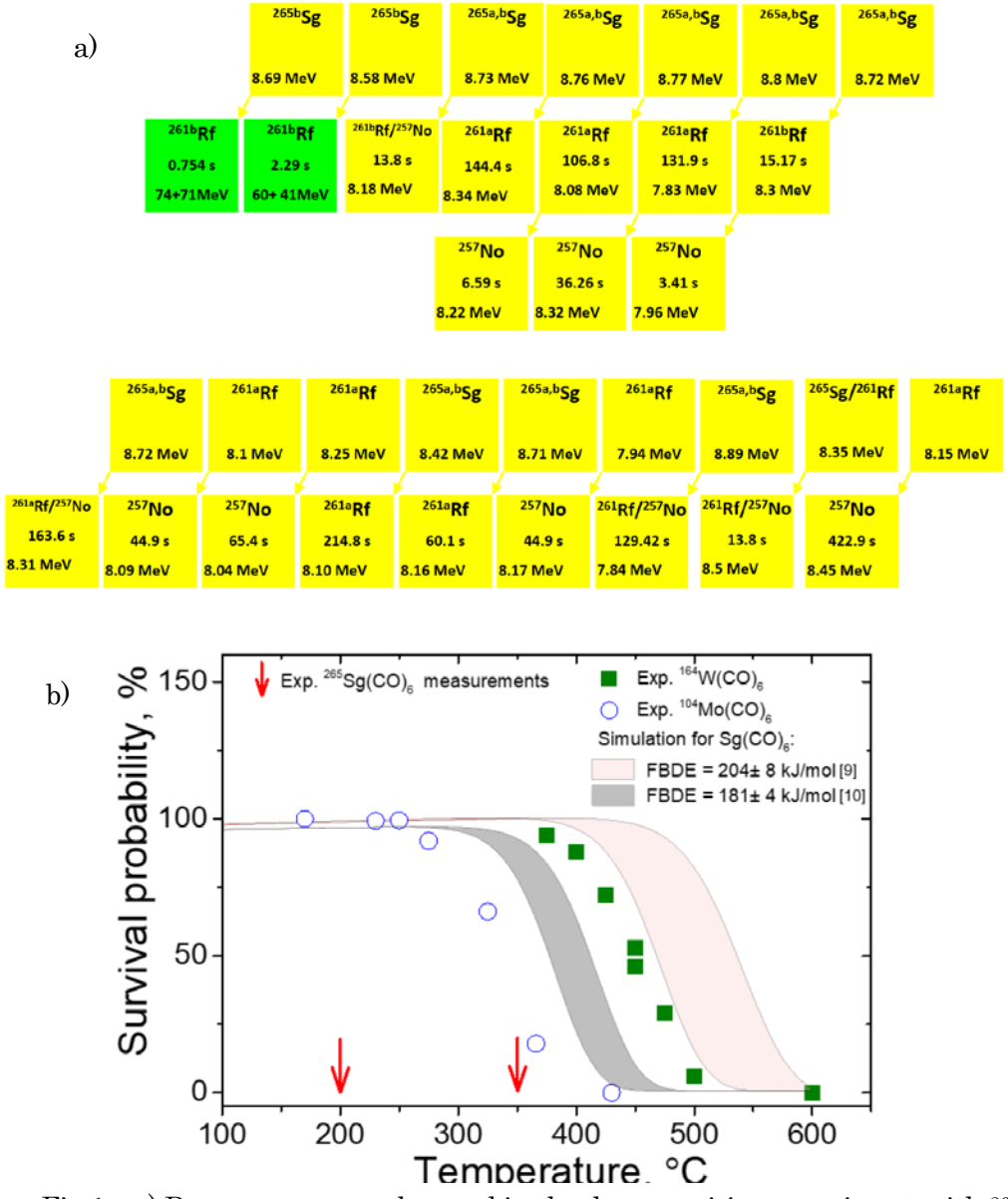
A separate set of experiments was performed at the research reactor TRIGA Mainz with the main scientific goal being to overcome the up to 90% losses of evaporation residues in the physical preseparator. As a beam-free environment is necessary for carbonyl-compound synthesis, a new two-chamber design was tested, whereby the beam is stopped in a first chamber, from which reaction products are flushed into a second, directly connected chamber with a rapid inert-gas flow. Such a design has first been tested previously in an exploratory study performed at JAEA Tokai. Similarly to those studies, in the TRIGA Mainz experiments, the chemical reaction chamber, directly connected to the recoil chamber, was flushed with carbon-monoxide containing gas, facilitating the synthesis of the carbonyl compounds [12]. These studies will guide the way to experiments with superheavy elements beyond Sg, which can only be produced at rates yet lower than those of Sg due to decreasing cross sections with increasing atomic number Z. Hence, highly efficient systems are required.

3. Research results

First decomposition experiments with $^{265}Sg(CO)_6$ have been performed successfully at the RILAC-GARIS facility. Preliminary results are shown in Figure 1, where panel a) gives an

overview of decay chains associated with ^{265}Sg. In panel b), red arrows indicate the temperatures, at which the stability of $Sg(CO)_6$ was studied. The results obtained previously [8,11] for $Mo(CO)_6$ (blue symbols) and $W(CO)_6$ (green symbols) are shown. A kinetic decomposition model was developed superimposing gas chromatographic transport of species through the open tubular reactor with heterogeneous decomposition of the species upon adsorption on the inner surfaces of the reactor [11]. This model is applied to relate the decomposition observations to the FBDE given for the hexacarbonyl complexes and was used in [11] to formulate an expectation for the behaviour of $Sg(CO)_6$ based on the predicted stability from [9] (red shaded area) and [10] (gray shaded area). The final data analysis is ongoing.

a)



b)

Fig 1 : a) Decay sequences observed in the decomposition experiment with ^{265}Sg.
b) Measured survival probability of $Mo(CO)_6$ and $W(CO)_6$. The red arrows indicate temperatures at which the Sg-decompositon was measured. For details, see text.

At TRIGA Mainz, overall yields for the two steps “flushing out of the recoil chamber” and

"chemical yield for carbonyl compound formation" of about 40% have been reached, supporting the effectiveness of this novel approach for experiments with higher yields.

4. Conclusion

First steps towards the determination of bond stability in a SHE-containing molecule have been successfully taken. Novel approaches for increased yield appear promising, supporting the exciting program which is available for carbonyl chemical studies of the superheavy transition metals.

5. References

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