Group 13 Oxyfluoride Radicals: A Combined Matrix-Isolation and Quantum-Chemical Study

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Oxygen-center radicals are extremely interesting and unstable species due to their high reactivity. Oxygen-centered radicals typically generated from many R-OX species (R = alkyl), which were detected by electron paramagnetic resonance (EPR).[1] Whereas, the stable synthesis of 13 main group oxyfluorides with terminal oxo radical elements is difficult due to the limitation of orbital number and energy. $^{\bullet}OScF_2$,[2] $^{\bullet}OHgF$[3] oxygen radical analogs have been identified under conditions of matrix isolation.

In this work, we firstly show the reaction between laser-ablated group 13 atoms M (M = B, Al, Ga, In) with OF_2 to form OBF, OAlF, OGaF, OInF molecules and $^{\bullet}OBF_2$, $^{\bullet}OAlF_2$, $^{\bullet}OGaF_2$, $^{\bullet}OInF_2$ oxygen-center radicals as well as MF, MF_2, MF_3, $(F_2)MF_2$ fluorides. These compounds have been characterized by matrix-isolation spectroscopy in neon and argon matrices at 4 K aided by quantum-chemical calculations with DFT and ab initio methods. Their vibrational band positions provide detailed insights into their molecular structures and the oxidation states at the metal centers. The calculations revealed the linear structure for OMF molecules in the singlet state. Moreover, the orbitals of OMF exhibit the multiple bond characteristics derived from two covalent bonds and a dative bond formed by oxygen $2p_\pi$ lone pair donating electrons to the M atoms *np* (n = 2, 3, 4, 5) empty orbital. While the $^{\bullet}OMF_2$ radicals have a $^2B_2$ ground state with C_{2v} symmetry, with the unpaired electron located mainly at the terminal oxygen atom. Furthermore, isotopic substitution experiments with $^{18}OF_2$ were performed to support these novel findings.

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