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<u>Electronic Supplementary Information</u>

Primary photodissociation mechanisms of pyruvic acid on S_1: observation of methylhydroxycarbene and its chemical reaction in the gas phase

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I. 351 nm fluence dependence of PA photoproducts

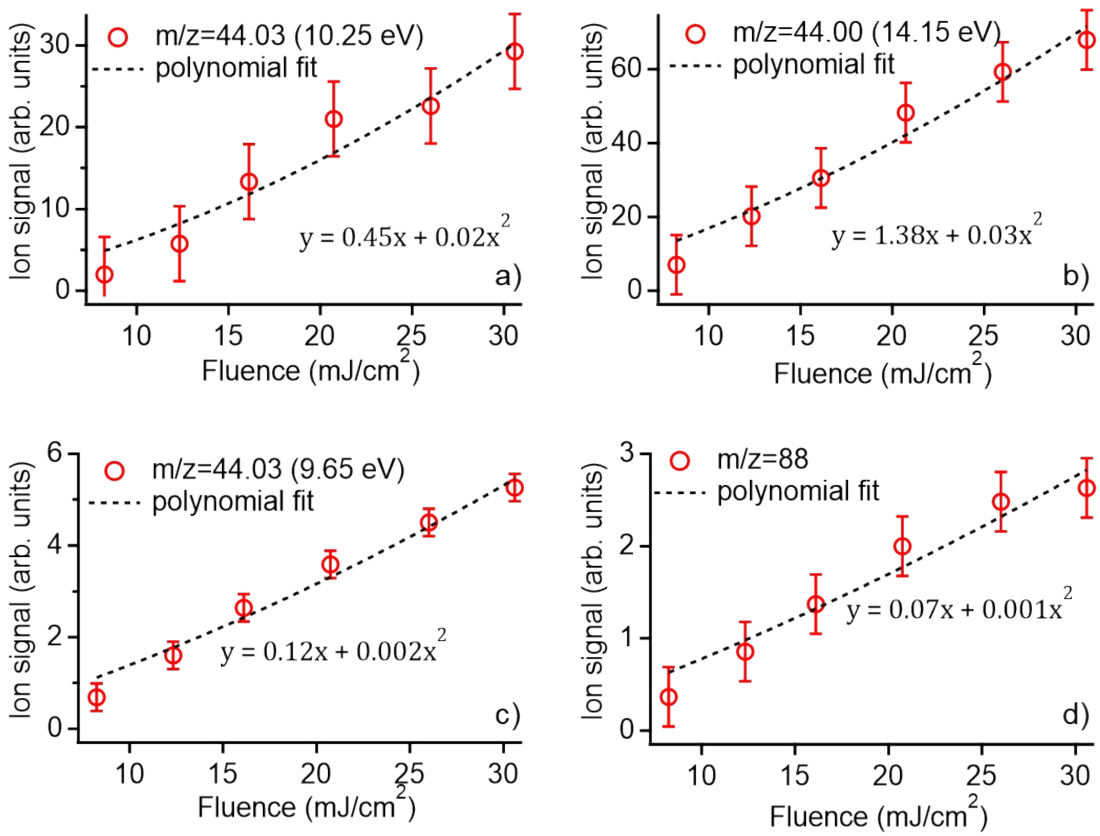

Figure S1: Fluence dependent signals of PA photoproducts a) acetaldehyde and vinyl alcohol at 10.25 eV b) vinyl alcohol at 9.65 eV c) CO_2 at 14.15 eV and d) species M at 9.65 eV. The plotted signal intensities fit to a zero-intercept quadratic equation show dominant linear contribution.

II. 351 nm fluence dependence of radical photoproducts of d_1-PA

Reactive radical species are consumed by wall collisions and/or secondary reactions and their signal intensity as a function of time, $S_i(t)$, can be fit to a first- and second-order decay kinetics profile. Equation S1 combines first and second order kinetics, and can be used to fit the nascent signal intensity, $S_i(t=0)$ for species *i*.[1]

$$S_i(t) = \frac{k_1 S_i(t=0)}{(2k' + k_1)e^{k_1 \cdot t} - 2k'} \tag{S1}$$

Here k_1 is the rate constant representing the sum of all first order losses (including wall-loss), and $k' = \sum k_2 \cdot [j]_{t=0}$ represents the sum of all second order reactions where j is any species with which the product reacts, including self-reaction.

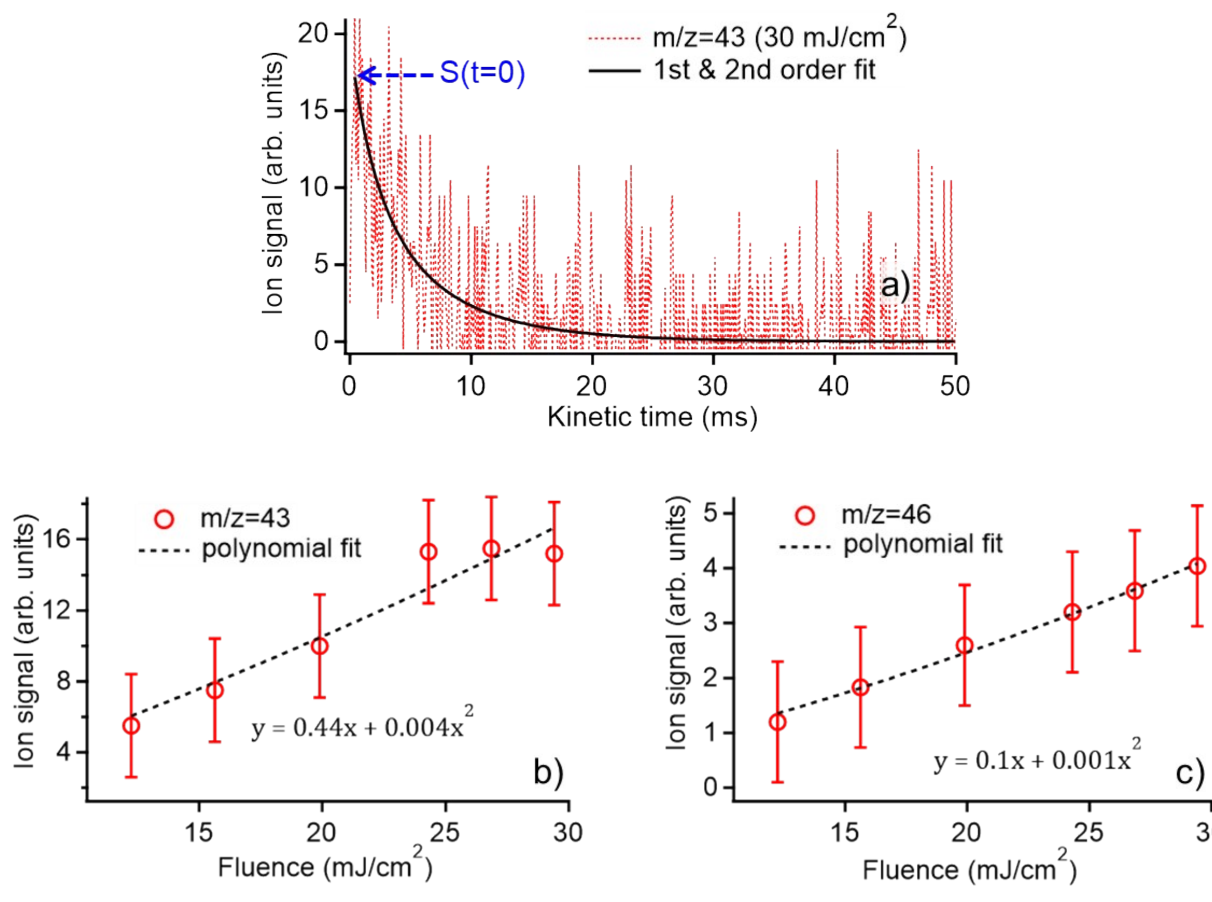

Figure S2: a) The signal intensities of unstable free radical species, obtained at 9.65 eV from d_1-PA photolysis, are extrapolated using equation S1 for m/z=43, as shown. The extrapolated signal intensities are plotted as a function of fluence for b) CH_3CO and c) DOCO radicals. The plotted signal intensities fit to a zero-intercept quadratic equation.

III. Photoionization spectra of species M

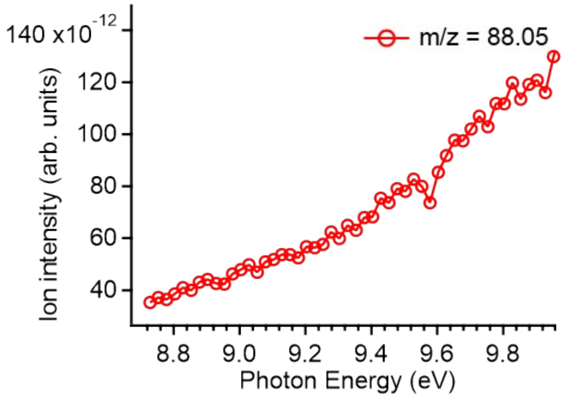

Figure S3: Photoionization spectra of species M (m/z = 88.05), a photoproduct of PA dissociation at 351 nm, in the 8.7 – 9.9 eV region.

IV. PA thermochemistry

Table S1: Summary of thermochemical values utilized in this work. Uncertainty in the values are less than 1 kcal mol^{-1}.

Thermodynamic entity (at 0 K)	(kcal mol^{-1})	Source
ΔH^0_f(PA)	-124.52 ± 0.55	Emel'yanenko et al. 2018[2]
ΔH^0_f(CH_3CHO)	-37.08 ± 0.06	ATcT[3]
ΔH^0_f(H_2C=CHOH)	-26.95 ± 0.16	ATcT[3]
ΔH^0_f(CO_2)	-93.955 ± 0.004	ATcT[3]
ΔH^0_f(CH_3CO)	-0.80 ± 0.08	ATcT[3]
ΔH^0_f(*trans*-HOCO)	-43.28 ± 0.11	ATcT[3]
ΔH^0_f(CH_3COOH)	-100.11 ± 0.10	ATcT[3]
ΔH^0_f(CO)	-27.200 ± 0.006	ATcT[3]
ΔH(Ac → MHC)	50.5 ± 0.8	da Silva 2016[4]
ΔE_{adiab}(PA; $S_1 \leftarrow S_0$)	76.37 ± 0.03	Sutradhar et al. 2019[5]
ΔE_{adiab}(PA; $S_1 \leftarrow T_1$)	6.0	da Silva[6]

ΔE_{adiab}(MHC; $T_1 \leftarrow S_0$)	30.1	Average of Samanta et al. 2018[7], Schreiner et al. 2011[8], and Matus et al. 2006[9]

V. References

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