

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

JOSHUA H MARKS, TIMOTHY B WARD, MICHAEL A DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA, USA.*

Zinc cation is studied as a model system for single atom catalysis in the gas phase with infrared photodissociation spectroscopy. $\text{Zn}(\text{C}_2\text{H}_2)_n^+$ ($n = 1-5$) 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. $\text{Zn}(\text{C}_2\text{H}_2)^+$ is found to consist of a C_{2v} three membered metallacycle, where zinc is equidistant from both carbon atoms of acetylene. $\text{Zn}(\text{C}_2\text{H}_2)_2^+$ 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 π -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 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 $\text{Zn}(\text{II})$. 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.