Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Fast Beam Photofragment Translational Spectroscopy of the Phenoxy Radical at 225 nm, 290 nm, and 533 nm

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Table S1: Anion Photoelectron Spectrum Peak Assignments

Peak Label	Energy (eV)	Assignment*
A	0.081	14_1^1
B	0.077	0_0^0
C	0.018	$11_0^1 14_1^1$
D	0.012	11_0^1

*Assignments correspond to notation provided in Kim et al.[1]

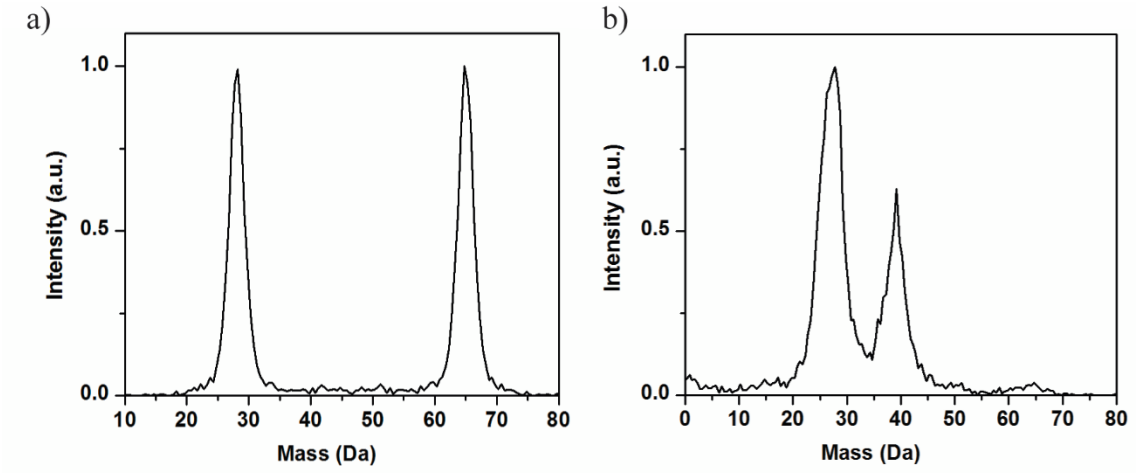

Figure S1: Two- and three-body mass distributions for C_6H_5O dissociation at 193 nm

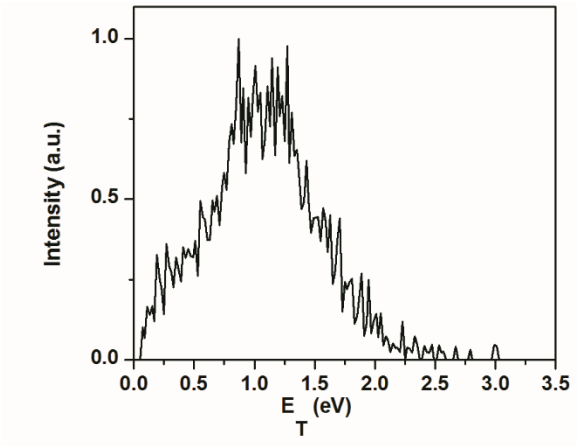

Figure S2: Translational energy distribution of C_6H_5O photodissociation to channel 1(CO + C_5H_5) at 193 nm

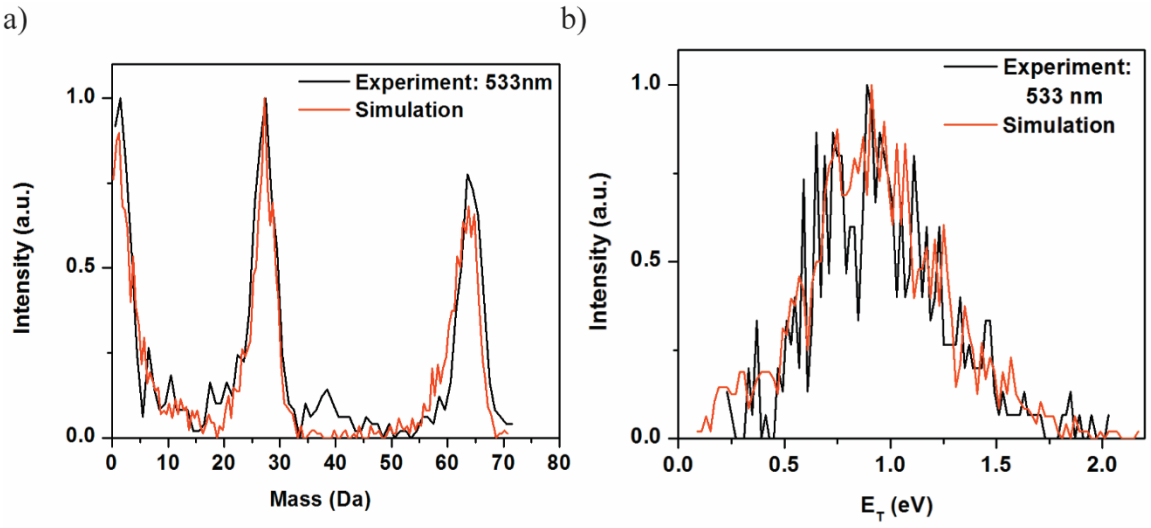

Figure S3: Comparison of experimental and simulated three-body mass (a) and translational energy distributions (b) of C_6H_5O at 533 nm. The simulations use the translational energy distribution of channel 1 formation with some probability of accepting a third fragment.

Table S2: RRKM Rate Constants (s^{-1})

Available Energy ($h\nu$-D_0)[a)]	$C_6H_5O \rightarrow CO + C_5H_5$ (channel 1)	$C_5H_5 \rightarrow C_2H_2 + C_3H_3$ (channel 4)[b)]	$C_5H_5 \rightarrow H + C_5H_4$ (channel 5)[b)]
532 nm (2.33 eV/ 1.29 eV)	1.5	N/A	N/A
290 nm (4.27 eV/ 3.23 eV)	2.8×10^7	N/A	N/A
225 nm (5.51 eV/ 4.47 eV)	6.0×10^8	3.2×10^6	4.3×10^3
225 nm – E_T (1.0 eV) (4.51 eV/ 3.47 eV)	N/A	N/A	N/A
532 nm + 533 nm (4.66 eV/ 3.62 eV)	8.9×10^7	N/A	N/A
532 nm + 290 nm (6.60 eV/5.56 eV)	3.3×10^9	1.8×10^8	3.7×10^7
532 nm + 225 nm (7.84 eV/ 6.80 eV)	1.3×10^{10}	1.4×10^9	1.1×10^9

[a)] D_0 refers to 0 eV for channel 1 formation and 1.04 eV for channels 4 and 5. Values in the parentheses next to each wavelength present the available energy in the following format ($h\nu$-0 eV/ $h\nu$-1.04 eV

[b)] The energy required for secondary dissociation of C_5H_5 to channels 4 and 5 is 3.25 eV and 3.92 eV, respectively. The minimum energy required to traverse all barriers to yield channel 4 is 3.65 eV.[2]

References:

1. J. B. Kim, T. I. Yacovitch, C. Hock and D. M. Neumark, *Phys. Chem. Chem. Phys.* **13**, 17378-17383 (2011).
2. M. Shapero, I. A. Ramphal and D. M. Neumark, *J. Phys. Chem. A* **122**, 4265-4272 (2018).