



Contribution ID: 758

Type: Poster

On the carbonyl complexes of Group VI-VIII transition metals: from molecular orbitals to structures

Tuesday, 15 May 2018 18:30 (15 minutes)

The first synthesis of a superheavy carbonyl, seaborgium hexacarbonyl, has witnessed the step of the studies on superheavy element chemistry into a new era. The carbonyl complexes of element 107 (bohrium) and 108 (hassium) are the next targets for the investigation. In “few-atom chemistry” condition, the structures, properties and stabilities of bohrium carbonyls are influenced by both the relativistic effect and the John-Teller effect. Previous isothermal chromatography (IC) and thermal chromatography (TC) have proved the existence of the mononuclear carbonyls $[M(\text{CO})_x]$, $M=\text{Mo}, \text{W}/\text{Tc}, \text{Re}/\text{Ru}, \text{Os}$ with the short-lived lighter homologues in Group VI-VIII. However, some of these carbonyls are not stable (in the form of radicals); some are radioactive (technetium carbonyls). This brings much difficulty in the structural characterization.

In our recent investigations, the laser ablation and ionization time-of-flight mass spectrometer (LAI-TOF-MS) technique and the theoretical approach, including the molecular orbital theory (MOT), the ligand field theory (LFT) and the density functional theory (DFT), are applied to give a systematical explanation of their structural information and the transition mechanism for these mononuclear carbonyl complexes.

In LAI-TOF-MS, it is found that the $17e$ cations, $[M(\text{CO})_6]^{+}$ ($M=\text{Mo}, \text{W}$) and $[M(\text{CO})_5]^{+}$ ($M=\text{Ru}, \text{Os}$) for Group VI and VIII, and $18e$ $[\text{Re}(\text{CO})_6]^{+}$ for Group VII can be formed spontaneously in gas phase. This is confirmed by the theoretical calculations on complexes formation energy. Also, by MOT, LFT predictions and DFT calculations, it can be determined that in ground-state the geometries of Group VII hexacarbonyl cations and Group VI neutral hexacarbonyls are in the same point group (O_h), while those of Group VII pentacarbonyl anions and Group VIII neutral pentacarbonyls are in the same point group (D_{3h}). By energy calculation, the coordination number of the most stable mononuclear carbonyls are determined to be 6 for Group VI molecules/cations and Group VII cations, 5 for Group VII radicals/anions, Group VIII molecules/cations and Group VI anions, and 4 for Group VIII anions. These results also accord well with the LAI-TOF-MS experiments.

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Session Classification: Poster TAN

Track Classification: Chemistry of Actinide and Trans-actinide Elements