PHOTOIONIZATION INDUCED BARRIERLESS PROTON TRANSFER ALONG THE WEAK C-H...O HYDROGEN BOND OF METHACROLEIN DIMER UNDER SUPERSONIC JET COLD CONDITION IN THE GAS PHASE

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An exceptional and remarkable chemical event, barrierless proton transfer (PT) at the interface of weak C-H...O hydrogen bond, has been found to be occurring within the dimer cation of an atmospherically significant α,β-unsaturated aldehyde, Methacrolein, produced in the gas phase under supersonic cooling condition. The reaction has been initiated upon non-resonant multiphoton ionization by 532 nm pulses (10 ns) of a Q-switched Nd:YAG laser and the fragment ions have been probed by means of time-of-flight (TOF) mass spectrometry. Prominent signatures of the protonated molecular ion [(MC)H^+] and dimer cation [$(MC)_2$]$^{\cdot+}$ have been observed in the TOF mass spectra whereby intensity of the former is found to increase proportionately with that of the latter as the cooling condition was improved by increasing the backing pressure of the carrier gas. The observations indicate that the intermolecular PT within the dimer cation and subsequent fragmentation lead to the formation of (MC)H^+. The laser power dependence study reveals that a 4-photon process is responsible for the photoionization of dimer and generation of the protonated molecular ion at 532 nm wavelength. The electronic structure theory calculations predict that the vertical ionization energy of the dimer is very much similar to the total four-photon excitation energy (9.32 eV) and thus it has been concluded that the dimer cations were formed with no excess energy under the experimental condition. The effect of excess vibrational energy on the PT process has also been experimentally verified by ionizing the compound with 355 nm laser light. Potential energy scans along the C-H...O coordinate of the dimer cations have revealed that the PT process occurs without encountering any effective energy barrier.