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

Supporting Information:

Unimolecular Decomposition of Methylketene and its Dimer in the Gas Phase: Theory and Experiment

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Table S1: Optimized geometries of MKE_2 and its cation MKE_2^+ and there calculated adiabatic ionization energies obtained at the PBE0/aug-cc-pVTZ and at the wB97XD/aug-cc-pVTZ levels of theory.

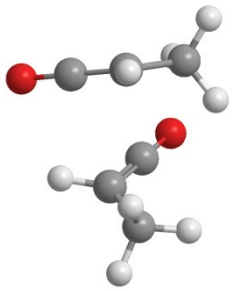
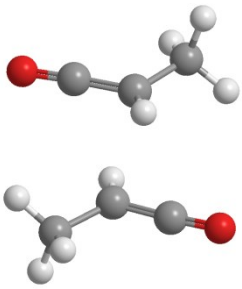
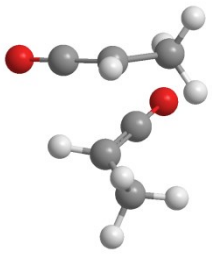
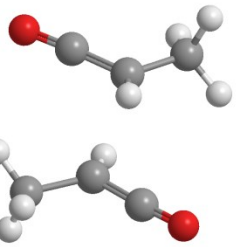
	MKE_2	MKE_2^+	Adiabatic ionization energies
PBE0/aug-cc-pVTZ			7.87
wB97XD/aug-cc-pVTZ			7.99

Table S2: Cartesian coordinates of neutral MKE_2, ionized MKE_2 as obtained after geometry optimizations at the PBE0/aug-cc-pVTZ and wB97XD/aug-cc-pVTZ levels of theory.

	MKE_2				MKE_2^+			
PBE0/aug-cc-pVTZ	C	1.226164	-1.021245	1.541321	C	0.977419	2.077796	-0.086779
	C	1.379187	-0.885781	0.053309	C	1.021153	0.724703	0.550486
	C	1.956057	0.136636	-0.519617	C	1.821348	-0.254862	0.100618
	O	2.461352	1.052823	-1.025248	O	2.451172	-1.113366	-0.305871
	H	1.690279	-1.942428	1.899641	C	-1.787814	0.252600	-0.214863
	H	0.169945	-1.041700	1.820752	C	-1.009754	-0.806921	-0.483437
	H	1.695335	-0.188396	2.064910	C	-1.047450	-2.059986	0.335140
	H	0.988196	-1.640896	-0.617997	O	-2.405943	1.177502	0.034405
	C	-1.942512	-0.441413	-0.411432	H	1.635218	2.759719	0.460718
	C	-2.060343	0.514606	0.472061	H	-0.030338	2.493163	-0.023109
	C	-1.183228	1.732987	0.504541	H	1.294302	2.057840	-1.127879
	O	-1.846071	-1.294921	-1.193611	H	0.665659	0.575230	1.566211
	H	-2.852930	0.377684	1.198056	H	-1.713330	-2.786879	-0.139565
	H	-1.782238	2.644235	0.447799	H	-0.056538	-2.515626	0.371130
	H	-0.598577	1.773249	1.426966	H	-1.400381	-1.883355	1.349477
	H	-0.484213	1.740302	-0.330349	H	-0.605834	-0.813156	-1.492253
wB97XD/aug-cc-pVTZ	C	1.135395	-0.548302	1.749262	C	0.810539	2.101735	0.004879
	C	1.349763	-0.838812	0.286575	C	0.955940	0.715924	0.566040
	C	2.003009	-0.041472	-0.515089	C	1.841254	-0.163186	0.065375
	O	2.577788	0.674189	-1.225050	O	2.538547	-0.938106	-0.388817
	H	1.524292	-1.357987	2.366655	C	-1.801915	0.155262	-0.255232
	H	0.071651	-0.435004	1.963943	C	-0.919245	-0.836496	-0.457950
	H	1.638947	0.369426	2.048213	C	-0.900762	-2.069501	0.401943
	H	0.943189	-1.732277	-0.166549	O	-2.500392	1.029989	-0.052866
	C	-1.965914	-0.501773	-0.353814	H	1.462064	2.786882	0.549741
	C	-2.071985	0.610651	0.323039	H	-0.211168	2.451937	0.144753
	C	-1.144098	1.784326	0.150224	H	1.064251	2.148081	-1.051178
	O	-1.880192	-1.492262	-0.951858	H	0.639196	0.493495	1.578466
	H	-2.882798	0.644186	1.037588	H	-1.493299	-2.854702	-0.069664
	H	-1.702808	2.685449	-0.102847	H	0.117371	-2.445929	0.492121
	H	-0.589054	1.979377	1.069117	H	-1.301515	-1.883443	1.395056
	H	-0.421209	1.603702	-0.642029	H	-0.497017	-0.853808	-1.456159

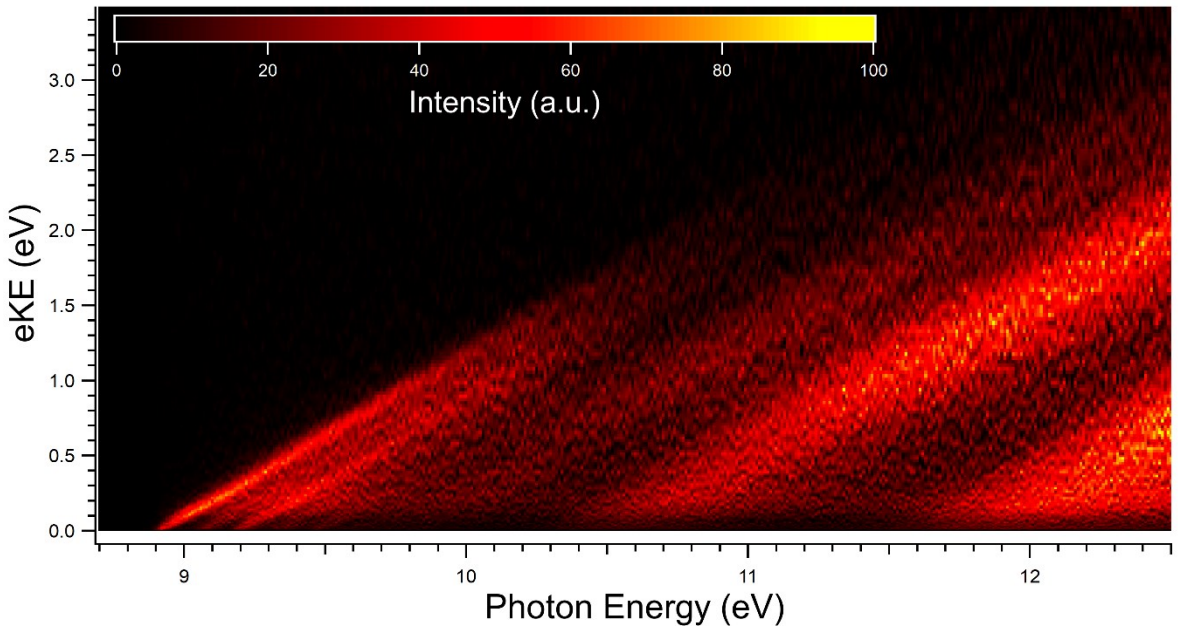


Figure S1. 2D-PES matrix of the *m/z* 56 mass signals.

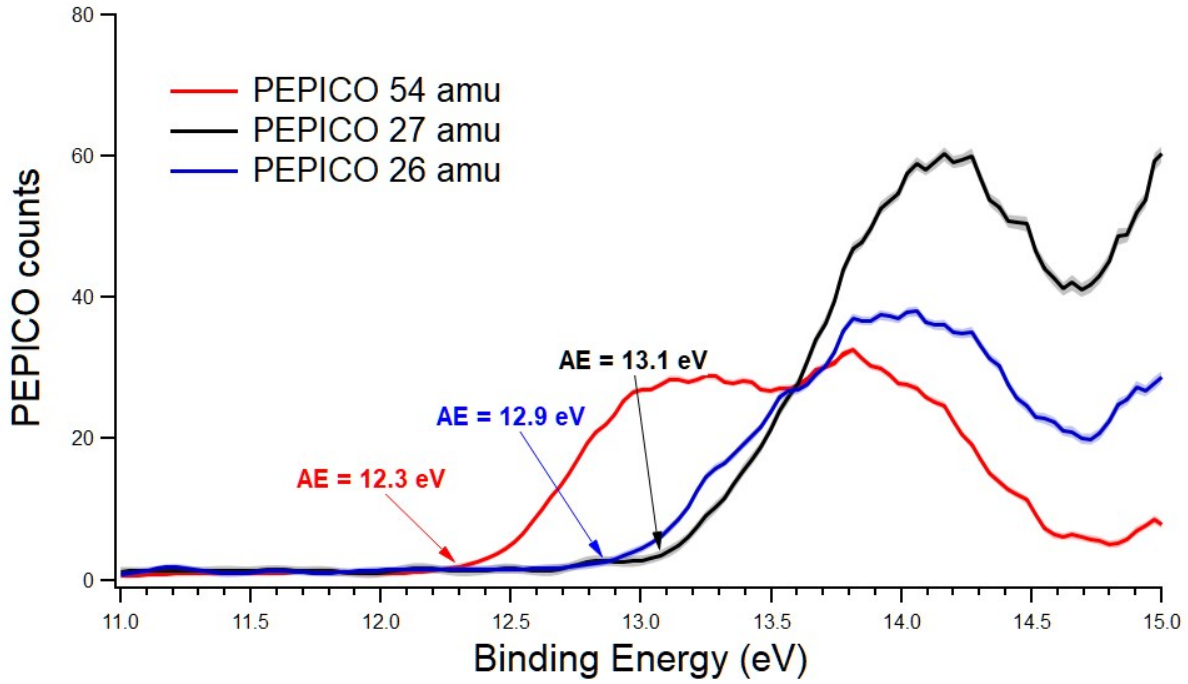


Figure S2. Mass selected PEPICO spectra obtained at 15.5 eV for *m/z* 54 (red), *m/z* 27 (black) and *m/z* 26 (blue). The appearance energies are derived as the first point where the signal increases above the background. This method is less accurate than using recorded SPES and hence we give an estimated error of 0.1 eV for the derived appearance energies.

Table S3: Cartesian coordinates of neutral MKE, ionized MKE and its fragments as obtained after geometry optimizations at the CCSD (T)-F12/cc-pVTZ-F12 level of theory.

	C_3H_4O				$C_3H_4O^+$		
C	-1.6835996785	-0.3306593240	-0.0000180628	C	-1.6771932832	-0.3442653468	0.0001182243
C	-0.4813060320	0.5822873294	0.0000257105	C	-0.5220531179	0.5837508947	0.0001138047
C	0.7526353148	0.1262125525	-0.0000361211	C	0.7844428304	0.1168639687	-0.0000887145
O	1.8448718328	-0.2845982987	-0.0001070977	O	1.8422077592	-0.2765816933	-0.0002865560
H	-2.3008893352	-0.1618850329	-0.8831006750	H	-2.2949103857	-0.1216438613	-0.8769343890
H	-2.3007023705	-0.1622351975	0.8832630473	H	-2.2939505177	-0.1227565128	0.8781521156
H	-1.3780280750	-1.3763389699	-0.0002606010	H	-1.3866719594	-1.3908983926	-0.0006637606
	$C_3H_3O^+$						
C	-1.3415905194	-0.4160344059	0.4546761816		$C_2H_3^+$		
C	-0.3239588476	0.4688524157	0.4505025777	C	-0.6125918687	-0.0772930734	-0.0000449781
C	0.9879869372	-0.0417745839	0.4446716469	C	0.6126722375	-0.0773587446	-0.0001313718
O	2.0333603206	-0.4481189207	0.4390378199	H	-1.6903309849	-0.0709653605	-0.0005232490
H	-2.3608732403	-0.0518705411	0.4591216137	H	1.6904116286	-0.0706727247	0.0002868030
H	-1.1778296628	-1.4865868159	0.4529499665	H	-0.0001340124	1.0473079032	-0.0000032041
H	-0.4130949877	1.5485328517	0.4520401936				
	$C_3H_2O^+$				$C_2H_4^+\_1$		
C	0.5117570972	-0.6259750498	0.0000000000	C	0.7253572054	-0.1328836903	-0.0942607431
C	0.0021893679	0.6681399976	0.0000000000	C	-0.6153527566	0.0422801726	-0.0589134432
O	-0.2023064021	-1.6349797642	0.0000000000	H	1.6132516684	0.4859531528	-0.0112312927
C	-0.3875368200	1.8169295191	0.0000000000	H	-1.2888589146	-0.8072373213	-0.1677649898
H	1.5977951174	-0.8459258166	0.0000000000	H	0.0587060314	-0.2295186937	1.0330641262
H	-0.7387433603	2.8298761139	0.0000000000	H	-1.0435072340	1.0435123799	0.0504473426
	C_2OH				C_2OH^+		
C	-0.9908396727	-0.0548506181	0.0000000000	C	-1.1153716462	-0.1226308642	0.0000000000
C	0.2402905378	-0.4825619496	0.0000000000	C	0.2673755009	-0.4811108247	0.0000000000
O	1.2518511619	-1.0721840225	0.0000000000	O	1.2539508361	-1.0307821896	0.0000000000
H	-1.4113020268	0.9325965901	0.0000000000	H	-1.3159546907	0.9575238785	0.0000000000
	HCO^+				CH_2O^+		
C	0.0000000000	0.0000000000	-0.5172798898	C	-0.0000035186	-0.5313459258	-0.0000000002
O	0.0000000000	0.0000000000	0.5905155470	O	0.0000075170	0.6626776664	-0.0000000004
H	0.0000000000	0.0000000000	-1.6108956572	H	-0.0000319992	-1.0779518700	-0.9705085941
				H	-0.0000319992	-1.0779518705	0.9705085942
	C_2H_4				$C_2H_4^+$		
C	0.6668209247	-0.0000184102	0.0002794630	C	0.7012972277	-0.0000206895	0.0001142941
C	-0.6668205986	0.0000274047	0.0002816600	C	-0.7012969173	0.0000258878	0.0001102854
H	1.2309854972	-0.9236495911	0.0005519684	H	1.2540868174	-0.9208237665	-0.1608712191
H	1.2310486376	0.9235742781	0.0005441274	H	1.2540228220	0.9206519565	0.1621335332
H	-1.2309851471	0.9236585929	0.0005803085	H	-1.2540869497	0.9208345838	-0.1608408218
H	-1.2310483137	-0.9235652744	0.0005734728	H	-1.2540220000	-0.9206409720	0.1621649282

CO			
C	0.0000000000	0.0000000000	-0.6465754168
O	0.0000000000	0.0000000000	0.4840774168

CO^+			
C	0.0000000000	0.0000000000	-0.6380070863
O	0.0000000000	0.0000000000	0.4788530863

C_2H_3			
C	-0.7105978953	-0.1520528045	-0.0001448734
C	0.5897028040	0.0273704924	-0.0000676627
H	-1.5921428740	0.4693229862	0.0000263161
H	1.0214515636	1.0279432494	0.0000225666
H	1.2842164018	-0.8052729235	0.0000456534

$C_2H_2^+$			
C	0.0000000000	0.0000000000	0.6250554878
C	0.0000000000	0.0000000000	-0.6250554878
H	0.0000000000	0.0000000000	1.7037339807
H	0.0000000000	0.0000000000	-1.7037339807

$C_2H_2^+$			
C	0.0000000000	0.0000000000	0.6027520933
C	0.0000000000	0.0000000000	-0.6027520933
H	0.0000000000	0.0000000000	1.6658833002
H	0.0000000000	0.0000000000	-1.6658833002

Table S4: Cartesian coordinates of neutral MKE_2, ionized MKE_2 and its fragments as obtained after geometry optimizations at the PBE0/aug-cc-pVTZ level of theory.

$(C_3H_4O)_2$				$(C_3H_4O)_2^+$			
C	1.226164	-1.021245	1.541321	C	0.977419	2.077796	-0.086779
C	1.379187	-0.885781	0.053309	C	1.021153	0.724703	0.550486
C	1.956057	0.136636	-0.519617	C	1.821348	-0.254862	0.100618
O	2.461352	1.052823	-1.025248	O	2.451172	-1.113366	-0.305871
H	1.690279	-1.942428	1.899641	C	-1.787814	0.252600	-0.214863
H	0.169945	-1.041700	1.820752	C	-1.009754	-0.806921	-0.483437
H	1.695335	-0.188396	2.064910	C	-1.047450	-2.059986	0.335140
H	0.988196	-1.640896	-0.617997	O	-2.405943	1.177502	0.034405
C	-1.942512	-0.441413	-0.411432	H	1.635218	2.759719	0.460718
C	-2.060343	0.514606	0.472061	H	-0.030338	2.493163	-0.023109
C	-1.183228	1.732987	0.504541	H	1.294302	2.057840	-1.127879
O	-1.846071	-1.294921	-1.193611	H	0.665659	0.575230	1.566211
H	-2.852930	0.377684	1.198056	H	-1.713330	-2.786879	-0.139565
H	-1.782238	2.644235	0.447799	H	-0.056538	-2.515626	0.371130
H	-0.598577	1.773249	1.426966	H	-1.400381	-1.883355	1.349477
H	-0.484213	1.740302	-0.330349	H	-0.605834	-0.813156	-1.492253
$C_3H_5O^+$				$C_3H_5O^+\_1$			
C	0.797992	0.133284	-0.000011	C	-0.898812	0.798235	0.000000
O	1.817881	-0.313257	0.000005	C	-0.934549	-0.761771	0.000000
C	-0.521914	0.663523	-0.000002	C	0.271325	-0.016567	0.000000
C	-1.581030	-0.460909	-0.000001	O	1.516343	-0.119357	0.000000
H	-0.583664	1.308666	0.888099	H	-1.155901	1.326192	0.916000
H	-0.583680	1.308672	-0.888074	H	-1.155901	1.326192	-0.916000
H	-1.496720	-1.078661	0.891699	H	-1.215462	-1.277818	-0.916000
H	-1.496770	-1.078613	-0.891737	H	-1.216462	-1.277818	0.916000
H	-2.552506	0.030602	0.000058	H	1.985198	0.738722	0.000000
$C_3H_5O^+\_2$				C_3H_5O			
C	-1.778340	0.135117	-0.000212	C	-1.867472	-0.161956	0.015726
C	-0.443592	-0.440572	0.000258	C	-0.486950	0.400861	-0.040666
C	0.729027	0.348201	0.000652	C	0.613046	-0.318578	-0.015841
O	1.879659	-0.113156	-0.000377	O	1.887098	0.043628	0.100548
H	-2.333126	-0.255026	-0.866791	H	-2.410638	0.218223	0.885335
H	-1.803254	1.222195	-0.000359	H	-1.844363	-1.249705	0.078969
H	-2.333521	-0.254754	0.866249	H	-2.445245	0.117654	-0.869391
H	-0.301151	-1.517590	0.000132	H	-0.372638	1.483622	-0.121101
H	0.691216	1.453947	-0.000402	H	2.424361	-0.440783	-0.533509
$C_3H_3O^+$				C_3H_3O			
C	1.606482	-0.382833	0.000008	C	1.699290	-0.348240	0.000002
C	0.629816	0.540848	-0.000003	C	0.578726	0.498553	0.000004
C	-0.693217	0.114470	0.000049	C	-0.696475	0.106171	0.000001

O	-1.760653	-0.217468	-0.000025	O	-1.808365	-0.222249	-0.000004
H	2.643132	-0.064385	-0.000057	H	2.687230	0.083594	-0.000060
H	1.403453	-1.448006	-0.000018	H	1.596732	-1.422646	0.000031
H	0.780158	1.617230	-0.000049	H	0.693708	1.578147	0.000021
	C_3H_6O				$C_3H_6O^+$		
C	-1.881030	0.113698	0.000050	C	1.858067	0.123779	0.000119
C	-0.491300	-0.425176	-0.000070	C	0.509909	-0.415674	-0.000099
C	0.589636	0.341352	-0.000087	C	-0.639603	0.382096	0.000085
O	1.851384	-0.175527	0.000065	O	-1.790249	-0.198645	0.000092
H	-2.440841	-0.220867	0.878470	H	2.408912	-0.279268	0.862976
H	-2.441267	-0.221703	-0.877771	H	1.906747	1.210432	0.000741
H	-1.884942	1.205699	-0.000469	H	2.408484	-0.277785	-0.863805
H	-0.355899	-1.502765	-0.000088	H	0.355103	-1.492168	-0.000463
H	0.518926	1.426584	-0.000087	H	-0.587208	1.469293	-0.000550
H	2.489115	0.538024	0.000068	H	-2.540281	0.417441	-0.000269
	C_3H_2O				$C_3H_2O^+$		
C	0.910473	1.581763	0.000000	C	0.498476	-0.621087	0.000000
C	0.000000	0.629043	0.000000	C	0.000000	0.665929	0.000000
C	-0.313538	-0.622530	0.000000	O	-0.195748	-1.640484	0.000000
O	-0.774037	-1.691621	0.000000	C	-0.381378	1.810136	0.000000
H	0.631735	2.632816	0.000000	H	1.590817	-0.832481	0.000000
H	1.978947	1.370499	0.000000	H	-0.727424	2.826482	0.000000
	$C_2H_3^+$				$C_2H_2^+$		
C	-0.609103	-0.075078	-0.000001	C	0.000000	0.000000	0.627339
C	0.609114	-0.075097	0.000005	C	0.000000	0.000000	-0.627339
H	-1.688902	-0.075838	-0.000007	H	0.000000	0.000000	1.714910
H	1.688914	-0.075745	-0.000020	H	0.000000	0.000000	-1.714910
H	-0.000078	1.052636	0.000000				

Table S5. Cartesian coordinates of the $C_3H_4O^+$ isomers, other than MKE as obtained after geometry optimizations at the PBE0/aug-cc-pVTZ level of theory.

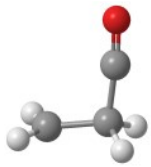
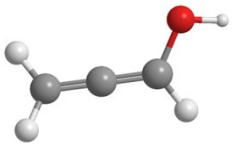
							
$CH_2CH_2CO^+$				$CH_2=C=CHOH^+$			
C	1.519231	-0.525248	-0.000002	C	1.923149	-0.192517	-0.000027
C	0.630976	0.683200	0.000039	C	0.647653	0.164274	-0.010207
C	-0.712120	0.169620	0.000082	C	-0.630969	0.513486	-0.022992
O	-1.709459	-0.330001	-0.000094	O	-1.641188	-0.468243	0.062419
H	1.793271	-0.978910	-0.941473	H	2.701527	0.514552	0.390421
H	1.792279	-0.979593	0.941440	H	2.221900	-1.213532	-0.356764
H	0.730732	1.316554	0.892403	H	-0.911580	1.585274	-0.205512
H	0.730872	1.316525	-0.892335	H	-2.521340	-0.051804	-0.128137

Table S6. Details on the calculations from Table 3 (energies in Hartree). ΔZPE is evaluated at the PBE0/aVTZ level using the corresponding anharmonic frequencies.

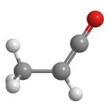
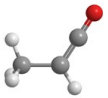
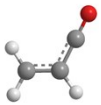
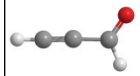
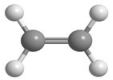
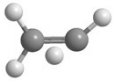
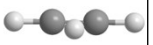
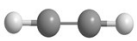
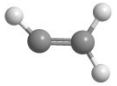
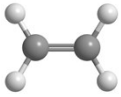
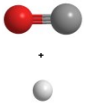
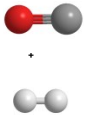
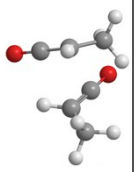
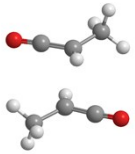
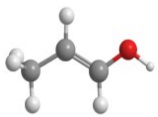
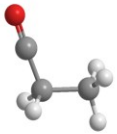
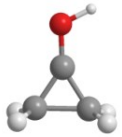
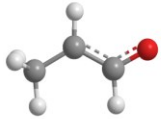
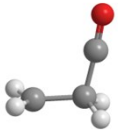
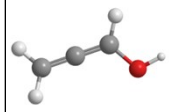
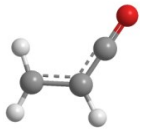
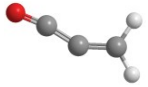
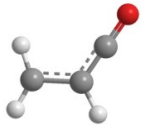
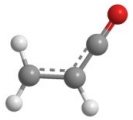
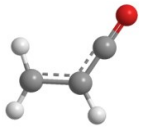
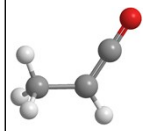
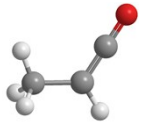
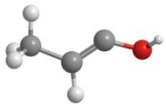
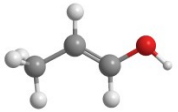
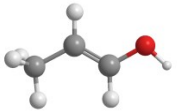
	Neutral	Ionization		Fragments									
	C_3H_4O	$C_3H_4O^{+\circ}$	$C_3H_3O^+$	$C_3H_2O^{+\circ}$	C_2HO^+	$CH_2O^{+\circ}$	HCO^+	$C_2H_4^{+\circ}$	$C_2H_4^{+\circ}$_1	$CO^{+\circ}$	$C_2H_3^+$	$C_2H_2^{+\circ}$	CH_3^+
													
			+ H	H_2	CH_3	C_2H_2	C_2H_3	+ CO	+ CO	C_2H_4	H+CO	H_2+CO	C_2HO
													
	MKE	**m/z = 56**	**m/z = 55**	**m/z = 54**	**m/z = 41**	**m/z = 30**	**m/z = 29**	**m/z = 28**	**m/z = 28**	**m/z = 28**	**m/z = 27**	**m/z = 26**	**m/z = 15**
$E(R)_{CCSD(T)\text{-}F12/cc\text{-}pVTZ\text{-}F12}$	-191.6727871	-191.3444769	-190.76708	-190.0170729	-151.34361	-113.978169	-113.434236	-78.08131501	-78.0383262	-112.684811	-77.46773556	-76.7976175	-39.4166771
ΔZPVE	0.061127	0.060027	0.05086	0.035518	0.018075	0.024017	0.016532	0.048681	0.045396	0.005307	0.034511	0.026117	0.031245
ΔCV	-0.19848764	-0.1980106	-0.19794229	-0.19788533	-0.14831673	-0.10090312	-0.1009479	-0.09619585	-0.09632495	-0.10023646	-0.09667361	-0.09612749	-0.04761424
ΔSR	0.00689882	0.00689129	0.00689727	0.00696941	0.00612191	0.0053068	0.00530276	0.0016243	0.00162836	0.00538693	0.00164178	0.0016518	0.00081066
$E_{corr}=E_{(R)CCSD(T)\text{-}F12}$ + ΔCV+ ΔSR+ ΔZPE	-191.8032489	-191.4755692	-190.907265	-190.1724708	-151.4677298	-114.049748	-113.513349	-78.12720556	-78.0876268	-112.774353	-77.52825639	-76.8659762	-39.4322357

Table S7. Details on the calculations from Table 4 (energies in Hartree). ΔZPE is evaluated at the PBE0/aVTZ level.

	Neutral	Ionization	Fragments									
	$(C_3H_4O)_2$	$(C_3H_4O)_2^{+\circ}$	$C_3H_6O^{+\circ}$	$C_3H_5O^+$	$C_3H_5O^+\_1$	$C_3H_5O^+\_2$	$C_3H_4O^{+\circ}$	$C_3H_4O^{+\circ}\_1$	$C_3H_3O^+$	$C_3H_2O^+$	$C_2H_3^+$	$C_2H_2^+$
												
	C_3H_2O	C_3H_3O	C_3H_3O	C_3H_3O	C_3H_4O	C_3H_4O	C_3H_5O	C_3H_6O	C_3H_6O	C_3H_4O		
										+CO		+HCO
	MKE_2	m/Z =112	m/Z =58	m/Z =57	m/Z =57	m/Z =57	m/Z =56	m/Z =56	m/Z =55	m/Z =54	m/Z =27	m/Z =26
PBE0/aug-cc-pVTZ	-383.41329	-383.124181	-192.590662	-192.021935	-191.973235	-191.923076	-191.362476	-191.31812	-190.805736	-190.075952	-77.477487	-76.818604

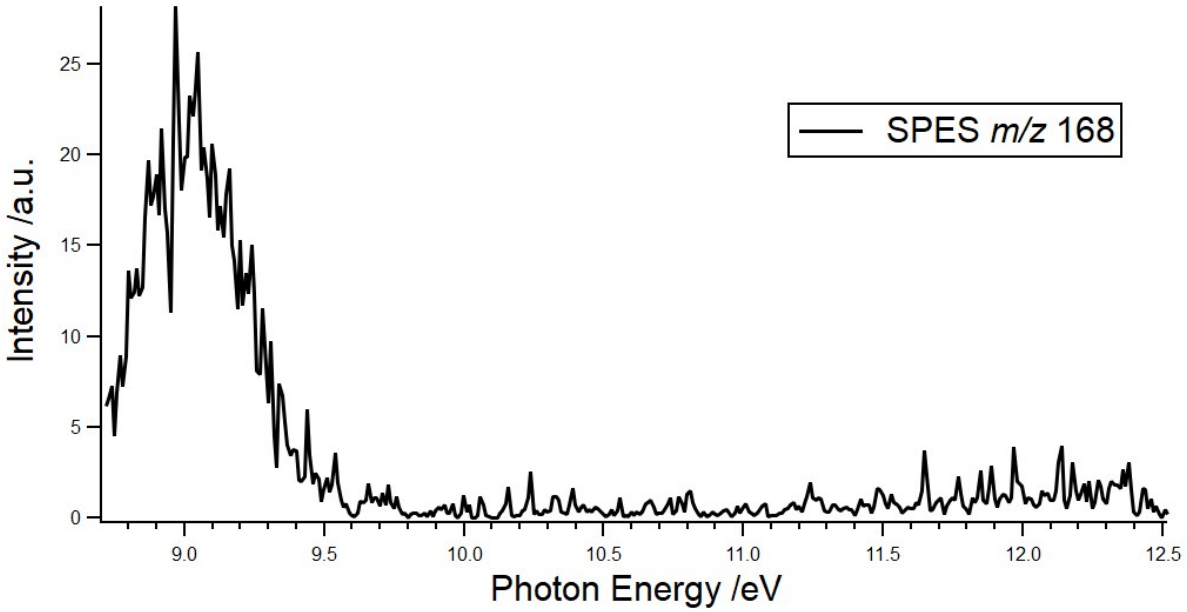


Figure S3. The SPES corresponding to the MKE trimer (*m/z* 168).

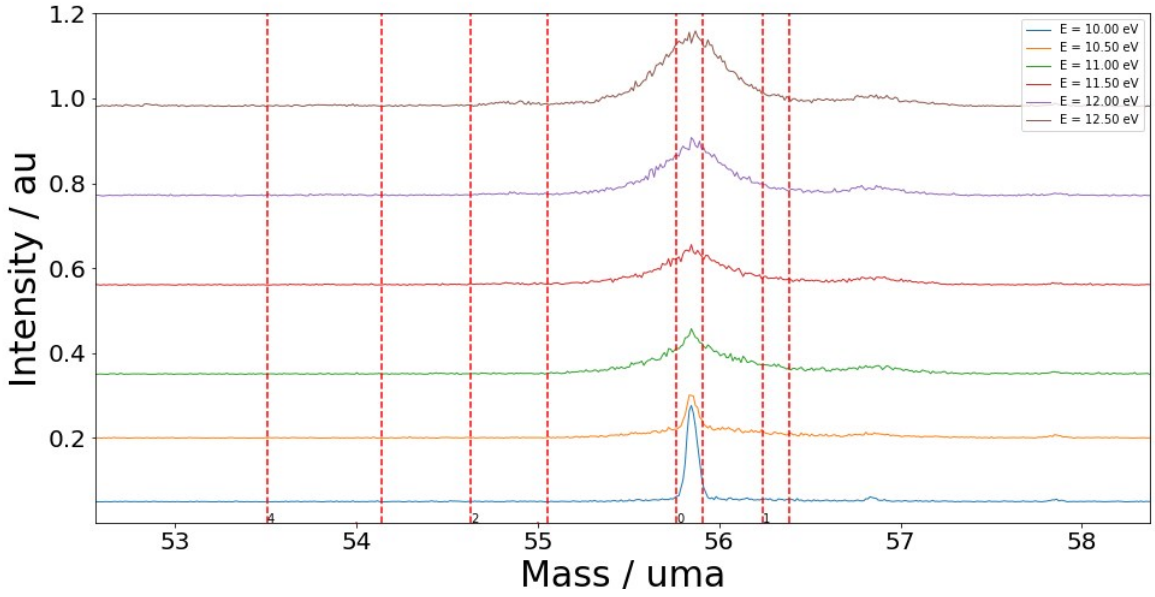


Figure S4. Peak evolution of the *m/z* 56 signal with increasing photon energy.

Table S8. Attribution of excited states of the MKE cation (*m/z* 56) calculated at the MRCI/aVTZ level of theory (in eV).

Ground State	8.917
1st excited state	13.51
2nd excited state	14.21

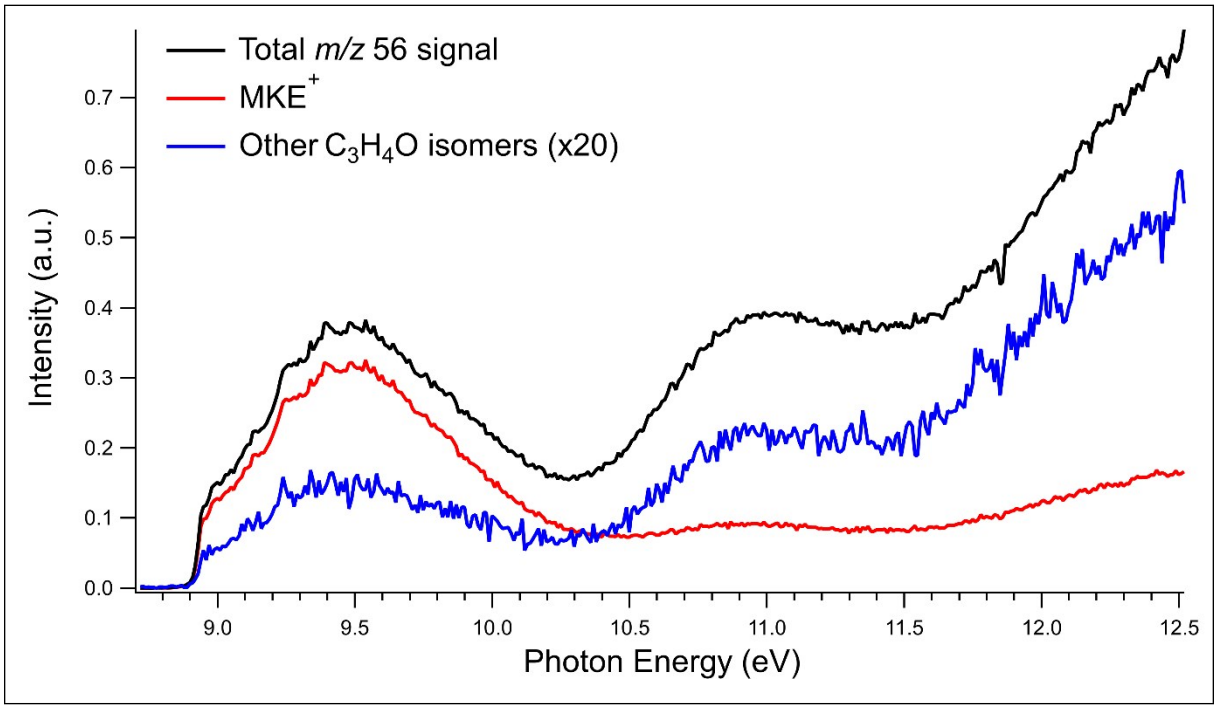


Figure S5. Total ion yield (TIY) of the *m/z* 56 signal (black). By employing the same filtering as was done on the *m/z* 56 SPES the signal can be disentangled into the contribution of the ionized MKE monomer (red) and that of the $C_3H_4O^+$ fragments formed by dissociative ionization of the MKE dimer.