

## INFRARED SPECTROSCOPY OF $Zn(\text{ACETYLENE})_{1-5}^+$ : EVIDENCE OF ACETYLENE ACTIVATION BY A METAL RADICAL

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Zinc cation is studied as a model system for single atom catalysis in the gas phase with infrared photodissociation spectroscopy.  $Zn(\text{C}_2\text{H}_2)_n^+$  ( $n = 1-5$ ) clusters are produced via laser vaporization of zinc in a supersonic expansion of acetylene and argon. Clusters are mass-selected and studied with infrared photodissociation spectroscopy in the C–H stretching region. Smaller clusters ( $n = 1-3$ ) are studied with the use of a weakly bound argon tag. These spectra are assigned with B3LYP/Def2TZVP computational studies.  $Zn(\text{C}_2\text{H}_2)^+$  is found to consist of a  $C_{2v}$  three membered metallacycle, where zinc is equidistant from both carbon atoms of acetylene.  $Zn(\text{C}_2\text{H}_2)_2^+$  does not contain a metallacycle, but features zinc binding more closely to one of the carbon atoms of each acetylene in a  $C_2$  configuration. The three-coordinate cluster is predicted to be lowest in energy as a  $\pi$ -bound  $D_{3h}$  structure, with a low energy  $C_3$  structure. When the spectrum of this cluster is measured with argon tagging the  $D_{3h}$  isomer is most abundant. When measured without the tag the  $C_3$  isomer is found to be in abundance. The spectra of the four and five coordinate clusters are found to contain a feature  $160\text{ cm}^{-1}$  to the red of the acetylene C–H asymmetric stretch. This is attributed to a fourth acetylene ligand forming a metal vinyl radical, accompanied by formation of Zn(II). This transfer of the radical center from zinc to a ligand activates the acetylene, and could be the first step in single atom catalysis by zinc.