Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplemental Material

Experimental Studies of High-Temperature Thermal Dissociation of *iso*-Propanol

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Table S1: Experimental conditions for HRRST/TOF-MS experiments for nominal reaction conditions 2053 K and 4.4 bar. T_5 and P_5 represent the average reflected shock conditions at each photon energy and σ the corresponding standard deviations.

hv [eV]	Num of shocks	T_5 (K)	σ_{T5} [K]	P_5 [bar]	σ_{P5} [bar]
12.80	500	2013	90	4.32	0.27
12.70	500	2004	91	4.35	0.29
12.45	500	2049	88	4.46	0.31
12.20	500	2016	91	4.36	0.31
11.95	500	2032	93	4.39	0.3
11.70	500	2066	93	4.47	0.32
11.45	500	2042	92	4.4	0.31
11.20	500	2075	92	4.51	0.3
10.95	500	2095	81	4.56	0.3
10.70	500	2060	87	4.44	0.33
10.45	500	2082	96	4.48	0.3
10.20	500	2036	92	4.34	0.31
9.95	500	2061	92	4.42	0.33
9.70	500	2076	96	4.46	0.32
9.45	500	2089	82	4.48	0.3

Table S2: Experimental conditions for HRRST/TOF-MS for nominal reaction conditions 1660 K and 3.9 bar. T_5 and P_5 represent the average reflected shock conditions at each photon energy and σ the corresponding standard deviations.

hv [eV]	Num of shocks	T_5 (K)	σ_{T5} [K]	P_5 [bar]	σ_{P5} [bar]
12.80	500	1624	58	3.79	0.32
12.70	500	1632	29	3.84	0.12
12.60	500	1636	29	3.86	0.13
12.50	500	1639	29	3.89	0.12
12.40	500	1644	31	3.9	0.12
12.30	500	1644	30	3.91	0.13
12.20	500	1648	29	3.93	0.13
12.10	500	1649	31	3.92	0.12
12.00	500	1654	31	3.94	0.12
11.90	500	1658	30	3.95	0.13
11.80	500	1655	30	3.96	0.12
11.70	500	1653	31	3.95	0.13
11.60	500	1658	42	3.94	0.22
11.50	500	1659	31	3.96	0.13
11.40	500	1660	31	3.98	0.12
11.30	500	1655	43	3.96	0.22
11.20	500	1664	32	3.97	0.13
11.10	500	1661	32	3.98	0.13
11.00	500	1658	32	3.98	0.13
10.90	500	1663	31	3.96	0.12
10.80	500	1660	31	3.97	0.13
10.70	500	1664	32	3.97	0.12
10.60	500	1661	43	3.95	0.22
10.50	500	1664	32	3.97	0.13
10.40	500	1668	33	3.98	0.13
10.30	500	1668	33	4	0.13

10.20	500	1643	30	3.83	0.13
10.10	500	1652	32	3.79	0.13
10.00	500	1660	31	3.82	0.14
9.90	500	1671	34	3.86	0.14
9.80	500	1675	32	3.85	0.14
9.70	500	1677	33	3.85	0.14
9.60	500	1686	34	3.86	0.14
9.50	500	1687	31	3.88	0.14
9.40	500	1700	40	3.89	0.15
9.30	500	1694	32	3.87	0.15

Table S3: Experimental conditions for HRRST/TOF-MS for nominal reaction conditions 1481 K and 3.7 bar. T_5 and P_5 represent the average reflected shock conditions at each photon energy and σ the corresponding standard deviations.

hv [eV]	Num of shocks	T_5 (K)	σ_{T5} [K]	P_5 [bar]	σ_{P5} [bar]
12.80	500	1470	38	3.59	0.16
12.7	500	1473	38	3.6	0.18
12.6	500	1473	38	3.58	0.18
12.5	500	1462	38	3.66	0.19
12.4	500	1471	37	3.68	0.19
12.3	500	1473	37	3.67	0.19
12.2	500	1478	40	3.65	0.19
12.1	500	1478	38	3.63	0.26
12	500	1486	38	3.64	0.19
11.9	500	1484	35	3.68	0.19
11.8	500	1481	37	3.76	0.18
11.7	500	1476	35	3.71	0.18
11.6	500	1490	34	3.74	0.17
11.5	500	1488	33	3.7	0.18
11.4	500	1484	37	3.67	0.17
11.3	500	1482	35	3.66	0.19
11.2	500	1478	37	3.74	0.19
11.1	500	1481	33	3.71	0.17
11	500	1481	34	3.67	0.17
10.9	500	1483	36	3.66	0.18
10.8	500	1484	36	3.65	0.18
10.7	500	1486	35	3.65	0.18
10.6	500	1487	37	3.65	0.18
10.5	500	1477	37	3.69	0.19
10.4	500	1481	36	3.71	0.17
10.3	500	1490	32	3.73	0.17

10.2	500	1483	34	3.67	0.16
10.1	500	1487	34	3.68	0.17
10	500	1486	36	3.66	0.18
9.9	500	1491	33	3.68	0.18
9.8	500	1483	33	3.75	0.17
9.7	500	1477	37	3.7	0.18
9.6	500	1480	34	3.72	0.18
9.5	500	1483	36	3.71	0.19

Table S4: List of observed m/z values from mass spectrometric measurements of *iso*-propanol pyrolysis along with corresponding species names, chemical formulae, and ionization energies. Structural formulae are provided for selected species (Ethenol, 1-hydroxyethyl radical, diacetylene, vinylacetylene, and 1,3,5-hexatriyne) to assist in identification.

m/z	Species	Chemical Formula	Ionization Energy (eV)
18	Water	H_2O	12.62
26	Acetylene	C_2H_2	11.4
28	Ethylene	C_2H_4	10.51
30	Ethane	C_2H_6	11.52
32	Oxygen	O_2	12.07
40	Propyne	C_3H_4	10.36
42	Propene	C_3H_6	9.73
44	Acetaldehyde	CH_3CHO	10.23
44	Ethenol	C_2H_3OH $H_2C{=}CH\text{-}OH$	9.33
45	1-Hydroxyethyl radical	sC_2H_4OH $H_3C\text{-}CH\text{-}OH$	6.85
50	Diacetylene	C_4H_2 $HC{\equiv}C\text{-}C{\equiv}CH$	10.17
52	Vinylacetylene	C_4H_4 $H_2C{=}CH\text{-}C{\equiv}CH$	9.58
58	Acetone	CH_3COCH_3	9.7
60	*iso*-propanol	iC_3H_7OH	10.17
74	1,3,5-Hexatriyne	C_6H_2 $HC{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}CH$	9.5

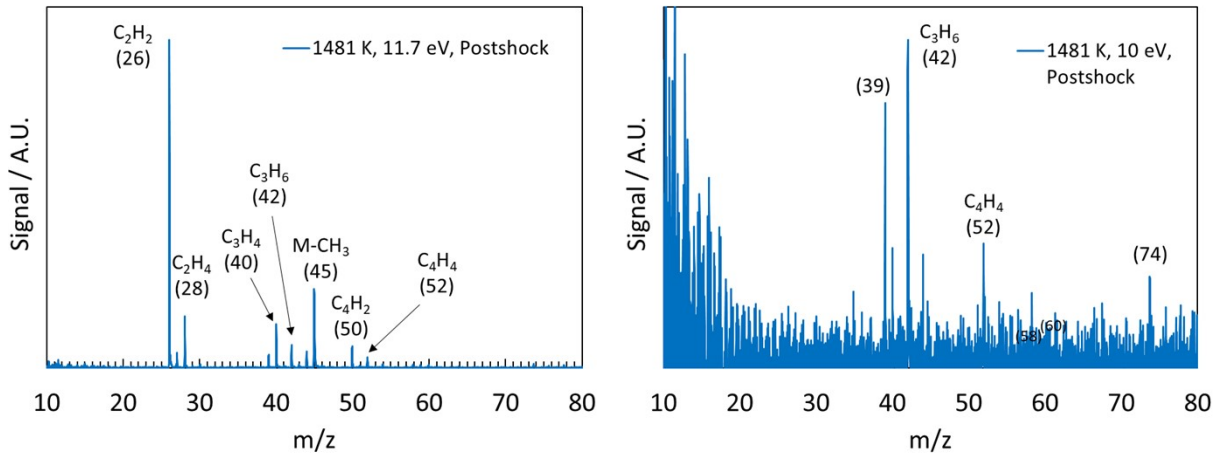


Figure S1: Mass spectra at T_5 = 1481 K and P_5 = 3.7 bar integrated over the first 500 µs of reaction in the post-shock region with photon energy of 11.7 eV and 10 eV.

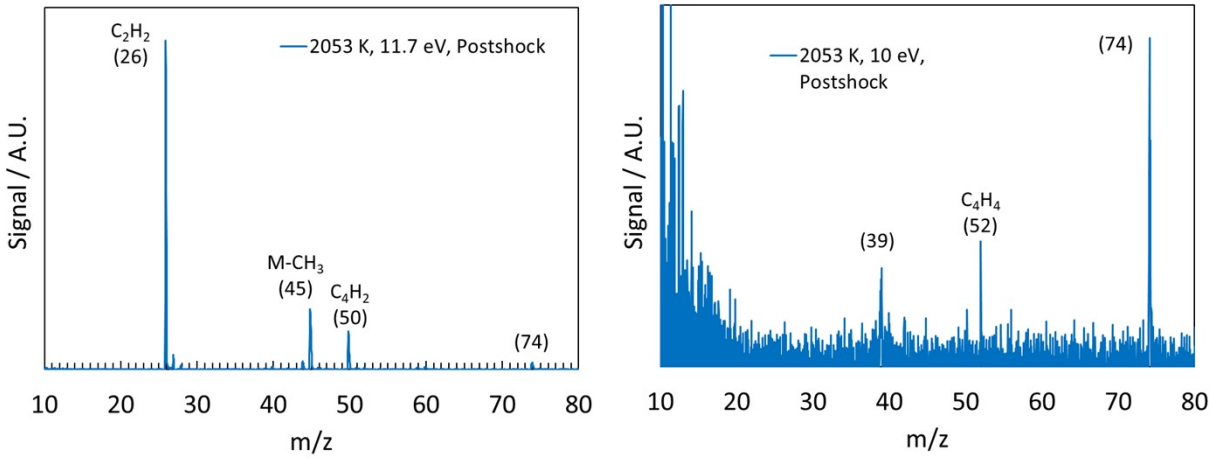


Figure S2: Mass spectra at T_5 = 2053 K and P_5 = 4.4 bar integrated over the first 500 µs of reaction in the post-shock region with photon energy of 11.7 eV and 10 eV.

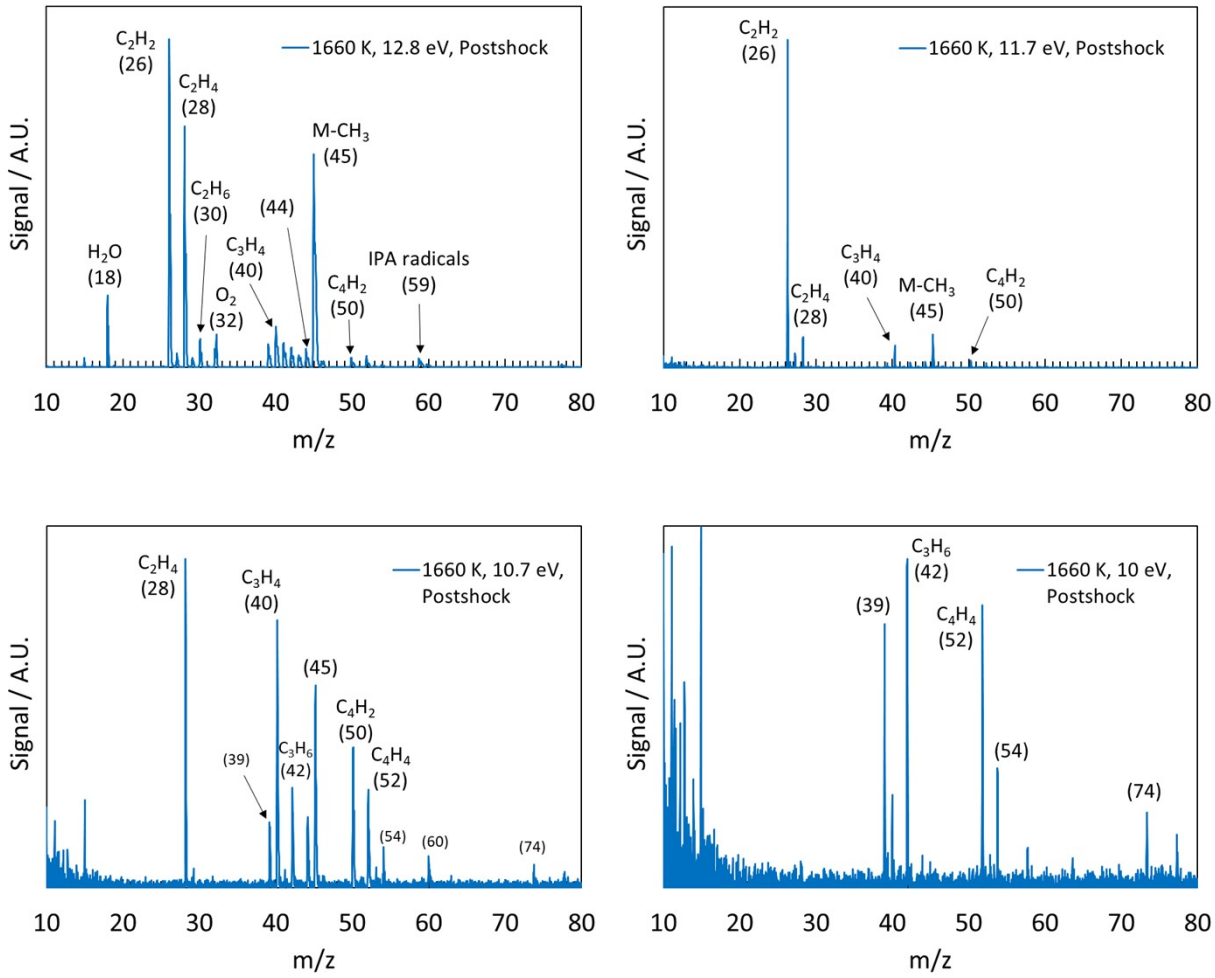


Figure S3: Mass spectra at T_5 = 1660 K and P_5 = 3.9 bar integrated over the first 500 µs of reaction in the post-shock region with photon energy of 12.8 eV, 11.7 eV, 10.7 eV, and 10 eV.

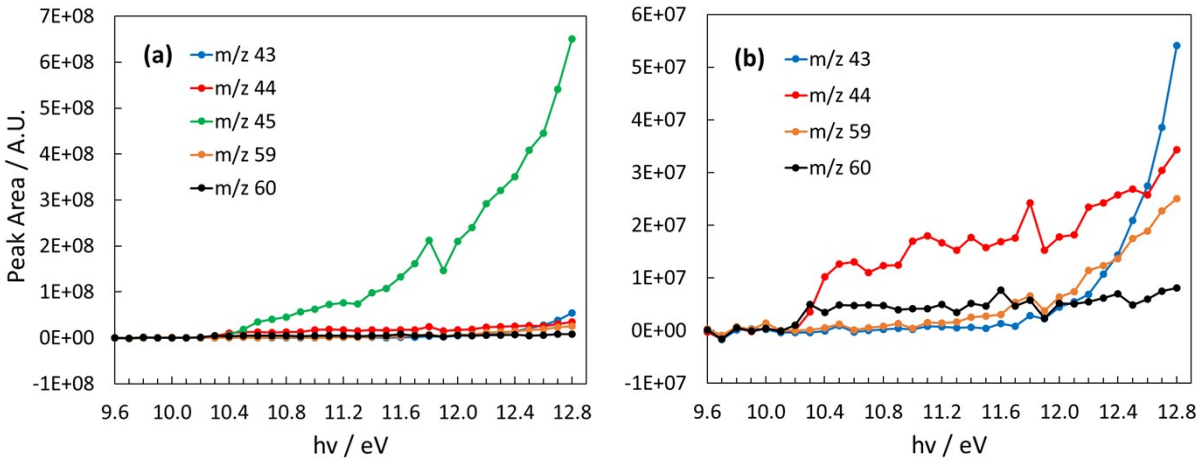
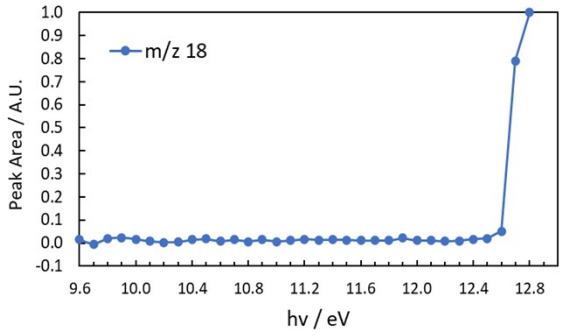
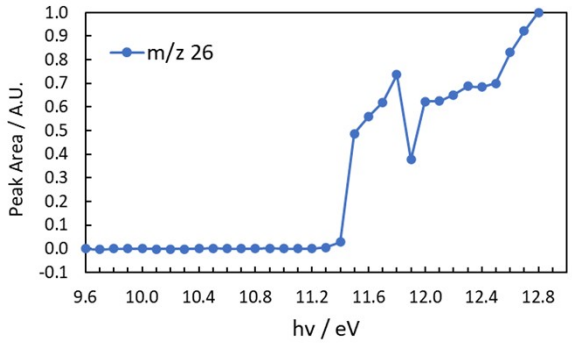
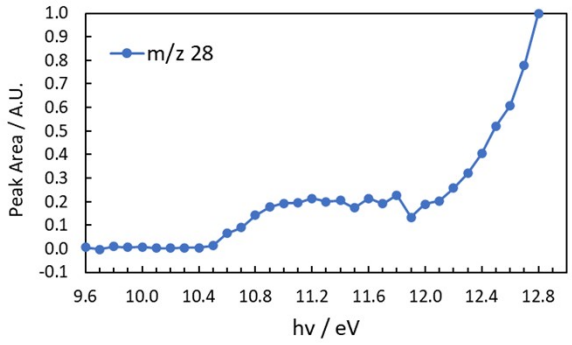


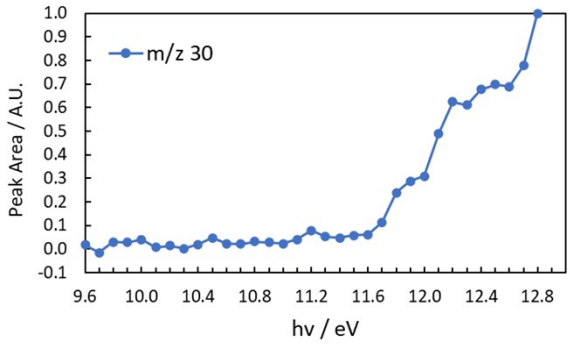
Figure S4: (a) Photoionization spectra of non-reacting *iso*-propanol and *iso*-propanol dissociative ionization products without normalization. (b) Same spectra as in (a), excluding m/z =45 for clearer comparison of the minor species.

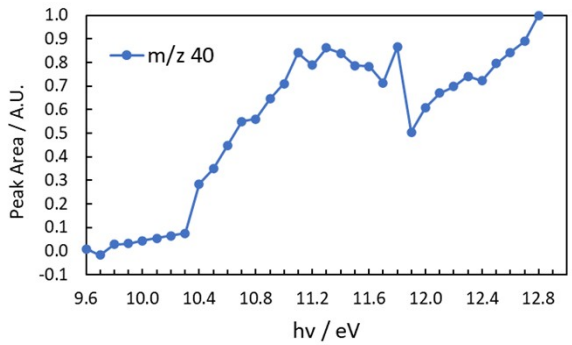
In Figs. S5-S7 the photoionization spectra from the three sets of mass spectra are shown.

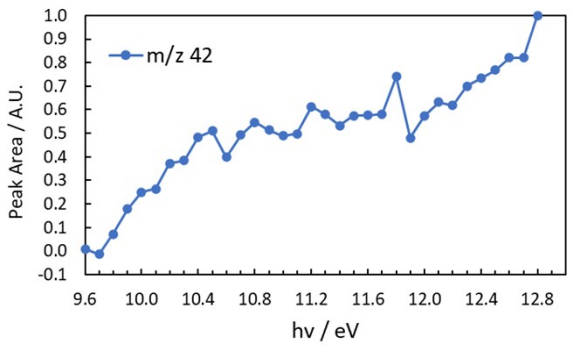


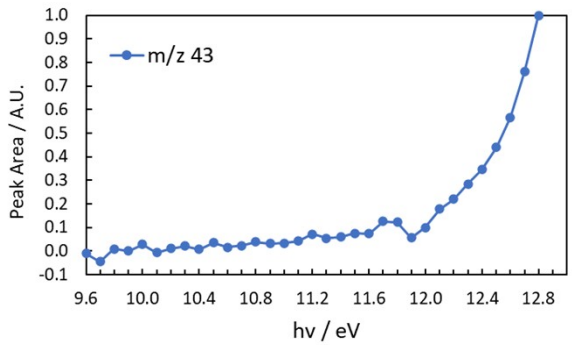


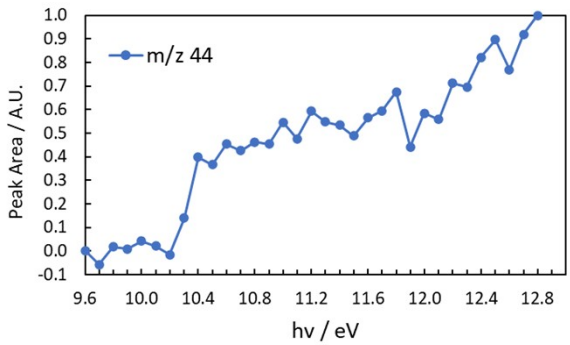












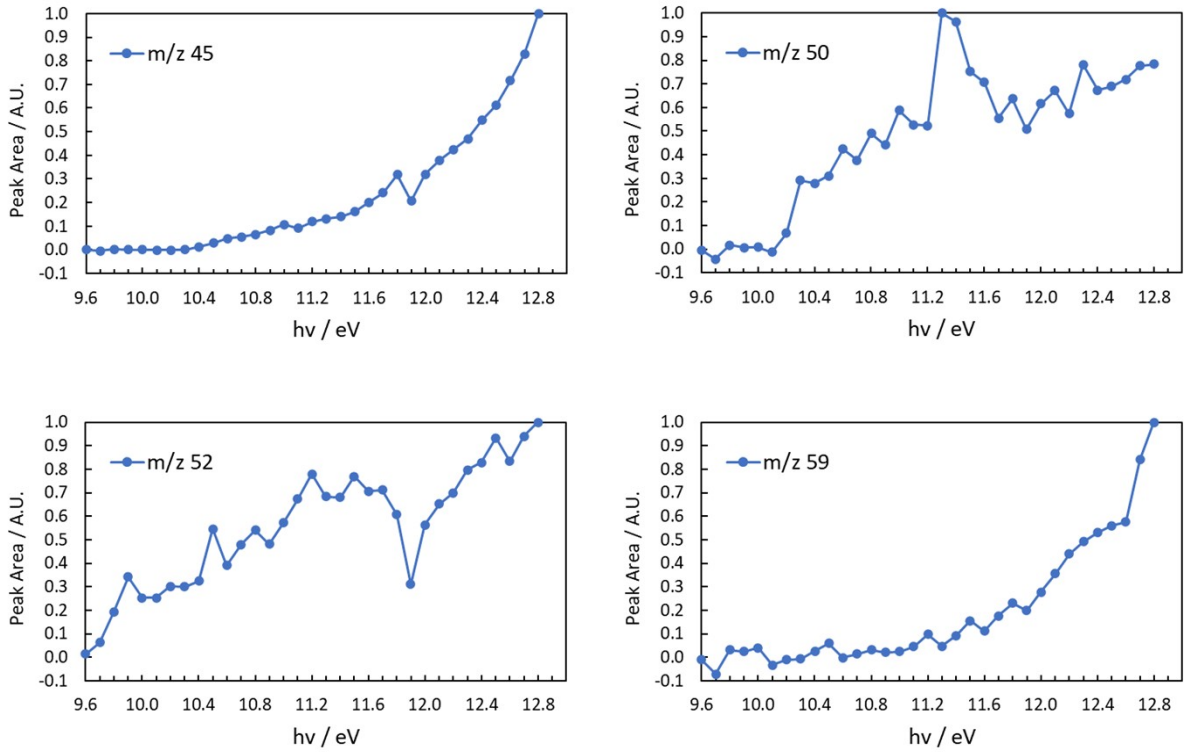
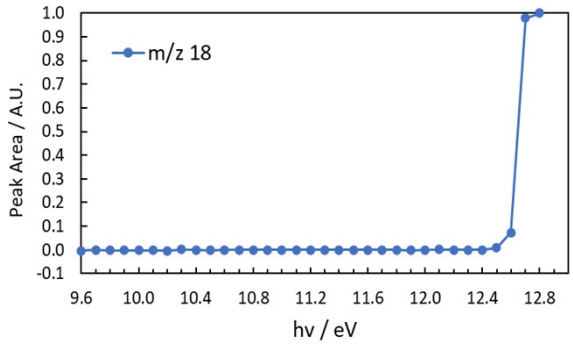


Figure S5: Photoionization spectrum of m/z 18, 26, 28, 30, 40, 42, 43, 44, 45, 50, 52, and 59 at T_5 = 1481 K in the post-shock region.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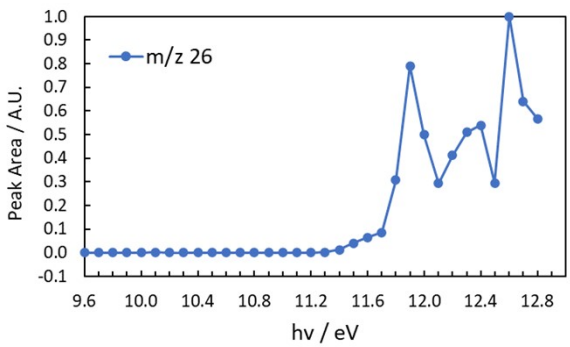
Peak Area / A.U.
hv / eV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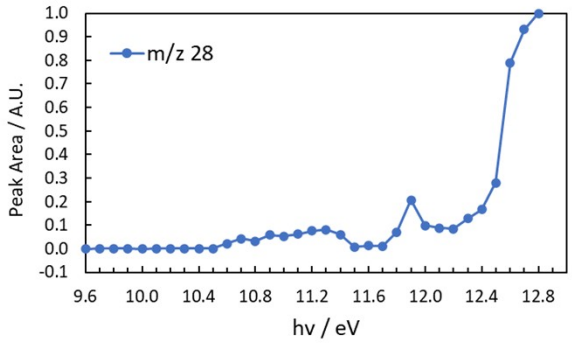
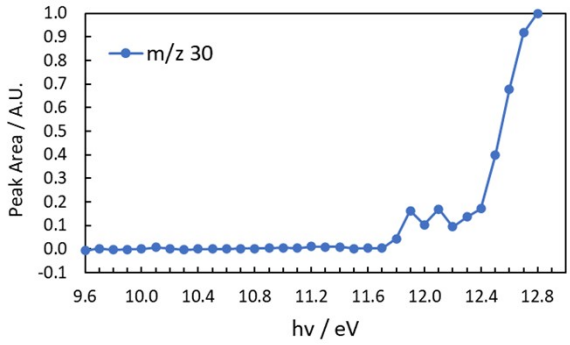
Peak Area / A.U.
hv / eV


m/z 28
Peak Area / A.U.
hv / eV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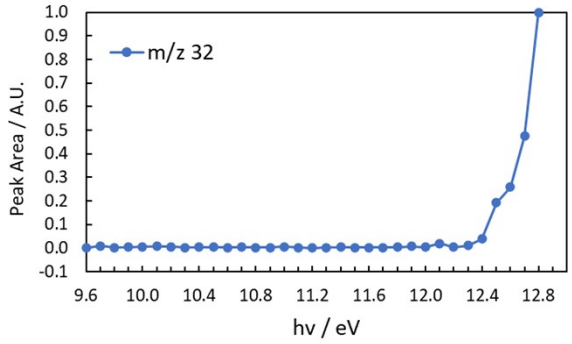
Peak Area / A.U.
hv / eV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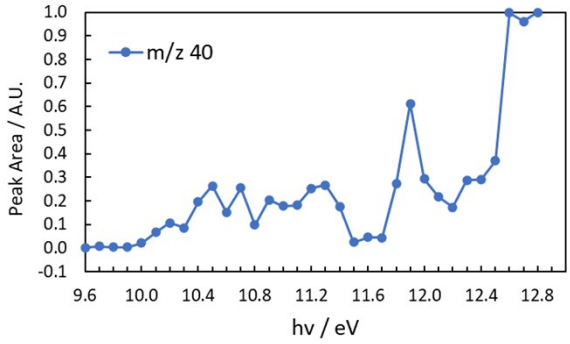
Peak Area / A.U.
hv / eV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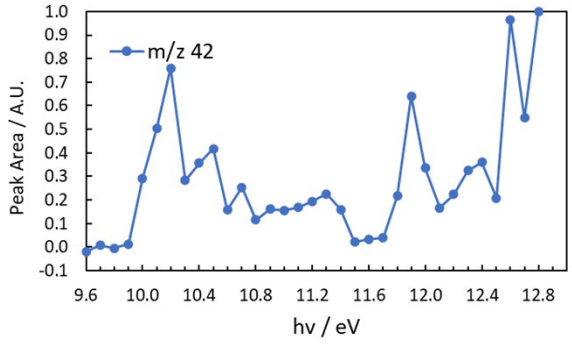
hv / eV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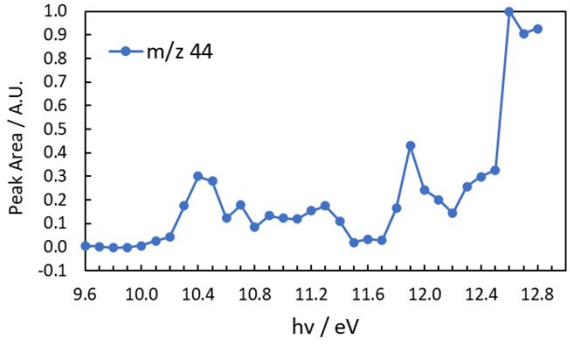
hv / eV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hv / eV

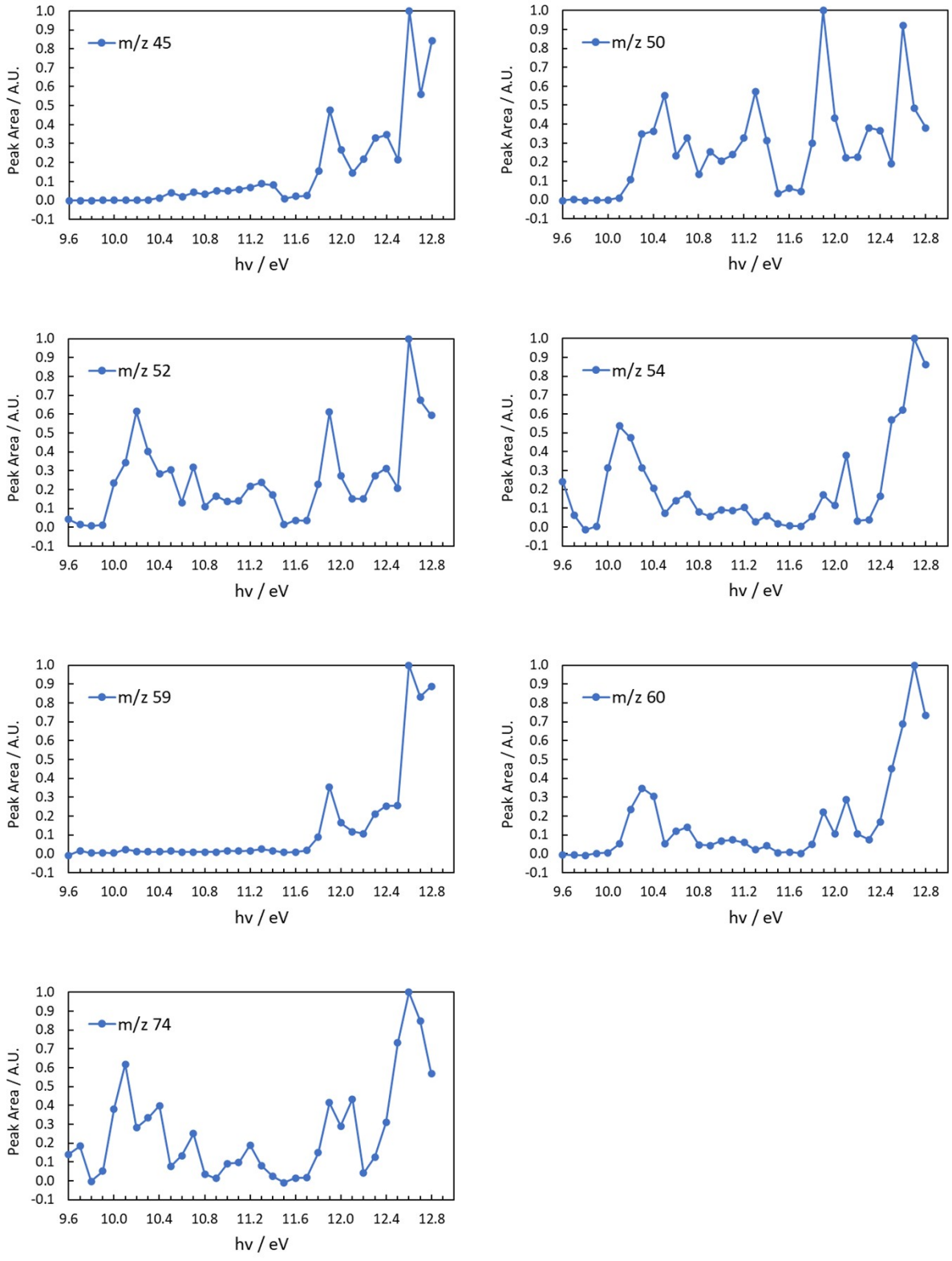
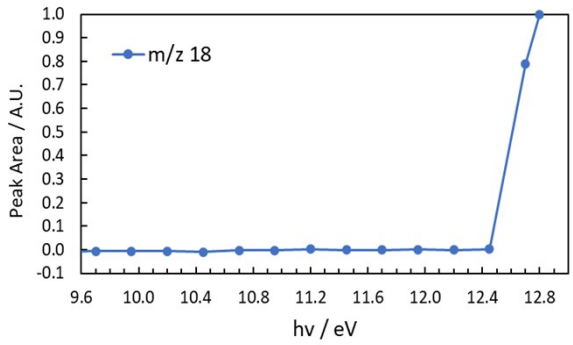


Figure S6: Photoionization spectrum of m/z 18, 26, 28, 30, 32, 40, 42, 44, 45, 50, 52, 54, 59, 60, 74 at T_5 = 1660 K in the post-shock region.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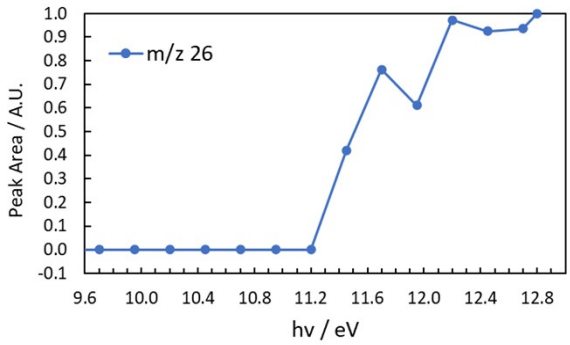
Peak Area / A.U.
hv / eV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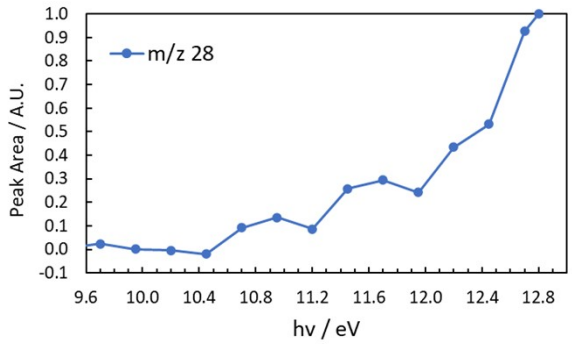
hv / eV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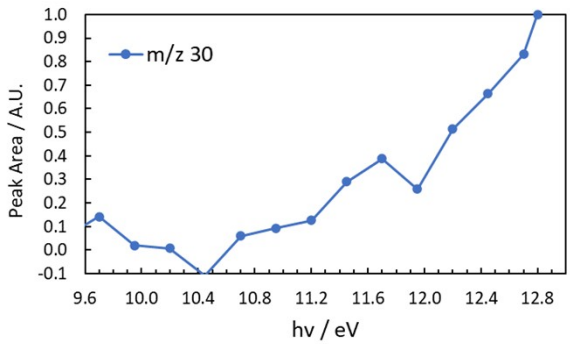
Peak Area / A.U.
hv / eV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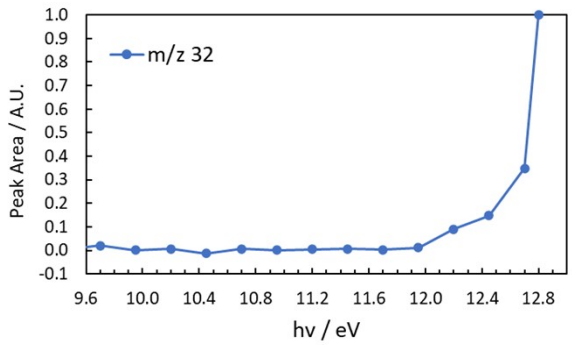
Peak Area / A.U.
hv / eV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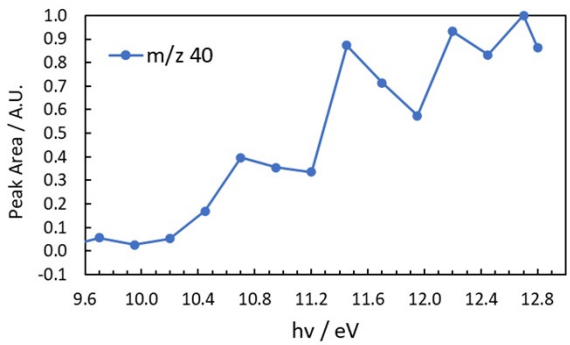
Peak Area / A.U.
hv / eV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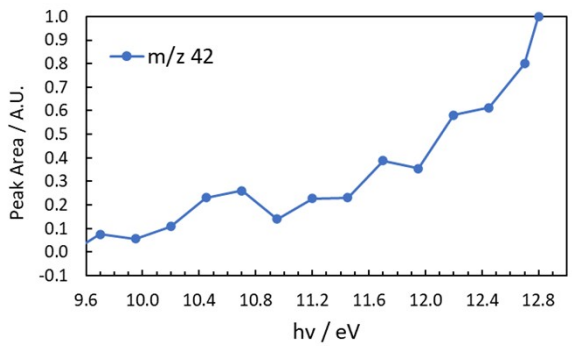
hv / eV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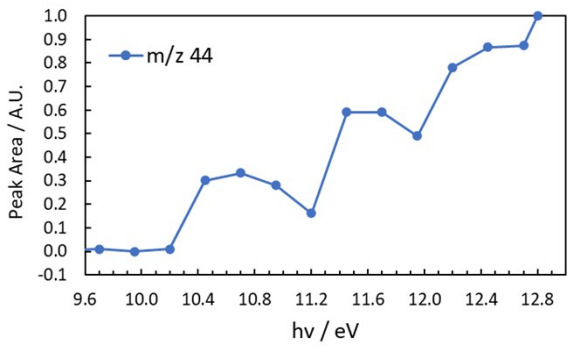
Peak Area / A.U.
hv / eV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hv / eV

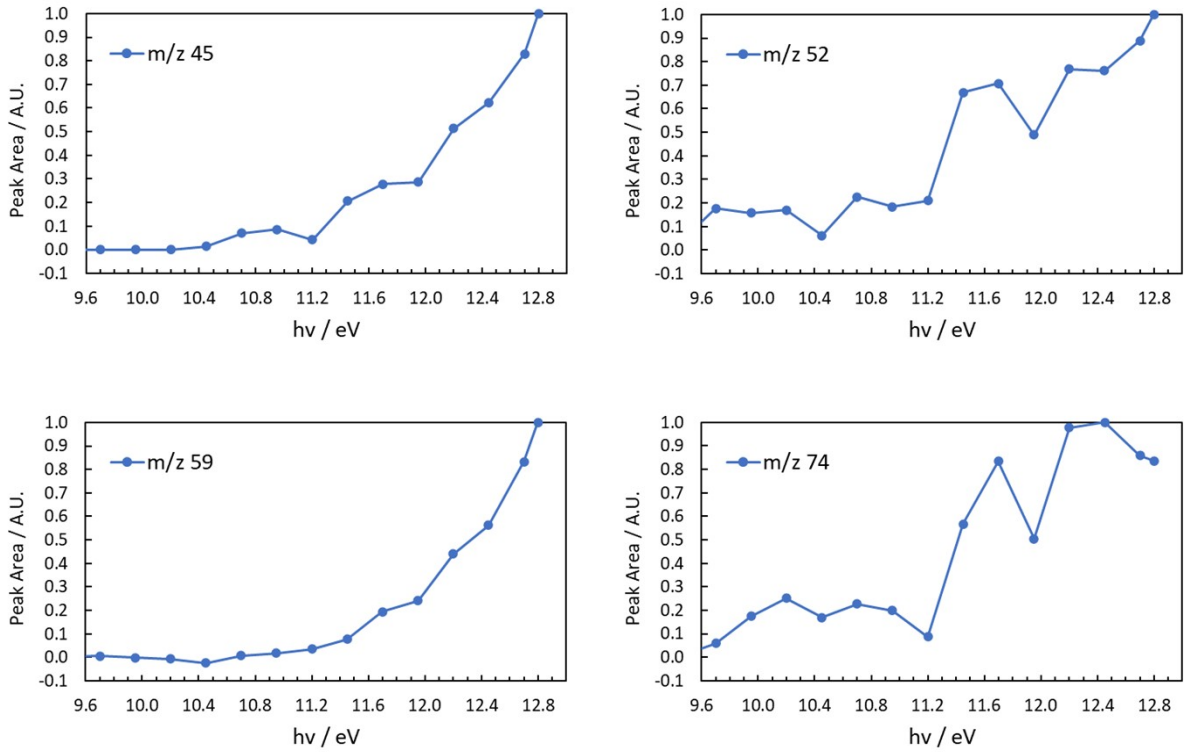

Figure S7: Photoionization spectrum of m/z 18, 26, 28, 30, 32, 40, 42, 44, 45, 52, 59, 74 at T_5 = 2053 K in the post-shock region.