REINVESTIGATION OF RYDBERG STATES OF KETENE BY TWO-PHOTON RESONANCE-ENHANCED MULTI-PHOTON IONIZATION SPECTROSCOPY

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The Rydberg states of CH_2CO and CD_2CO in the energy region of 54000 - 72000 cm^{-1} have been reinvestigated using the two-photon resonance enhanced multiphoton ionization (REMPI) spectroscopic technique. Better resolution and sensitivity allow us to identify more Rydberg states than the previous work. The transitions to the $3p_z$, $4p_y$, $4p_z$, $5p_y$, four components of 3d, three components of 4d and two components of 4f Rydberg states were identified, based on the analysis of the rotational structures, their quantum defects and the comparison with the theoretical calculations. The rotational and vibrational structures observed in the REMPI spectra provide evidence that the $3p_y$ state has almost identical geometry with C_{2v} symmetry as the ground electronic state of the corresponding cation. While the $3p_x$ state has significantly different geometry from the ground states of both neutral molecules and the cations, in consistent with the ab initio calculations suggesting that the $3p_x$ state possesses C_s symmetry. It is revealed that the difference in the energetic ordering of the three components of the 3p and four components of 3d Rydberg states from those of the theoretical predictions is due to the interactions occuring between the $3p_x$ and $3d_{xz}$ states, both having the same A_1 symmetry. Excitaions of vibrational modes of b_1(e.g. C=C=O out-of-plane bending, CH_2 and CD_2 wag) and b_2(e.g. C=C=O in-plane bending) symmetry have been observed for the first time in the Rydberg states of both ketene isotopomers. It is also indicated from the strong appearance of the two 4f Rydberg states and their rotational structures that the f orbitals might be the major channels of the zero kinetic energy (ZEKE) electron ejection of ketene molecules.