MASS-ANALYZED THRESHOLD IONIZATION SPECTROSCOPY AND SPIN-ORBIT COUPLING OF CERIUM-HYDROCARBON COMPLEXES

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Ce(C\textsubscript{2}H\textsubscript{2}) and Ce(C\textsubscript{4}H\textsubscript{6}) are produced by the Ce-mediated ethylene activation and investigated by mass-analyzed threshold ionization (MATI) spectroscopy, isotopic substitutions, and relativistic quantum chemical computations. The MATI spectrum of Ce(C\textsubscript{2}H\textsubscript{2}) exhibits two nearly identical band systems separated by 128 cm\textsuperscript{-1}, and that of Ce(C\textsubscript{4}H\textsubscript{6}) shows three similar band systems separated by 55 and 105 cm\textsuperscript{-1}. These separations are not affected by deuteration. The observed band systems for the two Ce-hydrocarbon species are attributed to the spin-orbit splitting arising from interactions of triplet and singlet states. Ce(C\textsubscript{2}H\textsubscript{2}) is a metallacyclopene in C\textsubscript{2v} symmetry, and Ce(C\textsubscript{4}H\textsubscript{6}) is a metallacyclopentene in C\textsubscript{s} symmetry. The low-energy valence electron configurations of the neutral and ionic states of each species are Ce 4f\textsuperscript{1}6s\textsuperscript{1} and Ce 4f\textsuperscript{1}, respectively. The remaining two electrons that are associated with the isolated Ce atom or ion are spin paired in a molecular orbital that is a bonding combination between a Ce 5d orbital and a hydrocarbon π* antibonding orbital.