

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

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$\text{Ce}(\text{C}_2\text{H}_2)$ and $\text{Ce}(\text{C}_4\text{H}_6)$ 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 $\text{Ce}(\text{C}_2\text{H}_2)$ exhibits two nearly identical band systems separated by 128 cm^{-1} , and that of $\text{Ce}(\text{C}_4\text{H}_6)$ shows three similar band systems separated by 55 and 105 cm^{-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. $\text{Ce}(\text{C}_2\text{H}_2)$ is a metallacyclopropene in C_{2v} symmetry, and $\text{Ce}(\text{C}_4\text{H}_6)$ is a metallacyclopentene in C_s symmetry. The low-energy valence electron configurations of the neutral and ionic states of each species are $\text{Ce } 4f^1 6s^1$ and $\text{Ce } 4f^1$, 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.