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

Excited state deactivation pathways of neutral/protonated anisole and p-fluoroanisole:

A Theoretical study

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This supplementary material section contains one Figure and two Tables:

Figure SM1: CC2 PE profiles of (a) protonated anisole (C4 isomer) and (b) protonated p-fluoroanisole (C2 isomer) in the electronic ground state (circles), the lowest $^1A'$ excited state (squares) and the lowest $^1A''$ state (triangles), as a function of the C-OCH_3 coordinate.

Table SM1: xyz coordinates revealed to the ground and S1 optimized geometry of neutral/protonated of anisole and p-fluoroanisole. All of the structures have been determined at the MP2, CC2 level of theory, respectively for the ground and excited state using the cc-pVDZ basis function. In all of relevant geometry optimizations, the Cs molecular symmetry has been taken to account.

Table SM2: Vertical transition energies of neutral/protonated anisole and p-fluoroanisole, computed at the CC2/ccpVDZ level of theory.

Figure SM:

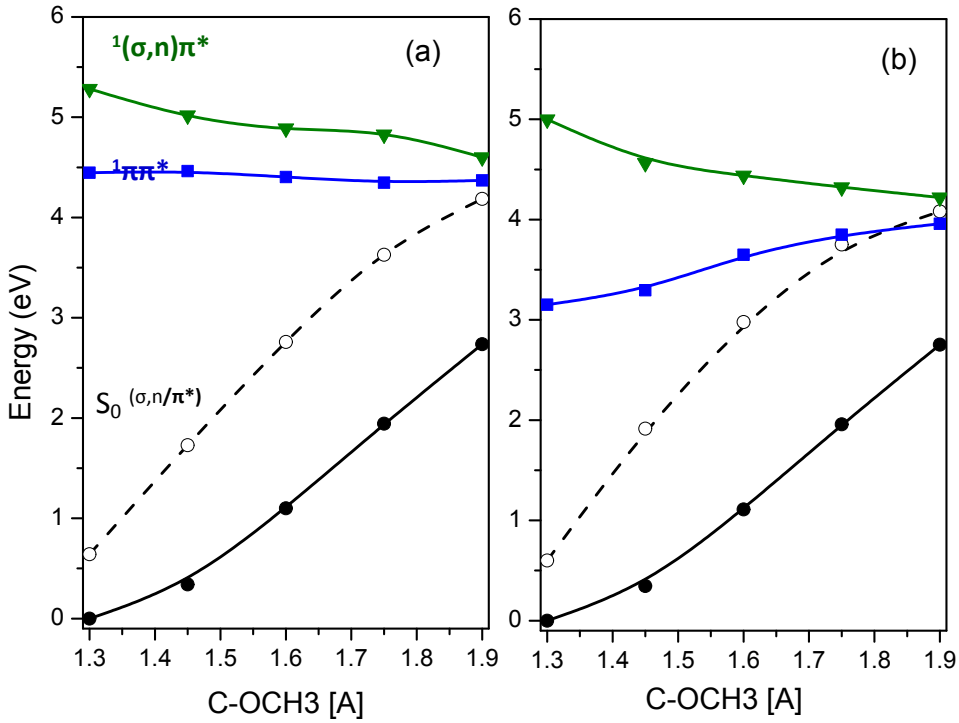
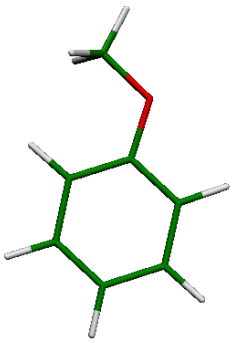
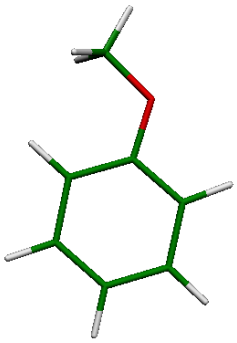
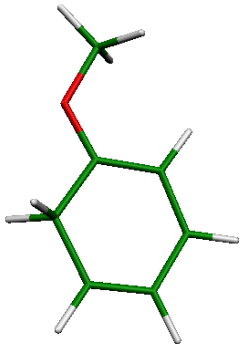
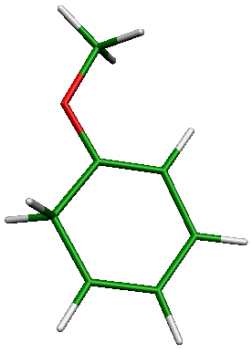
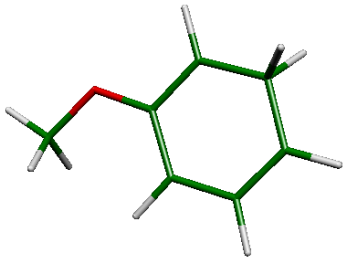
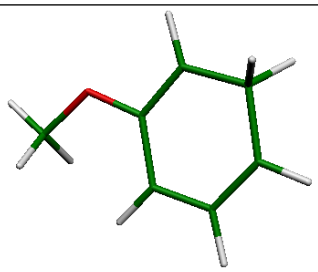


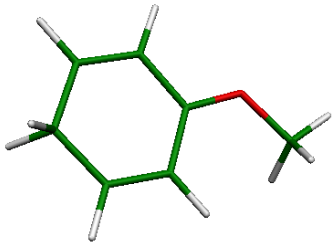
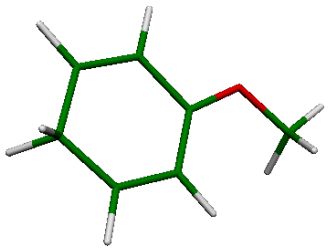
Figure SM: CC2 PE profiles of (a) protonated anisole (C4 isomer) and (b) protonated p-fluoroanisole (C2 isomer) in the electronic ground state (circles), the lowest $^1A'$ excited state (squares), the lowest $^1A''$ state (triangles), as a function of the C-OCH_3 coordinate.

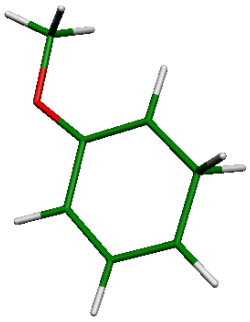
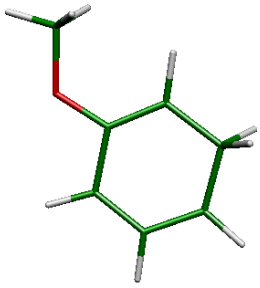
Table SM1:

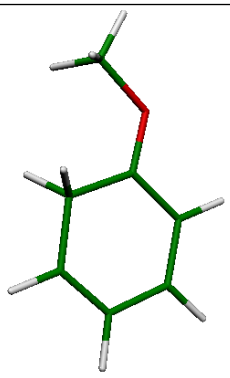
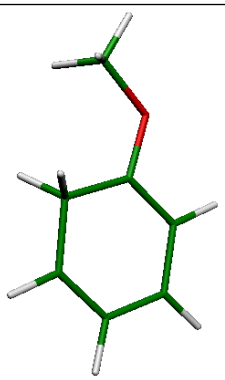
Neutral anisole							
S0				**S1**			
O	0.83274	1.69839	0	O	0.6573	1.7799	0
C	-1.21726	-1.4063	0	C	-1.42631	-1.32503	0
C	0.4201	0.39383	0	C	0.25262	0.48259	0
C	1.45312	-0.56649	0	C	1.33509	-0.45943	0
C	1.14832	-1.93233	0	C	1.02571	-1.87079	0
C	-0.19242	-2.36244	0	C	-0.34802	-2.27509	0
C	-0.92317	-0.0289	0	C	-1.13745	0.08698	0
C	-0.19243	2.68102	0	C	-0.35878	2.79712	0
H	-2.26513	-1.72487	0	H	-2.46301	-1.67305	0
H	2.48791	-0.21042	0	H	2.35803	-0.07483	0
H	1.96229	-2.66495	0	H	1.82428	-2.61714	0
H	-0.43201	-3.43016	0	H	-0.58917	-3.34428	0
H	-1.74451	0.69115	0	H	-1.94573	0.81962	0
H	0.32122	3.65192	0	H	0.18565	3.75029	0
H	-0.82938	2.60527	-0.89994	H	-0.98654	2.718	-0.90271
H	-0.82938	2.60527	0.89994	H	-0.98654	2.718	0.90271
							

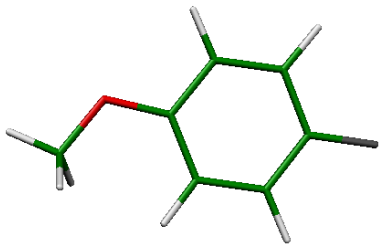
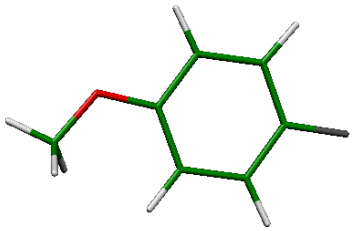
Protonated anisole (C2 isomer)							
S0				**S1**			
H	-2.04965	-0.36173	-0.87098	H	-2.04588	-0.26786	-0.87367
H	-2.04965	-0.36173	0.87098	H	-2.04588	-0.26786	0.87367
O	-0.71615	1.67186	0	O	-0.66991	1.75972	0
C	1.05851	0.03302	0	C	1.12048	0.09681	0
C	1.34052	-1.32862	0	C	1.48785	-1.32985	0
C	0.33619	-2.35597	0	C	0.44004	-2.27868	0
C	-0.98435	-1.99752	0	C	-0.92154	-1.87386	0
C	-1.3925	-0.56821	0	C	-1.37919	-0.46781	0
C	-0.29704	0.44128	0	C	-0.22163	0.48478	0
C	0.2513	2.7655	0	C	0.29488	2.85459	0
H	1.87484	0.757	0	H	1.92079	0.84211	0
H	2.39444	-1.63202	0	H	2.53991	-1.62594	0
H	0.63936	-3.40562	0	H	0.66466	-3.35014	0
H	-1.77758	-2.75264	0	H	-1.69099	-2.65783	0
H	-0.36065	3.67335	0	H	-0.31814	3.76272	0
H	0.86619	2.71102	0.90982	H	0.91359	2.79518	0.9095
H	0.86619	2.71102	-0.90982	H	0.91359	2.79518	-0.9095
							

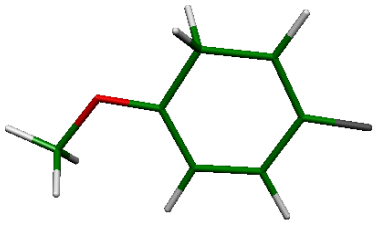
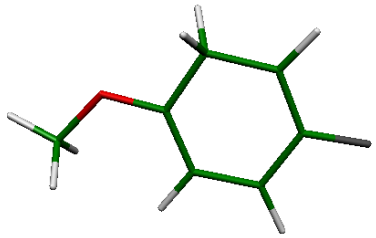
Protonated anisole (C3 isomer)							
S0				**S1**			
H	2.34791	1.58141	-0.8549	H	2.40584	1.53035	-0.87217
H	2.34791	1.58141	0.8549	H	2.40584	1.53035	0.87217
O	-1.81721	0.76377	0	O	-1.79318	0.6629	0
C	-0.5469	0.37047	0	C	-0.45911	0.26134	0
C	0.42985	1.38082	0	C	0.43365	1.29898	0
C	1.85559	1.05499	0	C	1.9131	1.0408	0
C	2.25308	-0.3556	0	C	2.23259	-0.42149	0
C	1.27547	-1.33674	0	C	1.27785	-1.4515	0
C	-0.09598	-0.98054	0	C	-0.09481	-1.16731	0
C	-2.84459	-0.25039	0	C	-2.87798	-0.32856	0
H	0.10594	2.42807	0	H	0.04873	2.32544	0
H	3.31781	-0.61095	0	H	3.29478	-0.70161	0
H	1.5457	-2.39648	0	H	1.61753	-2.49219	0
H	-0.8329	-1.79039	0	H	-0.84352	-1.96327	0
H	-3.78937	0.30435	0	H	-3.79228	0.27464	0
H	-2.77615	-0.87211	-0.90745	H	-2.78689	-0.93873	-0.9118
H	-2.77615	-0.87211	0.90745	H	-2.78689	-0.93873	0.9118
							

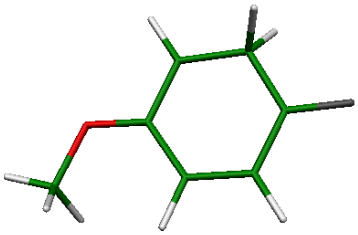
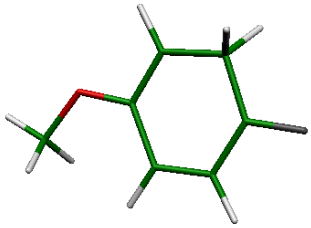
Protonated anisole (C2 isomer)							
S0				S1			
C	-2.28851	-0.3553	0	C	-2.38316	-0.36071	0
C	-1.24769	-1.40963	0	C	-1.28853	-1.40363	0
C	-1.78614	1.04028	0	C	-1.84268	1.02569	0
C	-0.45032	1.32661	0	C	-0.44824	1.29207	0
C	0.5104	0.25343	0	C	0.56103	0.18288	0
C	0.09183	-1.12544	0	C	0.09953	-1.12775	0
H	-2.96487	-0.51008	0.86868	H	-3.07173	-0.47157	0.87126
H	-1.57404	-2.45607	0	H	-1.60455	-2.45355	0
H	-2.51768	1.85598	0	H	-2.53504	1.87885	0
H	-0.06727	2.35054	0	H	-0.07394	2.32361	0
O	1.75087	0.63845	0	O	1.82027	0.68653	0
H	0.8267	-1.93226	0	H	0.79101	-1.97566	0
C	2.835	-0.34154	0	C	2.88733	-0.29466	0
H	3.74722	0.26391	0	H	3.81592	0.28728	0
H	2.77626	-0.95429	0.91059	H	2.81554	-0.91956	0.90642
H	2.77626	-0.95429	-0.91059	H	2.81554	-0.91956	-0.90642
H	-2.96487	-0.51008	-0.86868	H	-3.07173	-0.47157	-0.87126
							

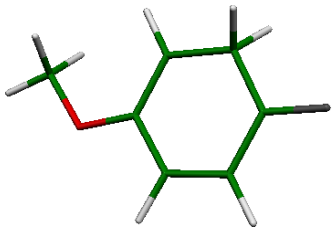
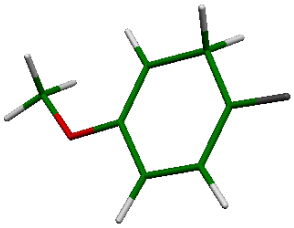
Protonated anisole (C5 isomer)							
S0				**S1**			
H	-1.81093	1.62237	-0.85733	H	-2.09271	1.64512	-0.87497
H	-1.81093	1.62237	0.85733	H	-2.09271	1.64512	0.87497
O	0.87995	-1.7928	0	O	0.61223	-1.77496	0
C	-0.14026	-2.81169	0	C	-0.37009	-2.87127	0
C	-0.85667	-0.06753	0	C	-1.11763	-0.08066	0
C	-1.13822	1.37497	0	C	-1.45316	1.39135	0
C	-0.01512	2.31552	0	C	-0.22881	2.26156	0
C	1.28654	1.83774	0	C	1.10714	1.79398	0
C	1.51081	0.44422	0	C	1.38082	0.43585	0
C	0.46938	-0.52618	0	C	0.19639	-0.48367	0
H	0.40285	-3.76312	0	H	0.24026	-3.78039	0
H	-0.76265	-2.7329	0.90668	H	-0.97925	-2.7801	0.9117
H	-0.76265	-2.7329	-0.90668	H	-0.97925	-2.7801	-0.9117
H	-1.70542	-0.75723	0	H	-1.93998	-0.80367	0
H	-0.22516	3.39077	0	H	-0.39654	3.34726	0
H	2.14097	2.51999	0	H	1.92307	2.524	0
H	2.53749	0.05639	0	H	2.38231	-0.00385	0
							

Protonated anisole (C6 isomer)							
S0				**S1**			
H	-1.42685	0.43304	-0.87369	H	-1.74648	0.53679	-0.87666
O	0.8675	1.65164	0	O	0.65663	1.77279	0
C	0.51018	0.40111	0	C	0.2503	0.48175	0
C	1.55361	-0.55684	0	C	1.3085	-0.45675	0
C	1.22996	-1.9038	0	C	1.06605	-1.88156	0
C	-0.12694	-2.38886	0	C	-0.29129	-2.30647	0
C	-1.16195	-1.49653	0	C	-1.35354	-1.374	0
C	-0.91611	-0.02636	0	C	-1.20279	0.11019	0
C	-0.14074	2.70293	0	C	-0.33107	2.8451	0
H	2.58944	-0.2078	0	H	2.32914	-0.05991	0
H	2.04784	-2.63375	0	H	1.89481	-2.59371	0
H	-0.31361	-3.46557	0	H	-0.5397	-3.37296	0
H	-2.20405	-1.83203	0	H	-2.37951	-1.76666	0
H	-1.42685	0.43304	0.87369	H	-1.74648	0.53679	0.87666
H	0.43236	3.6358	0	H	0.26606	3.76413	0
H	-0.75689	2.62699	-0.90814	H	-0.95054	2.79028	-0.90874
H	-0.75689	2.62699	0.90814	H	-0.95054	2.79028	0.90874
							

p-fluoroanisole							
S0				**S1**			
C	-0.4423	0.39282	0	C	-1.00636	0.26822	0
C	0.44139	1.49223	0	C	-0.1511	1.42079	0
C	1.82654	1.29522	0	C	1.27687	1.22445	0
C	2.32918	-0.01206	0	C	1.74448	-0.11943	0
C	1.4747	-1.11373	0	C	0.91014	-1.27856	0
C	0.08057	-0.91469	0	C	-0.51459	-1.08904	0
F	3.66801	-0.20642	0	F	3.0766	-0.32166	0
O	-1.77372	0.70867	0	O	-2.32776	0.57552	0
C	-2.67597	-0.38787	0	C	-3.27094	-0.51195	0
H	0.01556	2.49987	0	H	-0.61115	2.41138	0
H	2.51942	2.14129	0	H	1.99028	2.05053	0
H	1.89662	-2.12265	0	H	1.36906	-2.26945	0
H	-0.57334	-1.7892	0	H	-1.18536	-1.94867	0
H	-3.68292	0.05058	0	H	-4.25987	-0.03599	0
H	-2.55187	-1.01704	-0.90015	H	-3.1453	-1.1307	-0.90323
H	-2.55187	-1.01704	0.90015	H	-3.1453	-1.1307	0.90323
							

Protonated p-fluoroanisole (C2 isomer)							
S0				**S1**			
C	-0.48029	0.26025	0	C	-1.00151	0.23838	0
C	0.4244	1.44348	0	C	-0.16491	1.48921	0
C	1.88707	1.18204	0	C	1.28344	1.16928	0
C	2.34428	-0.10363	0	C	1.75972	-0.15048	0
C	1.43092	-1.20916	0	C	0.90799	-1.3359	0
C	0.05249	-1.05516	0	C	-0.48214	-1.08721	0
O	-1.74311	0.55978	0	O	-2.3011	0.55372	0
C	-2.7447	-0.50524	0	C	-3.30025	-0.51061	0
F	3.64125	-0.39401	0	F	3.06143	-0.33339	0
H	2.58375	2.02582	0	H	2.02832	1.97558	0
H	1.86177	-2.21774	0	H	1.34857	-2.33503	0
H	-0.58968	-1.93742	0	H	-1.16888	-1.93838	0
H	-3.70408	0.02215	0	H	-4.26154	0.01519	0
H	-2.633	-1.11117	-0.91048	H	-3.18831	-1.12059	-0.90991
H	-2.633	-1.11117	0.91048	H	-3.18831	-1.12059	0.90991
H	0.15097	2.07558	0.87136	H	-0.42981	2.12543	0.87652
H	0.15097	2.07558	-0.87136	H	-0.42981	2.12543	-0.87652
							

Protonated p-fluoroanisole (C3 isomer)							
S0				S1			
C	-1.00151	0.23838	0	O	-2.09874	0.53037	-1.01063
C	-0.16491	1.48921	0	C	-0.89774	0.26579	-0.42864
C	1.28344	1.16928	0	C	-0.22695	1.38057	0.01497
C	1.75972	-0.15048	0	C	1.1153	1.29776	0.6854
C	0.90799	-1.3359	0	C	1.54693	-0.12749	0.76964
C	-0.48214	-1.08721	0	C	0.84983	-1.27223	0.30992
O	-2.3011	0.55372	0	C	-0.3855	-1.13792	-0.30164
C	-3.30025	-0.51061	0	C	-2.94121	-0.55673	-1.53838
F	3.06143	-0.33339	0	F	2.7191	-0.31913	1.34391
H	2.02832	1.97558	0	H	1.09963	1.73833	1.70773
H	1.34857	-2.33503	0	H	1.89014	1.88525	0.14319
H	-1.16888	-1.93838	0	H	-0.70004	2.35816	-0.13226
H	-4.26154	0.01519	0	H	1.3229	-2.24864	0.45726
H	-3.18831	-1.12059	-0.90991	H	-0.94494	-2.00171	-0.66542
H	-3.18831	-1.12059	0.90991	H	-3.82164	-0.03954	-1.93467
H	-0.42981	2.12543	0.87652	H	-2.38495	-1.07628	-2.33233
H	-0.42981	2.12543	-0.87652	H	-3.20531	-1.22875	-0.70871
							

Protonated p-fluoroanisole (C5 isomer)							
S0				S1			
H	1.72491	1.70907	0.86792	H	0.88325	2.17714	0.84011
H	1.72491	1.70907	-0.86792	H	1.80097	1.63302	-0.56177
O	-1.84576	-0.78438	0	O	-2.01323	-0.5812	-1.09235
C	-0.56039	-0.4271	0	C	-0.87598	-0.24185	-0.47957
C	0.35375	-1.53005	0	C	-0.33212	-1.39169	0.32274
C	1.74743	-1.40208	0	C	0.84549	-1.15362	1.00124
C	2.27357	-0.11652	0	C	1.4692	0.11627	0.91666
C	1.42449	1.0781	0	C	1.00672	1.31492	0.14867
C	-0.0397	0.86505	0	C	-0.27896	1.00718	-0.57354
C	-2.81197	0.28446	0	C	-2.73421	0.38699	-1.94011
F	3.56744	0.0739	0	F	2.59834	0.3003	1.5844
H	-0.09386	-2.53196	0	H	-0.88119	-2.33606	0.32985
H	2.40404	-2.27595	0	H	1.33038	-1.91935	1.61587
H	-0.67793	1.75209	0	H	-0.72936	1.80196	-1.17686
H	-3.79014	-0.2089	0	H	-3.60731	-0.17013	-2.29543
H	-2.70039	0.90259	0.9064	H	-3.02175	1.24371	-1.31366
H	-2.70039	0.90259	-0.9064	H	-2.07064	0.67979	-2.76655
							

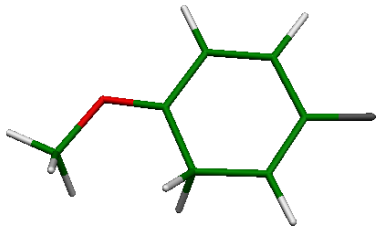
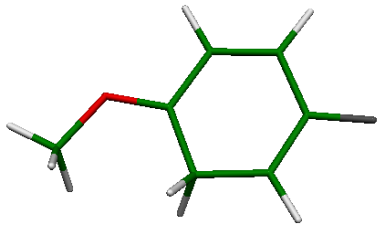
Protonated p-fluoroanisole (C6 isomer)							
S0				**S1**			
F	3.68144	-0.0937	0	F	3.06326	-0.30566	0
O	-1.71117	0.76821	0	O	-2.29215	0.6001	0
C	-0.44423	0.48426	0	C	-0.99511	0.2616	0
C	0.45105	1.58605	0	C	-0.10659	1.39434	0
C	1.81174	1.34247	0	C	1.28369	1.26668	0
C	2.35671	0.01182	0	C	1.76707	-0.10659	0
C	1.54648	-1.08466	0	C	0.94295	-1.24527	0
C	0.06762	-0.91356	0	C	-0.55017	-1.17655	0
C	-2.70408	-0.29963	0	C	-3.31373	-0.44082	0
H	-0.36815	-1.44481	0.87406	H	-0.94793	-1.73386	0.87942
H	-0.36815	-1.44481	-0.87406	H	-0.94793	-1.73386	-0.87942
H	0.04496	2.60092	0	H	-0.58414	2.38028	0
H	2.518	2.18098	0	H	1.98244	2.10522	0
H	1.96636	-2.09457	0	H	1.44157	-2.22318	0
H	-3.66791	0.21954	0	H	-4.26219	0.10821	0
H	-2.59034	-0.90925	-0.90861	H	-3.22765	-1.0559	-0.9089
H	-2.59034	-0.90925	0.90861	H	-3.22765	-1.0559	0.9089
							

Table SM2 :

State	Energy/eV	Oscillator Strength	Configuration*
Neutral anisole			
S1 (1A′/ππ*)	5.03	0.029	5a”-6a”(73%)/H->L
S2 (2A′/ππ*)	6.22	0.150	5a”-7a”(74%)/H->L+1
S3 (3A′/ππ*)	7.15	0.062	4a”-7a”(39%)/H-1->L+1, 4a”-6a”(14%) / H-1->L+1
S4 (1A″/πσ*)	7.31	0.002	5a"-25a′(83%)
Protonated Anisole (C4 isomer)			
S1 (1A′/ππ*)	4.77	0.142	5a"-6a"(80%)/H->L
S2 (2A′/ππ*)	5.24	0.374	4a"-6a"(88%)/H-1->L
S3 (1A″/σ,nπ*)	5.65	0.0003	24a'-6a"(96%)/H-2->L
S4 (2A″/ σ,nπ*)	6.94	0.0002	23a'-6a"(42%)/H-3->L , 22a'-6a"(30%)/H-4->L
p-Fluoroanisole			
S1 (1A′/ππ*)	4.81	0.048	6a"-7a"(81%)/H->L
S2 (2A′/ππ*)	6.29	0.095	6a"-8a"(77%)/H->L+1
S3 (1A″/πσ*)	7.22	0.078	6a"-29a' (78%)/H->L+2
S4 (2A″/πσ*)	7.94	0.0003	5a"-29a' (80%)/H-1->L+2
Protonated p-Fluoroanisole (C2 isomer)			
S1 (1A′/ππ*)	3.40	0.187	6a"-7a"(93%)/H->L
S2 (1A″/σ,nπ*)	5.43	0.002	27a'-7a"(94%)/H->L
S3 (1A″/σ,nπ*)	6.31	0.0006	26a'-7a"(52%)/H-2->L 25a'-7a"(32%)/H-3->L
S4 (2A″/ σ,nπ*)	3.35	0.0001	25a'-7a"(56%)//H-3->L 24a'-7a"(20%)/H-4->L

***H and L denotes to the HOMO and LUMO orbitales respectively.**