AN INFRARED PHOTODISSOCIATION SPECTROSCOPIC AND THEORETICAL STUDY OF $M(CO)^+_{6,7,8}$ (M = Ti, Zr, Hf)

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Spectroscopic and theoretical study of extreme coordinated metal carbonyl complexes has been a subject of intensive studies.[a] $M(CO)^+_n$ (M = Ti, Zr, Hf) ions were produced by ablating a metal target in a pulse of CO seeded helium, and further studied by mass-selected infrared photodissociation spectroscopy in the carbonyl stretching region. $Ti(CO)^+_6$ is formed as dominant species in the mass spectrum, while $M(CO)^+_{6,7,8}$ ions are of the most abundant species in the mass spectra for zirconium and hafnium. The infrared spectra of $M(CO)^+_6$ (M = Ti, Zr, Hf) show good agreement with previous reports.[b] $M(CO)^+_7$ (M = Zr, Hf) ions only dissociate under focused laser irradiation and have one broad band, indicating strongly coordinated complexes. $M(CO)^+_8$ (M = Zr, Hf) complexes can fragment by one CO molecule in unfocused light, and each exhibits an infrared band centered at 2084 cm^{-1}(Zr) and 2072 cm^{-1}(Hf). Theoretical calculations indicate that the $M(CO)^+_7$ (M = Zr, Hf) complexes are at doublet ground states with C_{2v} symmetry. The $M(CO)^+_8$ (M = Zr, Hf) complexes are identified as 19-electron octacarbonyls. Each of them has D_4 symmetry (distorted cubic geometry) and a doublet ground state. The results extend the knowledge of extreme coordinated carbonyl complexes to Group 4 metals, and provide insights into the ion growth mechanisms in the gas phase.

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[a] Zhou, M. F.; Frenking, G. Angew. Chem. Int. Ed. 2018, 57(21), 6236-6241; Science, 2018, 361(6405), 912-916.

[b] Duncan, M. A. J. Phys. Chem. A, 2013, 117(46), 11695–11703.