NONRESONANT TWO-PHOTON MASS-ANALYZED THRESHOLD IONIZATION AND ZERO KINETIC ENERGY PHOTOELECTRON SPECTROSCOPY OF KETENE

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The rotationally resolved nonresonant two-photon mass analyzed threshold ionization (MATI) spectra and zero kinetic energy (ZEKE) photoelectron spectra of CH$_2$CO$^+$ and CD$_2$CO$^+$ are presented. The MATI and ZEKE spectra of CH$_2$CO$^+$ are dominated by the totally symmetric modes $\nu_1$ (C=C stretch) and $\nu_2$ (C=O stretch), with weaker excitation of $\nu_3$ (CH$_2$ scissor), while those of CD$_2$CO$^+$ are dominated by approximately equally intense $\nu_2$, $\nu_5$, and $\nu_4$. This is consistent with the theoretical calculations of Takeshita$^a$, which indicate a strong coupling of $\nu_2$ and $\nu_4$ modes of CD$_2$CO$^+$ in the ground state. In addition, weak excitations to the nontotally symmetric vibrations $\nu_5$ (CH$_2$ wag), $\nu_6$ (C=C=O linear bend) and $\nu_9$ (C=C=O linear bend) are also observed in the MATI spectra of both isotopomers. Rotational structure is dominated by very strong $\Delta K_a=\pm 1$ manifolds with two orders of magnitude weaker $\Delta K_a=\pm 3$ features. Analysis of the ZEKE spectra provides the ionization potentials (77538.8±2 cm$^{-1}$ for CH$_2$CO and 77533.7±2 cm$^{-1}$ for CD$_2$CO) and rotational constants for the ground states of both ketene cations.