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

Supplementary Information

Electron ionization induced fragmentation pathways of Trichloroanisole

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Table S1. List of the observed cationic fragments under electron ionization at 70 eV incident electron energy (iso = isotope).

Cation	m/Z	Cation	m/Z	Cation	m/Z	Cation	m/Z
29	CHO^+	66	CH_3ClO^+ / $C_5H_2Cl_2^{2+}$	109	$C_3HCl_2^+$ iso / $C_3H_3Cl_2^+$	160	$C_6H_2Cl_2O^+$
30	CH_2O^+	66.5	$C_5HCl_2^{2+}$ iso	110	$C_3H_2Cl_2^+$ iso	162	$C_6H_2Cl_2O^+$ iso
31	CH_3O^+	67	$C_5H_2Cl_2^{2+}$ iso	111	$C_3HCl_2^+$ iso /$C_3H_3Cl_2^+$ iso	167	$C_5H_2Cl_3^+$
32	Cont. O_2^+	68	$C_5H_2Cl_2^{2+}$ iso	112	$C_3H_2Cl_2^+$ iso	168	$C_5H_2Cl_3^+$ iso
35	Cl^+	71	C_3Cl^+	113	$C_3H_3Cl_2^+$ iso	169	$C_5H_2Cl_3^+$ iso
36	ClH^+	71.5	$Cl_3C_3H_2^{2+}$	114	$C_3H_3Cl_2^+$ iso	170	$C_5H_2Cl_3^+$ iso
37	ClH_2^+	72	C_3HCl^+	117	CCl_3^+	171	$C_5H_2Cl_3^+$ iso
38	$C_3H_2^+$	72.5	$Cl_3C_3H_2^{2+}$ iso	118	$CHCl_3^+$	172	$C_5H_2Cl_3^+$ iso
43	$C_2H_3O^+$	73	$C_3H_2Cl^+$	119	CCl_3^+ iso	173	$C_5H_2Cl_3^+$ iso
44	$C_2H_4O^+$	74	$C_3H_3Cl^+$	120	$CHCl_3^+$ iso	175	$(M-Cl)^+$
45	$C_2H_5O^+$	75	$C_3H_4Cl^+$ / $C_6H_3^+$	121	CCl_3^+ iso	177	$(M-Cl)^+$ iso
47	CCl^+	76	$C_3H_5Cl^+$ / $C_6H_4^+$	122	$CHCl_3^+$ iso	179	$(M-OCH_3)^+$
48	$CHCl^+$	77	$C_2H_2ClO^+$	123	CCl_3^+ iso	180	$(M-OCH_3)^+$ iso
49	CH_2Cl^+	83	$CHCl_2^+$	124	$C_7H_5Cl^+$	181	$(M-OCH_3)^+$ iso
50	CH_3Cl^+	84	$CH_2Cl_2^+$ / $Cl_3C_5H_2^{2+}$ iso	125	?	182	$(M-OCH_3)^+$ iso
51	ClO^+ ?	84.5	$Cl_3C_5H_2^{2+}$ iso	126	$C_7H_5Cl^+$ iso	183	$(M-OCH_3)^+$ iso
53	C_4H_5+	85	$CHCl_2^+$ iso / $Cl_3C_5H_2^{2+}$ iso	127	?	195	$(M-CH_3)^+$
54	$C_3H_2O^+$	85.5	$Cl_3C_5H_2^{2+}$ iso	130	$C_2HCl_3^+$	196	$(M-CH_3)^+$ iso
54.5	$C_3HCl_2^{2+}$ iso / $C_3H_3Cl_2^{2+}$	86	$CH_2Cl_2^+$ iso / Cl_2O+	131	$C_5HCl_2^+$	197	$(M-CH_3)^+$ iso
55	$C_3H_2Cl_2^{2+}$ iso	87	$CHCl_2^+$ iso	132	$C_5H_2Cl_2^+$	198	$(M-CH_3)^+$ iso
55.5	$C_3HCl_2^{2+}$ iso /$C_3H_3Cl_2^{2+}$ iso	89	?	133	$C_5HCl_2^+$ iso	199	$(M-CH_3)^+$ iso
56	$C_3H_4O^+$	90	?	134	$C_5H_2Cl_2^+$ iso	200	$(M-CH_3)^+$ iso
57	$C_3H_5O^+$	95	C_5Cl^+	135	$C_5HCl_2^+$ iso	201	$(M-CH_3)^+$ iso
58	?	96	$C_2H_2Cl_2^+$	136	$C_5H_2Cl_2^+$ iso	210	M^+
59	?	97	$C_2H_3Cl_2^+$	141	?	211	M^+ iso
60	C_2HCl^+	98	$C_2H_3Cl_2^+$ iso	143	$C_3H_2Cl_3^+$	212	M^+ iso
61	C_5H^+ / $C_2H_2Cl^+$	99	$C_2H_3Cl_2^+$ iso	144	$C_3H_2Cl_3^+$ iso	213	M^+ iso
62	$C_5H_2^+$	100	$C_2H_3Cl_2^+$ iso	145	$C_3H_2Cl_3^+$iso	214	M^+ iso
63	$C_2H_2Cl^+$ iso	105	M^{2+}	146	$C_3H_2Cl_3^+$iso	215	M^+ iso
65	?	105.5	M^{2+} iso	147	$C_3H_2Cl_3^+$iso	216	M^+ iso
65.5	$C_5HCl_2^{2+}$	106	M^{2+} iso	148	$C_3H_2Cl_3^+$ iso		

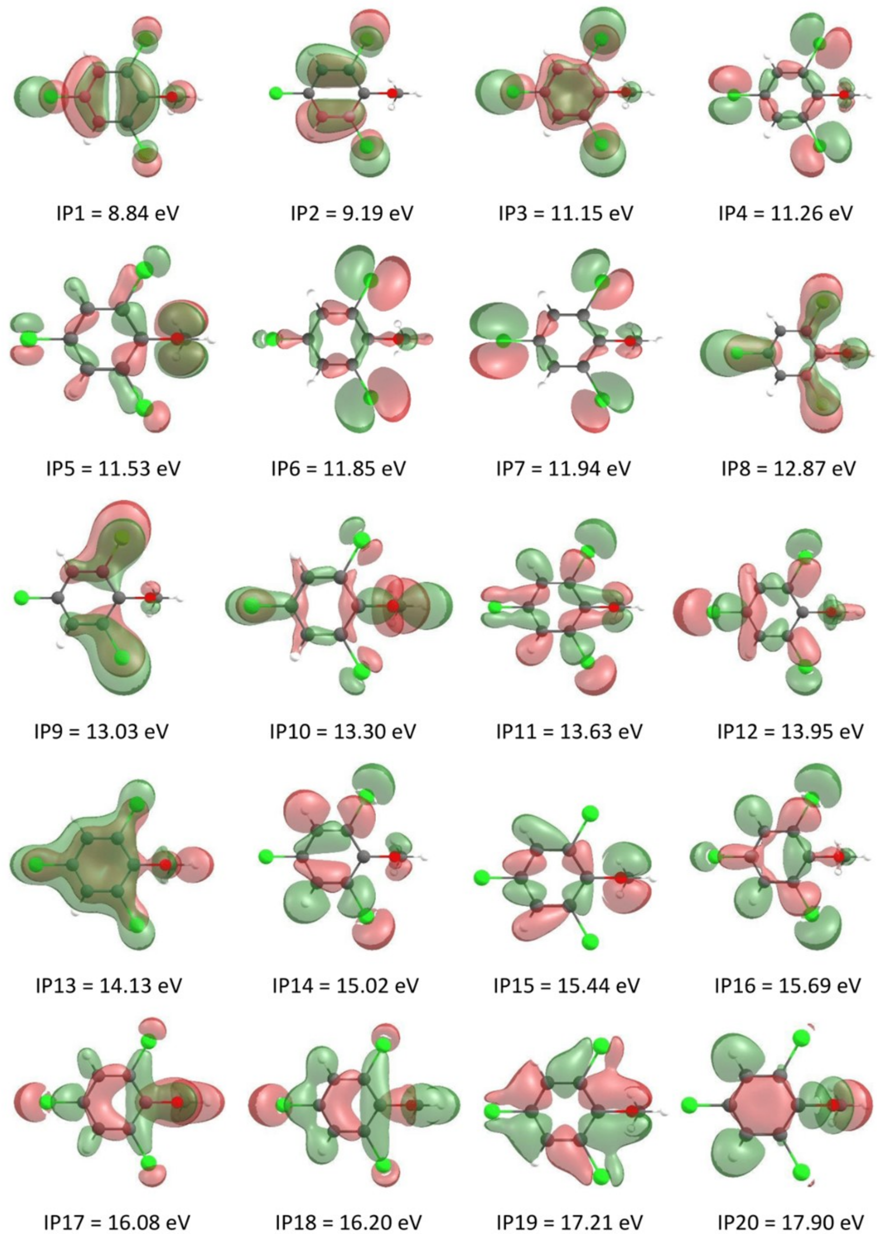

Fig. S1. Twenty first ionization potentials of TCA, in eV, and the corresponding molecular orbitals. The IPs were obtained at the EPT-OVGF/6-311G++(2df,2p) level of theory. The IPs correspond to molecular orbitals HOMO to HOMO-19 and IP1 is related to the threshold for the formation of the parent cation.

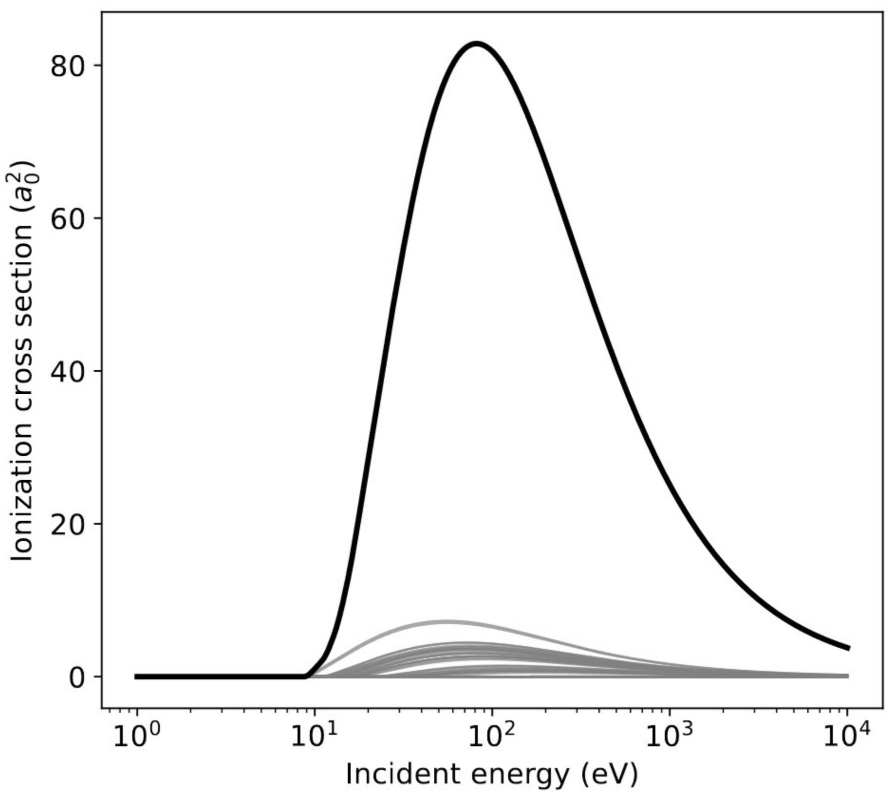

Fig. S2. Total ionization cross section for the electron impact ionization, in a_0^2, as a function of the incident electron energy, in eV. The thin gray lines denote the ionization cross section from each molecular orbital individually, while the black line is the sum over all molecular orbitals (TICS).

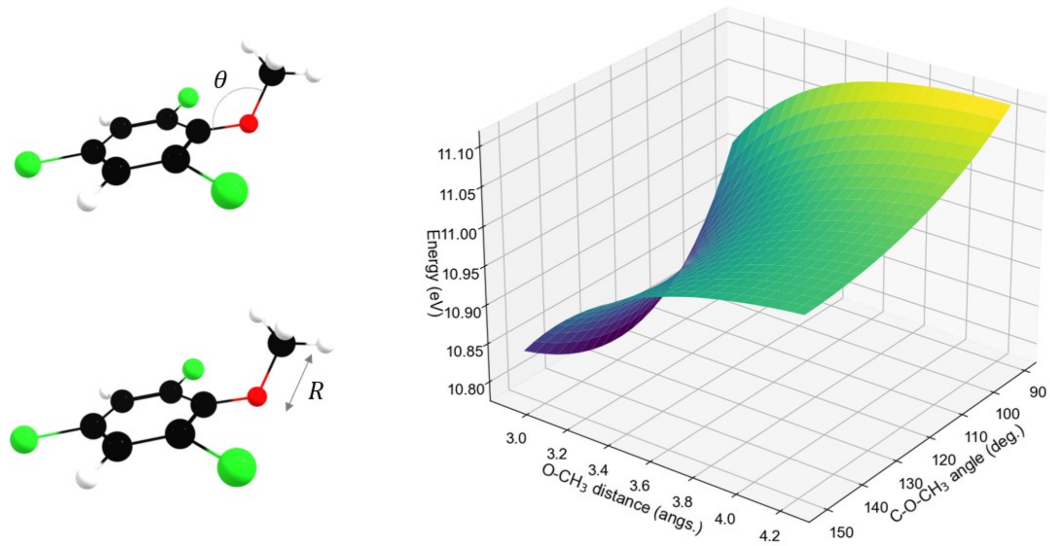

Fig. S3. Two-dimensional potential energy surface, in eV, for the lowest-lying cationic TCA against the O-CH3 bond length and the C-O-CH3 planar angle. The plot focused on the dissociation region. The calculations were done at the DFT/B3LYP/aug-cc-pVTZ level of theory.

Table S2. Wannier-type fitting parameters obtained for the experimental thresholds of the ten most abundant cations for three different measurements. The Wannier function is defined by $f(E) = \begin{cases} b + a(E - AE)^d & E \geq AE \\ b & E < AE \end{cases}$, where *E* represents the electron energy and *b*, *a*, *d*, and *AE* are variable fitting parameters.

Measurement 1	Wannier-type fitting parameters			
m/Z	**a**	**b**	**AE**	**d**
210	2.14	0.44	8.68	4.02
195	0.36	0.14	10.57	6.04
167	32.03	0.15	14.39	2.05
143	0.16	0.09	16.35	3.30
107	0.17	0.03	15.97	3.79
97	0.24	0.91	16.58	3.16
74	0.08	0.18	18.73	2.98
73	0.67	0.20	17.72	2.14
62	0.002	0.24	20.08	4.88
61	0.001	0.45	17.24	3.90
Measurement 2	**Wannier-type fitting parameters**			
m/Z	**a**	**b**	**AE**	**d**
210	1.15	0.59	9.12	3.82
195	0.51	0.32	10.92	4.73
167	8.85	0.27	14.34	2.31
143	0.19	0.20	16.93	3.05
107	0.01	0.30	15.52	4.94
97	0.11	0.59	16.52	3.33
74	0.02	0.23	18.22	3.17
73	0.32	0.25	17.55	2.11
62	0.005	0.22	20.60	4.18
61	0.001	0.41	18.39	3.67
Measurement 3	**Wannier-type fitting parameters**			
m/Z	**a**	**b**	**AE**	**d**
210	1.71	0.26	8.57	1.87
195	0.13	0.15	10.52	2.86
167	0.16	0.16	14.27	2.47
143	0.06	0.16	18.28	2.74
107	0.002	0.13	15.26	4.43
97	0.01	0.16	16.68	3.79
74	0.01	0.18	18.72	3.50
73	0.06	0.18	17.71	2.42
62	0.001	0.21	20.13	4.54
61	0.001	0.22	17.78	3.68

Table S3. Appearance energy values of the three measurements and the corresponding average value.

m/Z	Measurement 1	Measurement 2	Measurement 3	Average
210	8.68	9.12	8.57	8.79
195	10.57	10.92	10.52	10.67
167	14.39	14.34	14.27	14.33
143	16.35	16.93	18.28	16.64
107	15.97	15.52	15.26	15.49
97	16.58	16.52	16.68	16.59
74	18.73	18.22	18.72	18.56
73	17.72	17.55	17.71	17.66
62	20.08	20.60	20.13	20.27
61	17.24	18.39	17.78	17.80