**Supporting Information**

for

# Barrierless Proton Transfer in the Weak C-H···O Hydrogen Bonded Methacrolein Dimer upon Non-Resonant Multi-Photon Ionization in the Gas Phase

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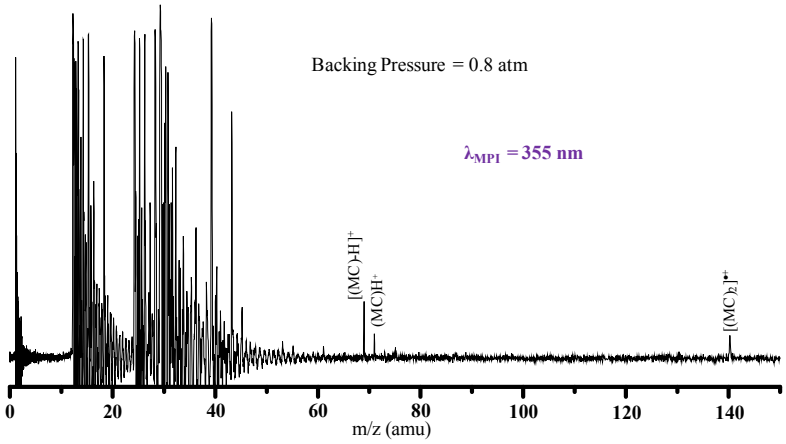


**Figure S1.** Multi-photon ionization mass spectrum of MC for 355 nm wavelength recorded with 2 mV unit division in the oscilloscope. Backing pressure of the carrier gas argon was kept 0.8 atm.

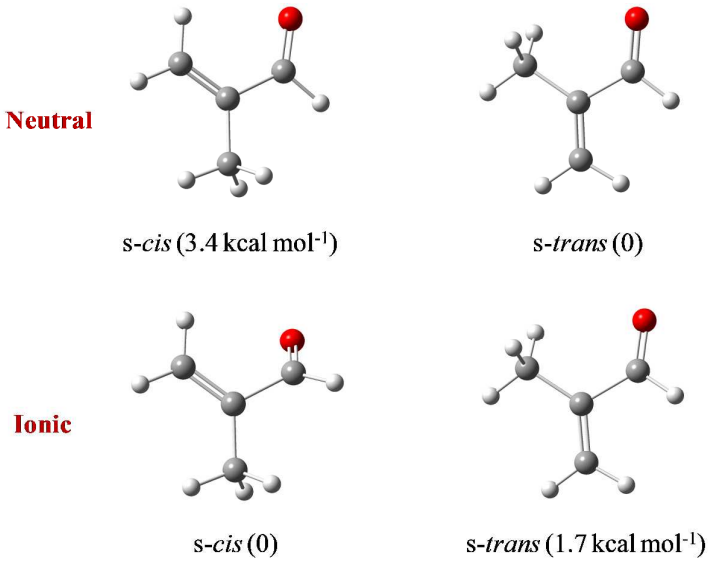


**Figure S2.** Geometric structures and relative energies of the 's-*cis*' and 's-*trans*' isomers of MC in neutral ($S_0$) and cationic ($D_0$) ground states, optimized at the *DFT/B3LYP/6-311++G(d,p)* level.

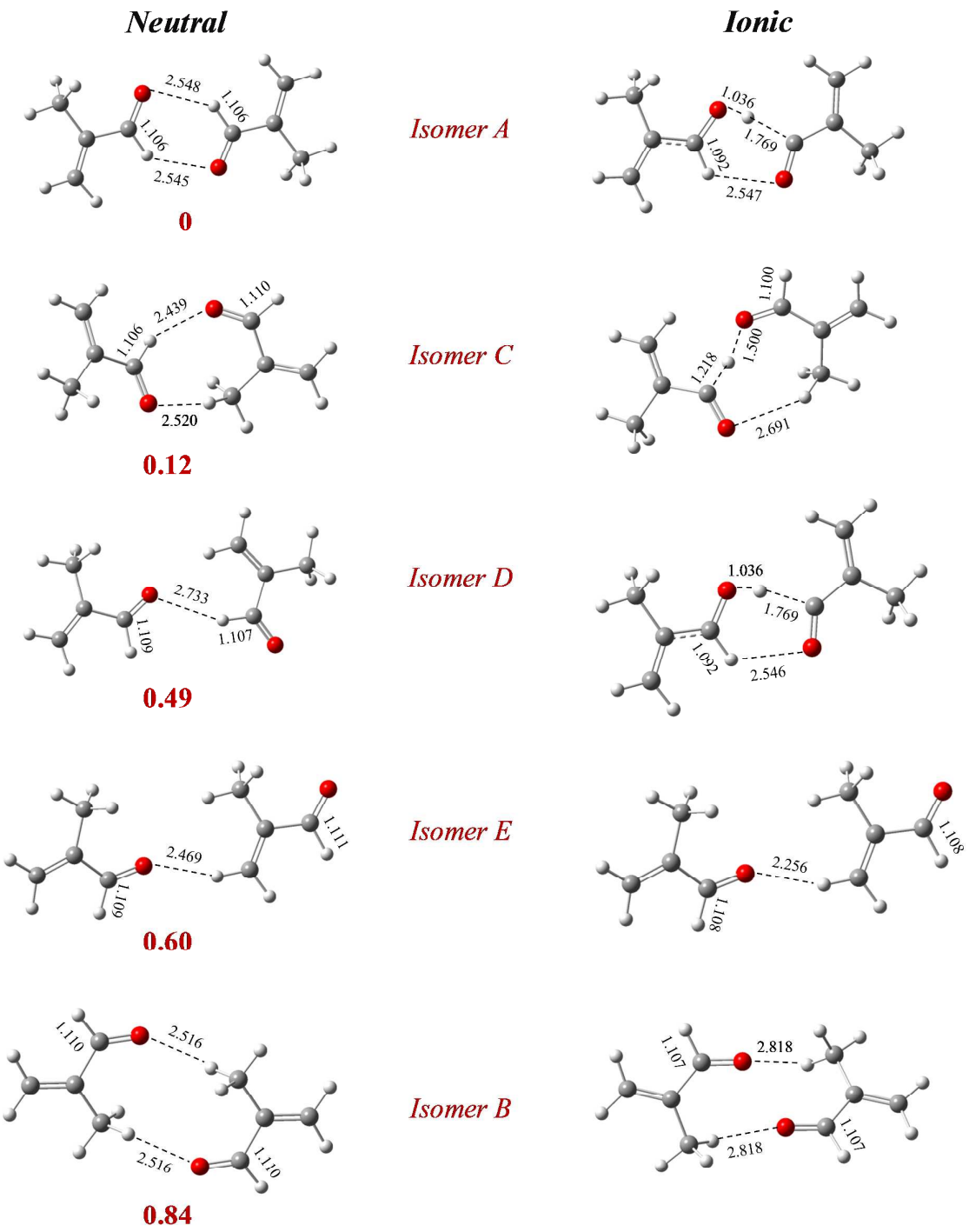


**Figure S3.** Geometric structures, BSSE corrected relative energies (in kcal $mol^{-1}$) of five structural isomers of MC dimer in neutral ($S_0$) and cationic ($D_0$) ground states, optimized at the *DFT/B3LYP/6-311++G(d,p)* level. Bond lengths are given in Å units.

| | Monomer (s-*trans*) | Dimer | | | | |
|---|---|---|---|---|---|---|
| | | *Isomer A* | *Isomer B* | *Isomer C* | *Isomer D* | *Isomer E* |
| VIE (eV) | 9.84 | 8.73 | 8.97 | 8.92 | 8.87 | 8.98 |
| AIE (eV) | 9.77 | 8.28 | 8.68 | 8.55 | 8.26 | 8.94 |

**Table S1a.** VIEs and AIEs of MC monomer and five dimer isomers calculated at *DFT/B3LYP/6-311++G(d,p)* level.

| | Monomer (s-*trans*) | Dimer | | | | |
|---|---|---|---|---|---|---|
| | | *Isomer A* | *Isomer B* | *Isomer C* | *Isomer D* | *Isomer E* |
| VIE (eV) | 10.02 | 9.30 | 9.71 | 9.42 | 9.51 | 9.62 |
| AIE (eV) | 9.96 | 8.35 | 8.09 | 8.50 | 8.31 | 9.48 |

**Table S1b.** VIEs and AIEs of MC monomer and five dimer isomers calculated at *M06-2X/6-311++G(3df,3pd)* level.

| | Monomer (s-*trans*) | Dimer | | | | |
|---|---|---|---|---|---|---|
| | | *Isomer A* | *Isomer B* | *Isomer C* | *Isomer D* | *Isomer E* |
| VIE (eV) | 9.84 | 9.03 | 9.55 | 9.18 | 9.29 | 9.46 |
| AIE (eV) | 9.78 | 8.23 | 8.59 | 8.38 | 8.20 | 9.29 |

**Table S1c.** VIEs and AIEs of MC monomer and five dimer isomers calculated at *ωB97X-D/6-311++G(3df,3pd)* level.

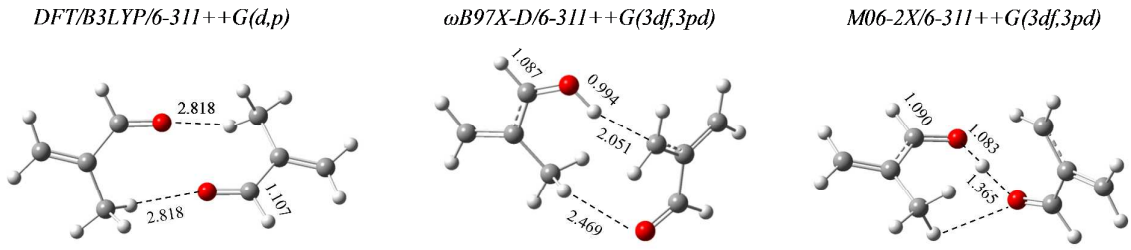


**Figure S4.** Geometric structures of the isomer B in the cationic ground state, optimized at *DFT/B3LYP/6-311++G(d,p)*, *ωB97X-D/6-311++G(3df,3pd)* and *M06-2X/6-311++G(3df,3pd)* level. Bond lengths are given in Å units.

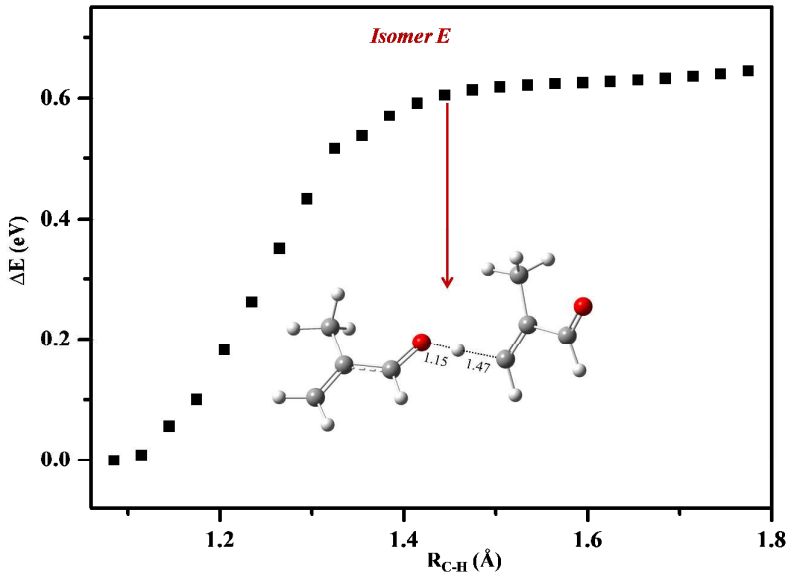


**Figure S5.** Constrained geometry optimization of the vertically ionized MC dimer (isomer E) at *DFT/B3LYP/6-311++G(d,p)* level, relative energies (ΔE) in eV are plotted as a function of C-H bond length, $R_{C\text{-}H}$, of the proton donating monomer. Transition state geometry is shown. Bond lengths are given in Å units.

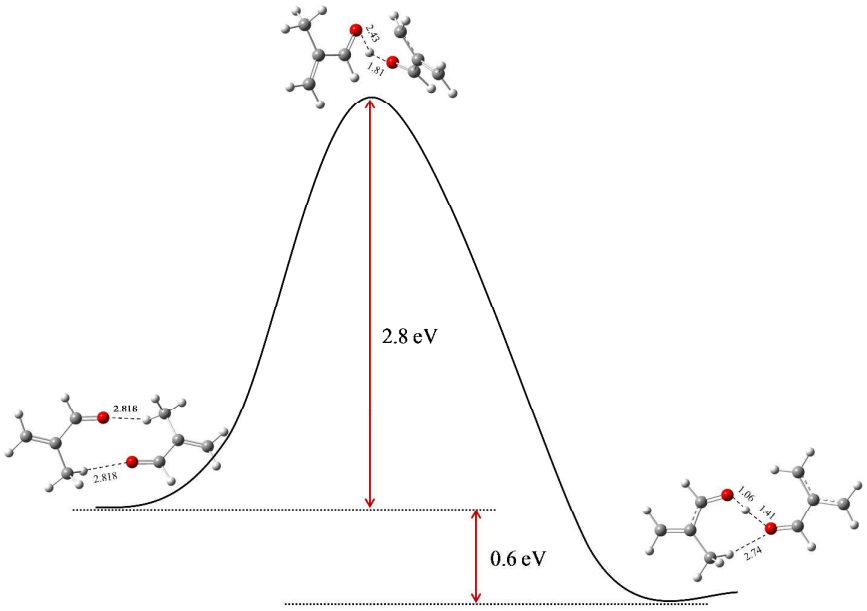


**Figure S6.** Energy diagram for PT in isomer B in the $D_0$ state calculated at *DFT/B3LYP/6-311++G(d,p)* level. Transition state geometry is shown. Bond lengths are given in Å units.

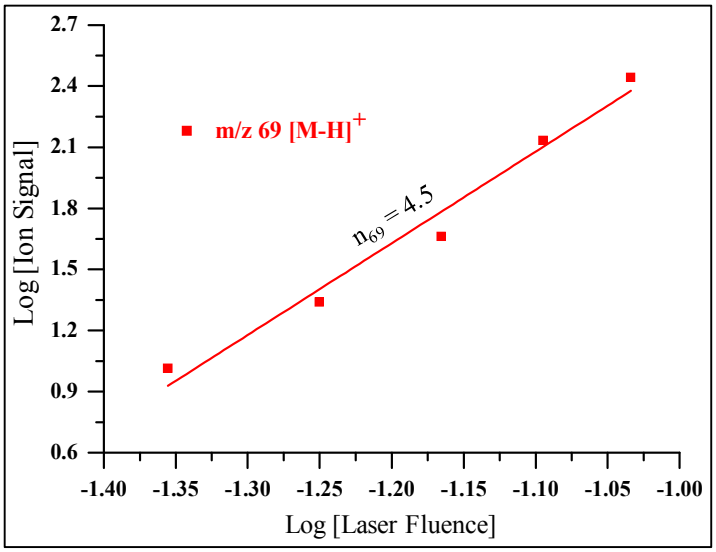


**Figure S7.** Logarithmic plot for the variation of yield of $(MC-H)^+$ ion with increasing laser pulse energies of 532 nm excitation wavelength.

| | Channel 1 | Channel 2 | Channel 3 |
|---|---|---|---|
| Isomer A | 0.8 | 1.4 | 2.4 |
| Isomer C | 0.6 | 1.2 | 2.2 |
| Isomer D | 0.8 | 1.4 | 2.4 |
| Isomer B | 1.0 | 1.7 | 2.7 |

**Table S2.** Dissociation energies from proton transferred structures of different isomers calculated at *DFT/B3LYP/6-311++G(d,p)* level.