MULTIPHOTON IONIZATION AND DISSOCIATION OF DIAZIRINE

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Multiphoton ionization and dissociation processes in diazirine have been studied experimentally via 304-325 nm two-photon absorption, and theoretically by using the EOM-CCSD and B3LYP methods. The electronic structure calculations indicate the strongest one-photon absorption is to the $2^1A_1(3p_x \leftarrow$n) Rydberg state. However, in two-photon absorption at comparable energies the first photon excites the low-lying $1^1B_2(\Pi^* \leftarrow$n) valence state, from which the strongest absorption is to the dissociative valence $1^1A_2(\Pi^* \leftarrow \sigma_{NN})$ state. In the experimental studies, resonance enhanced multiphoton ionization (REMPI) experiments show no ions at the parent diazirine mass but only CH_2^+ ions from dissociative photoionization. It is proposed that weak one-photon absorption to the 1^1B_2 state is immediately followed by more efficient absorption of another photon to reach the 1^1A_2 state from which competition between ionization and fast dissociation takes place. Strong signals of CH^+ ions are also detected and assigned to 2+1 of CH fragments. Velocity map CH^+ images show that CH fragments are born with substantial translational energy indicating that they arise from absorption of two photons in diazirine. It is argued that two-photon processes via the 1^1B_2 intermediate state are very efficient in this wavelength range, leading predominantly to dissociation of diazirine from the 1^1A_2 state. The most likely route to CH(X) formation is isomerization to isodiazirine followed by dissociation to CH + HN_2.