HIGHLY ACCURATE QUARTIC FORCE FIELDS, VIBRATIONAL FREQUENCIES, AND SPECTROSCOPIC CONSTANTS FOR CYCLIC AND LINEAR $C_3H_3^+$ INCLUDING ^{13}C AND DEUTERIUM ISOTOPOLOGUES

TIMOTHY J. LEE, *MS 245-1, NASA Ames Research Center, Moffett Field, CA, 94035*; XINCHUAN HUANG, *SETI Institute, 189 Bernardo Ave, Suite 100, Mountain View, CA, 94043*; and PETER R. TAYLOR, *Victorian Life Sciences Computation Initiative and Department of Chemistry, University of Melbourne, Vic 3010, Australia*.

High levels of theory have been used to compute quartic force fields (QFFs) for the cyclic and linear forms of the $C_3H_3^+$ molecular cation, referred to as c-$C_3H_3^+$ and l-$C_3H_3^+$. Specifically the singles and doubles coupled-cluster method that includes a perturbational estimate of connected triple excitations, CCSD(T), has been used in conjunction with extrapolation to the one-particle basis set limit and corrections for scalar relativity and core correlation have been included. The QFFs have been used to compute highly accurate fundamental vibrational frequencies and other spectroscopic constants using both 2nd-order perturbation theory and exact variational methods to solve the nuclear Schrdinger equation. Agreement between our best computed fundamental vibrational frequencies and recent infrared photodissociation experiments is reasonable for most bands, but there are a few exceptions. Possible sources for the discrepancies are discussed. Fundamental vibrational frequencies and spectroscopic constants for ^{13}C and deuterium isotopologues will also be presented. It is expected that the fundamental vibrational frequencies and spectroscopic constants presented here for c-$C_3H_3^+$ and l-$C_3H_3^+$ are the most reliable available for the free gas-phase species. It is hoped that these will be useful in the assignment of future high-resolution laboratory experiments or astronomical observations.