

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

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Spectroscopic and theoretical study of extreme coordinated metal carbonyl complexes has been a subject of intensive studies.<sup>a</sup>  $M(\text{CO})_n^+$  ( $M = \text{Ti}, \text{Zr}, \text{Hf}$ ) 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.  $\text{Ti}(\text{CO})_6^+$  is formed as dominant species in the mass spectrum, while  $M(\text{CO})_{6,7,8}^+$  ions are of the most abundant species in the mass spectra for zirconium and hafnium. The infrared spectra of  $M(\text{CO})_6^+$  ( $M = \text{Ti}, \text{Zr}, \text{Hf}$ ) show good agreement with previous reports.<sup>b</sup>  $M(\text{CO})_7^+$  ( $M = \text{Zr}, \text{Hf}$ ) ions only dissociate under focused laser irradiation and have one broad band, indicating strongly coordinated complexes.  $M(\text{CO})_8^+$  ( $M = \text{Zr}, \text{Hf}$ ) complexes can fragment by one CO molecule in unfocused light, and each exhibits an infrared band centered at  $2084 \text{ cm}^{-1}$  (Zr) and  $2072 \text{ cm}^{-1}$  (Hf). Theoretical calculations indicate that the  $M(\text{CO})_7^+$  ( $M = \text{Zr}, \text{Hf}$ ) complexes are at doublet ground states with  $C_{2v}$  symmetry. The  $M(\text{CO})_8^+$  ( $M = \text{Zr}, \text{Hf}$ ) 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.

<sup>a</sup>Zhou, M. F.; Frenking, G. *Angew. Chem. Int. Ed.* 2018, 57(21), 6236-6241; *Science*, 2018, 361(6405), 912-916.

<sup>b</sup>Duncan, M. A. *J. Phys. Chem. A*, 2013, 117(46), 11695-11703.