INFRARED SPECTROSCOPY AND STRUCTURES OF METAL CARBONYL CATIONS, $M(CO)_n^+$ (M= Nb,Ta,Mn), (n=1-11)

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$M(CO)_n^+$ complexes (M=Nb,Ta,Mn), (n=1-11) are produced in the gas phase by laser vaporization in a pulsed nozzle source and detected with a time of flight mass spectrometer. The carbonyl stretching region is studied using mass selected infrared photodissociation spectroscopy. The coordination number, geometry, and electronic structure of these complexes can be determined from the number of infrared-active bands, their positions, their relative intensities, and the fragmentation patterns. Complexes with CO ligands in excess of the coordination sphere are eliminated readily, leaving behind a core ion with its complete coordination sphere. Complexes at or below the coordination number do not fragment efficiently, and the argon-tagged analogues of the form $M(CO)_n(Ar)_m^+$, are investigated instead. The $Mn(CO)_6^+$ and $Ta(CO)_7^+$ complexes have a completed coordination sphere, consistent with their expected 18 electron stability. However, $Nb(CO)_n^+$ shows evidence of two isomers, one with a completed coordination sphere at n=6, yielding a 16 electron complex, and another with a completed coordination sphere at n=7, yielding an 18 electron complex. $V(CO)_n^+$, not discussed here, is exclusively six coordinate. The geometries and electronic structure of the complexes are determined by comparison of the measured spectra to the spectra predicted by theoretical calculations.