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_2CO^+ and CD_2CO^+ are presented. The MATI and ZEKE spectra of CH_2CO^+ are dominated by the totally symmetric modes ν_4 (C=C stretch) and ν_2 (C=O stretch), with weaker excitation of ν_3 (CH_2 scissor), while those of CD_2CO^+ are dominated by approximately equally intense ν_2, ν_3, and ν_4. This is consistent with the theoretical calculations of Takeshita[a], which indicate a strong coupling of ν_3 and ν_4 modes of CD_2CO^+ in the ground state. In addition, weak excitations to the nontotally symmetric vibrations ν_5 (CH_2 wag), ν_6 (C=C=O linear bend) and ν_9 (C=C=O linear bend) are also observed in the MATI spectra of both isotopomers. Rotational structure is dominated by very strong $\Delta K_a=\pm1$ manifolds with two orders of magnitude weaker $\Delta K_a=+3$ features. Analysis of the ZEKE spectra provides the ionization potentials (77538.8±2 cm^{-1} for CH_2CO and 77533.7±2 cm^{-1} for CD_2CO) and rotational constants for the ground states of both ketene cations.

[a]K. Takeshita, J. Chem. Phys. 96, 1199, (1992)