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Supplementary Material: Examining the degradation of environmentally-daunting per- and poly-fluoroalkyl substances from a fundamental chemical perspective

Antonio H. da S. Filho[a] and Gabriel L. C. de Souza*[a,b]

[a] *Departamento de Química, Universidade Federal de Mato Grosso, Cuiabá, Mato Grosso, 78060-900 Brazil; E-mail: gabriellcs@pq.cnpq.br*

[b] *Department of Chemistry, Washington State University, Pullman, Washington, 99164 USA.*

Table 1 Cartesians coordinates of the 1^1A PFES optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
O	-1.417624	-1.049348	-1.201511
O	-2.360542	0.899226	-0.050255
F	0.287275	1.403990	1.092000
O	-1.456798	-0.971859	1.249855
F	0.291736	1.404092	-1.091242
C	1.455090	-0.283026	0.000329
S	-1.448680	-0.231822	-0.000500
F	1.518153	-1.023871	-1.100450
F	1.477153	-1.084218	1.059935
C	0.205170	0.615738	0.000204
F	2.547576	0.487644	0.041990

Table 2 Cartesians coordinates of the 1^1A PFES optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
O	-1.337598	-1.149411	-1.123838
O	-2.354417	0.878647	-0.192532
F	0.283355	1.407634	1.091848
O	-1.496790	-0.859710	1.305955
F	0.296623	1.409306	-1.087479
C	1.442956	-0.282597	0.000810
S	-1.437777	-0.231896	-0.001856
F	1.555118	-0.942420	-1.143583
F	1.402239	-1.154915	0.999292
C	0.202420	0.623582	0.001157
F	2.534066	0.470196	0.151167

Table 3 Cartesians coordinates of 1^1A PFBS optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	2.766585	-0.301963	-0.065682
F	2.934169	-0.520375	-1.363196
F	3.802799	0.400309	0.381452
C	1.467774	0.501410	0.196811
F	2.734513	-1.467895	0.571284
F	1.487438	1.566985	-0.620433
C	0.161148	-0.310390	-0.023166
F	1.507697	0.927157	1.467463
F	0.310095	-1.054020	-1.133348
F	0.017605	-1.134051	1.026806
C	-1.098890	0.575425	-0.178597
F	-1.079769	1.099558	-1.419190
S	-2.726504	-0.298850	0.073411
F	-1.018720	1.594910	0.703534
O	-3.674320	0.681737	-0.430297
O	-2.785764	-0.523030	1.507249
O	-2.592175	-1.498519	-0.736967

Table 4 Cartesians coordinates of 2^1A PFBS optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	2.903684	-0.435894	0.007505
F	3.035630	-0.925022	-1.219409
F	3.999883	0.259791	0.302282
C	1.674698	0.499293	0.103674
F	2.799269	-1.444272	0.866857
F	1.805532	1.421404	-0.867234
C	0.291301	-0.189939	-0.028875
F	1.737405	1.116813	1.295141
F	0.348640	-1.033885	-1.081117
F	0.104045	-0.915064	1.096897
C	-0.908512	0.720291	-0.214781
F	-0.878608	1.292976	-1.435184
S	-3.060729	-0.200225	-0.052513
F	-0.896788	1.702480	0.712345
O	-4.525177	0.241407	-0.034547
O	-2.974217	-0.503196	1.434717
O	-2.911909	-1.442696	-0.825184

Table 5 Cartesians coordinates of 1^1A PFBS optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	2.741776	-0.299398	-0.074819
F	2.900182	-0.482449	-1.376279
F	3.785376	0.374563	0.388861
C	1.454441	0.505411	0.209610
F	2.690385	-1.479675	0.529179
F	1.458671	1.570976	-0.603749
C	0.158093	-0.315228	-0.005694
F	1.504783	0.922513	1.479124
F	0.322662	-1.075610	-1.098950
F	-0.000705	-1.114640	1.056964
C	-1.087526	0.576731	-0.187355
F	-1.055578	1.077661	-1.433932
S	-2.704331	-0.295619	0.070043
F	-1.000705	1.605940	0.679279
O	-3.653459	0.655759	-0.480733
O	-2.779813	-0.470748	1.508737
O	-2.538858	-1.518596	-0.697456

Table 6 Cartesians coordinates of 2^1A PFBS optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	2.782564	-0.315741	-0.059715
F	2.960418	-0.472300	-1.362133
F	3.827863	0.331729	0.436824
C	1.502624	0.500575	0.218339
F	2.701975	-1.507723	0.516665
F	1.534220	1.586093	-0.570182
C	0.189274	-0.283728	-0.049486
F	1.526012	0.889616	1.496822
F	0.354253	-0.991609	-1.175057
F	0.000294	-1.114983	0.979015
C	-1.003072	0.652661	-0.218483
F	-1.097232	1.132723	-1.433939
S	-3.025225	-0.459776	0.130346
F	-1.027339	1.615579	0.675879
O	-3.583125	0.703727	-0.647627
O	-2.722437	-0.257290	1.593345
O	-2.375551	-1.594977	-0.633780

Table 7 Cartesians coordinates of 2^1A PFBS optimized at the CAM-B3LYP/6-311++G(2d,2p) level of theory and the cluster-continuum solvation model (considering one water molecule explicitly plus the IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-3.151899	0.683213	-0.240892
F	-3.292486	0.467708	-1.543130
F	-4.313237	0.423833	0.356018
C	-2.064466	-0.239435	0.359894
F	-2.851794	1.962289	-0.043604
F	-2.404028	-1.502054	0.044164
C	-0.611779	0.031365	-0.110429
F	-2.117857	-0.099160	1.695020
F	-0.621017	0.111252	-1.458199
F	-0.251181	1.231931	0.393356
C	0.438001	-0.988267	0.291993
F	0.217647	-2.163534	-0.327234
S	2.702937	-0.530072	-0.160051
F	0.411550	-1.196407	1.622873
O	4.006530	-1.266535	-0.464488
O	2.957991	0.595475	0.762203
O	2.494245	0.001832	-1.567416
O	5.112998	2.410526	0.514275
H	5.140983	2.735469	-0.388769
H	4.380382	1.771333	0.536236

Table 8 Cartesians coordinates of 2^1A PFBS optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory and the cluster-continuum solvation model (considering one water molecule explicitly plus the IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-3.152685	0.684252	-0.240218
F	-3.290098	0.477116	-1.544169
F	-4.315115	0.420008	0.352379
C	-2.065925	-0.241624	0.356913
F	-2.854227	1.962290	-0.033955
F	-2.404330	-1.502257	0.032420
C	-0.612372	0.032894	-0.108524
F	-2.122133	-0.109823	1.692819
F	-0.618317	0.117016	-1.456177
F	-0.255087	1.232326	0.400020
C	0.438200	-0.986204	0.293176
F	0.218266	-2.161500	-0.326179
S	2.703143	-0.530100	-0.157364
F	0.412296	-1.194592	1.624083
O	4.009655	-1.268935	-0.443717
O	2.952198	0.611330	0.746740
O	2.499487	-0.023096	-1.574580
O	5.117533	2.413756	0.509593
H	5.151065	2.739427	-0.392991
H	4.383057	1.776578	0.527273

Table 9 Cartesians coordinates of 2^1A PFBS optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory and the cluster-continuum solvation model (considering three water molecules explicitly plus the IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-3.661390	-0.876872	0.181680
F	-3.836657	-0.815587	1.495695
F	-4.838061	-0.687778	-0.409579
C	-2.676835	0.217661	-0.295532
F	-3.214036	-2.086294	-0.140097
F	-3.116874	1.389252	0.197114
C	-1.197588	0.012035	0.125681
F	-2.741989	0.261885	-1.635622
F	-1.178046	-0.345333	1.425062
F	-0.711323	-1.008559	-0.612944
C	-0.283938	1.212422	-0.054103
F	-0.549598	2.157897	0.859123
S	2.004759	0.834294	0.130526
F	-0.430189	1.740485	-1.281201
O	3.379887	1.523355	-0.001406
O	2.123986	0.103649	-1.204305
O	2.032942	-0.121258	1.248834
O	4.036869	-1.895958	-1.910239
H	3.854787	-2.781402	-1.583626
H	3.272137	-1.354680	-1.655465
O	5.648727	-0.279887	-0.269563
H	4.991473	0.433054	-0.235800
H	5.251444	-0.928711	-0.878197
O	4.560458	-1.281297	2.150958
H	3.676580	-0.942780	1.948752
H	5.083940	-1.008205	1.377391

Table 10 Cartesians coordinates of 2^1A PFBS optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory and the cluster-continuum solvation model (considering five water molecules explicitly plus the IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	3.716786	1.187306	-0.021913
F	3.747600	1.782609	1.163722
F	4.935703	0.729901	-0.297276
C	2.729760	-0.004450	-0.016920
F	3.379506	2.078744	-0.946445
F	3.121037	-0.838207	0.961867
C	1.235691	0.350783	0.194536
F	2.858571	-0.632366	-1.198726
F	1.143145	1.102761	1.308583
F	0.839483	1.084538	-0.866899
C	0.278228	-0.818897	0.338608
F	0.502536	-1.501204	1.465824
S	-2.017663	-0.303069	0.393085
F	0.382468	-1.660559	-0.710334
O	-3.387050	-1.006355	0.357443
O	-2.074720	0.124801	-1.073483
O	-2.064243	0.886200	1.257601
O	-3.982975	2.316579	-1.753133
H	-3.908399	2.770069	-0.891679
H	-3.249284	1.687459	-1.743567
O	-5.718767	0.200718	-1.027593
H	-5.032533	-0.284165	-0.549711
H	-5.253096	0.994978	-1.343726
O	-3.633187	3.190099	0.865030
H	-3.080612	2.418739	1.084129
H	-3.089319	3.963809	1.035707
O	2.234630	-4.005068	-1.409069
H	1.685008	-3.246904	-1.189066
H	2.976202	-3.642254	-1.900866
O	-3.587569	-3.794066	0.982076
H	-3.518591	-3.872314	1.936674
H	-3.488946	-2.847971	0.793063

Table 11 Cartesians coordinates of 1^1A PFOS optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	5.364900	0.179950	0.205312
F	5.499764	-0.354751	1.410697
F	6.382841	-0.212073	-0.551005
C	4.043595	-0.285962	-0.457852
F	5.390253	1.504339	0.308886
F	3.988797	-1.622811	-0.357154
C	2.768640	0.334517	0.176755
F	4.092891	0.055238	-1.751075
F	2.905858	0.336844	1.510631
F	2.660950	1.600760	-0.251687
C	1.469063	-0.440884	-0.186122
F	1.415797	-1.548294	0.567877
C	0.177299	0.396082	0.046975
F	1.522494	-0.793189	-1.478783
F	0.308410	1.078436	1.194551
F	0.050730	1.264629	-0.966534
C	-1.106214	-0.480817	0.134791
F	-1.139678	-1.048405	1.349947
C	-2.417885	0.327104	-0.094405
F	-1.029228	-1.447221	-0.794260
F	-2.299430	1.508123	0.536918
F	-2.532688	0.551553	-1.411839
C	-3.684201	-0.394564	0.429689
F	-3.702487	-0.268813	1.770321
S	-5.303266	0.238374	-0.246571
F	-3.582240	-1.709019	0.136754
O	-6.265542	-0.402355	0.635140
O	-5.323052	-0.237982	-1.618525
O	-5.190935	1.679760	-0.092108

Table 12 Cartesians coordinates of 2^1A PFOS optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-5.460685	0.286499	-0.176145
F	-5.630586	-0.295525	-1.354899
F	-6.480635	-0.037130	0.609519
C	-4.147014	-0.193784	0.491554
F	-5.443329	1.605151	-0.337904
F	-4.143934	-1.535250	0.461385
C	-2.859491	0.344232	-0.191012
F	-4.164356	0.216580	1.765555
F	-3.014569	0.278802	-1.521477
F	-2.702620	1.627628	0.165872
C	-1.583010	-0.455926	0.198453
F	-1.581773	-1.605038	-0.493090
C	-0.265191	0.318243	-0.095159
F	-1.631883	-0.735243	1.509529
F	-0.389200	0.942933	-1.277257
F	-0.097927	1.237958	0.866760
C	0.988157	-0.601153	-0.149167
F	0.980847	-1.241311	-1.331076
C	2.341303	0.150003	0.003140
F	0.893287	-1.514543	0.833601
F	2.271224	1.280783	-0.730964
F	2.467359	0.484432	1.307089
C	3.585889	-0.610998	-0.409958
F	3.637570	-0.748959	-1.749961
S	5.721641	0.276426	0.184963
F	3.582093	-1.844638	0.140957
O	7.058829	0.426068	-0.519864
O	5.889482	-0.021161	1.617430
O	5.287924	1.733193	0.057134

Table 13 Cartesians coordinates of 1^1A PFOS optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	5.321907	0.165080	0.198363
F	5.457983	-0.417083	1.378142
F	6.336335	-0.190766	-0.575046
C	4.002878	-0.272979	-0.475705
F	5.336284	1.482045	0.354005
F	3.932163	-1.608835	-0.411145
C	2.744527	0.336999	0.187360
F	4.047802	0.107351	-1.754834
F	2.899602	0.315238	1.516428
F	2.619767	1.606436	-0.218817
C	1.455258	-0.440168	-0.181596
F	1.392821	-1.547903	0.566392
C	0.175854	0.400311	0.059010
F	1.515434	-0.781296	-1.474200
F	0.316854	1.066505	1.212193
F	0.044932	1.275014	-0.945183
C	-1.097589	-0.479605	0.136339
F	-1.132062	-1.066065	1.339834
C	-2.398870	0.337214	-0.071564
F	-1.017741	-1.423739	-0.811424
F	-2.272228	1.490890	0.602103
F	-2.514546	0.604947	-1.377999
C	-3.655892	-0.408123	0.428039
F	-3.685465	-0.313128	1.767826
S	-5.254265	0.237473	-0.259379
F	-3.535822	-1.710890	0.103539
O	-6.234279	-0.384440	0.614173
O	-5.263129	-0.245522	-1.628009
O	-5.114993	1.676158	-0.108379

Table 14 Cartesians coordinates of 2^1A PFOS optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-5.347923	0.158754	-0.187714
F	-5.504165	-0.525645	-1.308773
F	-6.359414	-0.110977	0.623035
C	-4.026643	-0.237358	0.508625
F	-5.346427	1.456448	-0.462444
F	-3.956971	-1.574546	0.530404
C	-2.771884	0.329659	-0.199343
F	-4.062971	0.224468	1.760976
F	-2.939704	0.238493	-1.523945
F	-2.638196	1.617934	0.138805
C	-1.482480	-0.432099	0.198464
F	-1.431837	-1.579450	-0.488349
C	-0.202553	0.388218	-0.099820
F	-1.530693	-0.701706	1.508439
F	-0.353139	0.994378	-1.284410
F	-0.055646	1.313518	0.855204
C	1.066594	-0.498058	-0.147405
F	1.096307	-1.135081	-1.326758
C	2.381066	0.317226	0.007949
F	0.999247	-1.403752	0.837254
F	2.260971	1.427559	-0.732271
F	2.507409	0.644044	1.296417
C	3.595155	-0.472683	-0.470725
F	3.758966	-0.410027	-1.769058
S	5.587824	0.380611	0.410301
F	3.592695	-1.718598	-0.051349
O	6.193832	-0.364088	-0.750953
O	5.209524	-0.403624	1.641037
O	4.971511	1.739552	0.153214

Table 15 Cartesians coordinates of 1^1A PFOA optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.259513	-0.207280	-0.229106
F	4.345170	-0.228925	-1.551780
F	5.287755	0.480601	0.252706
C	2.945340	0.476111	0.227625
F	4.319690	-1.451436	0.233375
F	2.851983	1.648247	-0.418707
C	1.669963	-0.370084	-0.039655
F	3.042953	0.707408	1.542640
F	1.771138	-0.933464	-1.252767
F	1.612256	-1.339630	0.885479
C	0.359966	0.468286	0.011512
F	0.258813	1.153177	-1.137204
C	-0.915113	-0.403682	0.204194
F	0.446386	1.336483	1.031142
F	-0.788818	-1.508522	-0.549797
F	-0.979019	-0.763161	1.495856
C	-2.228632	0.328469	-0.188991
F	-2.300796	0.343006	-1.535383
C	-3.518226	-0.321874	0.363580
F	-2.143432	1.598254	0.246725
F	-3.352678	-1.665935	0.302109
F	-3.617859	0.001964	1.678291
C	-4.799121	0.143737	-0.412784
O	-5.085137	1.333543	-0.217385
O	-5.342865	-0.719127	-1.110416

Table 16 Cartesians coordinates of 2^1A PFOA optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.268137	-0.141913	-0.238078
F	4.356357	-0.074713	-1.559134
F	5.283746	0.530176	0.290686
C	2.941062	0.487211	0.257771
F	4.349726	-1.412866	0.141077
F	2.823864	1.692251	-0.320645
C	1.682954	-0.368328	-0.057286
F	3.036004	0.645639	1.583894
F	1.796343	-0.861065	-1.300256
F	1.647231	-1.389635	0.811814
C	0.355383	0.437157	0.039237
F	0.243702	1.186635	-1.068137
C	-0.904236	-0.465209	0.179635
F	0.424513	1.247495	1.107864
F	-0.762630	-1.519816	-0.643684
F	-0.947607	-0.912308	1.445476
C	-2.236736	0.258303	-0.164555
F	-2.301573	0.354300	-1.507834
C	-3.547923	-0.410924	0.338845
F	-2.181161	1.506471	0.347621
F	-3.437911	-1.735607	0.018821
F	-3.530148	-0.285622	1.699597
C	-4.832074	0.119612	-0.185331
O	-5.228910	1.333155	0.109455
O	-5.216530	-0.112841	-1.415187

Table 17 Cartesians coordinates of 1^1A PFOA optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.220583	-0.194775	-0.254402
F	4.287190	-0.145915	-1.574767
F	5.258779	0.454041	0.250599
C	2.920056	0.469738	0.249690
F	4.266770	-1.460341	0.140345
F	2.803942	1.658312	-0.356182
C	1.655268	-0.378417	-0.030666
F	3.035557	0.654850	1.567213
F	1.760733	-0.925447	-1.247938
F	1.588996	-1.353754	0.884113
C	0.357581	0.464798	0.029844
F	0.253576	1.161631	-1.108695
C	-0.908511	-0.411589	0.208403
F	0.450526	1.314244	1.061372
F	-0.767844	-1.508456	-0.549905
F	-0.989823	-0.774946	1.494963
C	-2.206576	0.329403	-0.196845
F	-2.277983	0.329343	-1.539853
C	-3.489749	-0.312661	0.367483
F	-2.103647	1.599045	0.228601
F	-3.313355	-1.653503	0.324981
F	-3.586985	0.035988	1.671730
C	-4.763015	0.142930	-0.424940
O	-5.024399	1.343997	-0.266520
O	-5.314563	-0.734294	-1.097305

Table 18 Cartesians coordinates of 2^1A PFOA optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-4.224028	0.133790	-0.264147
F	-4.289982	-0.004649	-1.578195
F	-5.247744	-0.503067	0.284284
C	-2.910456	-0.466055	0.283520
F	-4.298813	1.421525	0.045376
F	-2.779398	-1.698395	-0.224444
C	-1.659318	0.373451	-0.071552
F	-3.018280	-0.545642	1.612445
F	-1.773231	0.805180	-1.333813
F	-1.610287	1.429583	0.750136
C	-0.347339	-0.439265	0.066513
F	-0.229705	-1.235704	-1.003473
C	0.905176	0.466214	0.168921
F	-0.431198	-1.194155	1.170761
F	0.763932	1.477554	-0.702959
F	0.954288	0.968582	1.410275
C	2.222387	-0.287329	-0.141583
F	2.298826	-0.430434	-1.474956
C	3.512140	0.408729	0.362919
F	2.143487	-1.510517	0.416069
F	3.374550	1.728133	0.066006
F	3.503938	0.272423	1.716523
C	4.799158	-0.105908	-0.198021
O	5.108094	-1.370776	-0.025293
O	5.138183	0.205087	-1.427924

Table 19 Cartesians coordinates of 1^1A PFOA (protonated) optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.295121	-0.221217	-0.216856
F	4.381784	-0.304379	-1.536920
F	5.321050	0.490397	0.233670
C	2.979609	0.480723	0.206703
F	4.355914	-1.442177	0.303403
F	2.887552	1.625624	-0.486656
C	1.703972	-0.372859	-0.032330
F	3.071224	0.763819	1.511694
F	1.799756	-0.974092	-1.226548
F	1.641492	-1.311466	0.923507
C	0.395767	0.469293	-0.005837
F	0.286550	1.117941	-1.174073
C	-0.879424	-0.395977	0.210316
F	0.476659	1.365321	0.987855
F	-0.774011	-1.513437	-0.523250
F	-0.953696	-0.728989	1.506744
C	-2.187969	0.340725	-0.194431
F	-2.301343	0.306495	-1.533574
C	-3.471070	-0.289324	0.403262
F	-2.114269	1.617335	0.204939
F	-3.378861	-1.635180	0.295327
F	-3.563184	0.030037	1.699914
C	-4.739604	0.220126	-0.325819
O	-5.048801	1.368643	-0.246611
O	-5.422360	-0.679656	-1.004551
H	-5.038681	-1.566076	-0.935045

Table 20 Cartesians coordinates of 2^1A PFOA (protonated) optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.285788	-0.194303	-0.235890
F	4.361352	-0.288801	-1.555871
F	5.308273	0.532329	0.198423
C	2.966796	0.497381	0.193637
F	4.364947	-1.409745	0.294870
F	2.856428	1.634933	-0.509153
C	1.698210	-0.371965	-0.025077
F	3.067981	0.793608	1.495119
F	1.788987	-0.981701	-1.215739
F	1.657786	-1.303921	0.938506
C	0.380305	0.454660	0.007694
F	0.255824	1.095249	-1.163605
C	-0.883378	-0.422445	0.243569
F	0.460208	1.359519	0.994215
F	-0.770984	-1.547468	-0.479754
F	-0.934910	-0.745355	1.543625
C	-2.206955	0.287461	-0.159993
F	-2.304555	0.260941	-1.498732
C	-3.497564	-0.347660	0.432203
F	-2.161055	1.567849	0.246315
F	-3.430253	-1.684403	0.252937
F	-3.522475	-0.076382	1.750747
C	-4.788390	0.131232	-0.199274
O	-5.018865	1.418579	-0.098643
O	-5.175209	-0.383218	-1.380466
H	-5.154300	-1.348911	-1.335477

Table 21 Cartesians coordinates of 3^1A PFOA (protonated) optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.275958	-0.190618	-0.238475
F	4.345928	-0.299480	-1.557639
F	5.298928	0.542367	0.183519
C	2.957547	0.503607	0.188813
F	4.359103	-1.400056	0.305240
F	2.840360	1.631337	-0.528514
C	1.689997	-0.371502	-0.012423
F	3.064096	0.817180	1.485666
F	1.776939	-0.997944	-1.194460
F	1.653557	-1.289249	0.964734
C	0.371106	0.453479	0.013862
F	0.238632	1.075760	-1.166594
C	-0.890564	-0.422415	0.265866
F	0.452726	1.372232	0.986581
F	-0.780273	-1.556119	-0.441934
F	-0.944073	-0.724510	1.570378
C	-2.215841	0.285773	-0.137614
F	-2.323842	0.225290	-1.487992
C	-3.504497	-0.347143	0.448717
F	-2.160068	1.569187	0.230571
F	-3.420747	-1.686093	0.296996
F	-3.563042	-0.058782	1.754805
C	-4.829971	0.193526	-0.150604
O	-5.088657	1.393992	-0.146281
O	-4.964848	-0.553057	-1.452775
H	-4.238389	-0.345808	-2.088624

Table 22 Cartesians coordinates of 1^1A PFOA (protonated) optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.255342	-0.230519	-0.224612
F	4.332497	-0.336146	-1.540541
F	5.294182	0.464575	0.211757
C	2.956194	0.497312	0.188410
F	4.286416	-1.442062	0.315344
F	2.847459	1.605773	-0.554761
C	1.688537	-0.370317	-0.001404
F	3.063529	0.835660	1.475596
F	1.784147	-1.027624	-1.163171
F	1.621485	-1.254565	1.001176
C	0.390895	0.475168	-0.011421
F	0.276130	1.071625	-1.203841
C	-0.871869	-0.387720	0.236874
F	0.474306	1.406383	0.945288
F	-0.751403	-1.529053	-0.451700
F	-0.957792	-0.665969	1.542559
C	-2.170400	0.331118	-0.206500
F	-2.283127	0.235540	-1.539358
C	-3.443058	-0.276837	0.424215
F	-2.093260	1.621297	0.136937
F	-3.333241	-1.621170	0.383849
F	-3.535703	0.113006	1.697162
C	-4.702676	0.192067	-0.343550
O	-5.051316	1.327989	-0.255233
O	-5.315519	-0.713789	-1.079308
H	-4.913717	-1.590666	-1.002415

Table 23 Cartesians coordinates of 2^1A PFOA (protonated) optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.245880	-0.153582	-0.272451
F	4.302318	-0.092446	-1.592668
F	5.275223	0.509380	0.231546
C	2.937454	0.483646	0.245798
F	4.316381	-1.421404	0.111230
F	2.796454	1.675924	-0.347426
C	1.684777	-0.381438	-0.036478
F	3.056285	0.656942	1.564341
F	1.787074	-0.910873	-1.261203
F	1.637302	-1.368731	0.866205
C	0.375150	0.441506	0.044986
F	0.244009	1.148550	-1.083911
C	-0.875440	-0.455532	0.224348
F	0.458700	1.279358	1.085746
F	-0.742779	-1.535471	-0.557089
F	-0.942220	-0.845233	1.502267
C	-2.185449	0.278226	-0.158265
F	-2.288814	0.286422	-1.493335
C	-3.463962	-0.368875	0.433815
F	-2.118184	1.545144	0.279888
F	-3.376166	-1.696756	0.251878
F	-3.479852	-0.097710	1.752070
C	-4.745077	0.123541	-0.183971
O	-5.029683	1.386413	-0.052695
O	-4.997622	-0.338968	-1.445373
H	-5.953149	-0.382382	-1.587998

Table 24 Cartesians coordinates of 3^1A PFOA (protonated) optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.234992	-0.170594	-0.273551
F	4.286152	-0.144397	-1.595068
F	5.270170	0.498565	0.209327
C	2.932194	0.488152	0.232328
F	4.298374	-1.428408	0.143027
F	2.792210	1.662655	-0.395442
C	1.674437	-0.379340	-0.018540
F	3.057417	0.699714	1.544544
F	1.765095	-0.941445	-1.229275
F	1.626962	-1.341361	0.910716
C	0.368806	0.450909	0.049917
F	0.232391	1.131443	-1.094504
C	-0.884644	-0.438518	0.251831
F	0.457479	1.310629	1.070974
F	-0.761304	-1.534304	-0.505395
F	-0.961219	-0.794498	1.538505
C	-2.193199	0.297877	-0.136815
F	-2.301407	0.285581	-1.481942
C	-3.467748	-0.366957	0.442993
F	-2.119759	1.560645	0.281474
F	-3.342410	-1.697943	0.339460
F	-3.579968	-0.034428	1.725099
C	-4.788603	0.124304	-0.243983
O	-4.997868	1.386282	-0.154559
O	-4.944768	-0.486677	-1.457387
H	-4.197981	-0.323883	-2.083020

Table 25 Cartesians coordinates of 1^1A PHBS optimized at the CAM-B3LYP/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-3.830858	0.364888	0.001819
H	-3.834339	0.990649	-0.891291
H	-4.768275	-0.189632	0.023501
C	-2.630697	-0.572170	0.007177
H	-3.814812	1.026350	0.868661
H	-2.682458	-1.238455	-0.856788
C	-1.301928	0.176116	-0.011607
H	-2.670136	-1.213344	0.890576
H	-1.260382	0.823329	-0.888570
H	-1.238560	0.824337	0.863415
C	-0.113955	-0.769182	-0.027536
H	-0.109818	-1.388215	-0.923193
S	1.476431	0.055679	0.001933
H	-0.117332	-1.427558	0.839715
O	2.473185	-1.024949	-0.054723
O	1.527650	0.809308	1.264335
O	1.516395	0.928612	-1.181622

Table 26 Cartesians coordinates of 1^1A PHBS optimized at the M06-2X/6-311+G(2d,2p) level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-3.817915	0.370052	0.002810
H	-3.807115	1.004207	-0.884735
H	-4.760796	-0.175464	0.015115
C	-2.624158	-0.578303	0.003377
H	-3.794325	1.021434	0.877571
H	-2.674716	-1.237688	-0.866543
C	-1.293397	0.169999	-0.009943
H	-2.664110	-1.223169	0.884642
H	-1.245512	0.814006	-0.890454
H	-1.232132	0.818803	0.866295
C	-0.109061	-0.781881	-0.016879
H	-0.104956	-1.409003	-0.908334
S	1.471982	0.056732	0.001329
H	-0.110865	-1.428385	0.860746
O	2.481305	-1.011503	-0.023200
O	1.503080	0.840727	1.244400
O	1.504365	0.899320	-1.202670

Table 27 Cartesians coordinates of 1^1A PFBS optimized at the CAM-B3LYP/aug-cc-pVTZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	2.777147	-0.303528	-0.066561
F	2.945988	-0.523969	-1.363910
F	3.814195	0.398959	0.379323
C	1.475121	0.502902	0.197405
F	2.746274	-1.469263	0.571314
F	1.494476	1.568874	-0.619357
C	0.163661	-0.308953	-0.021218
F	1.516827	0.930556	1.467426
F	0.312114	-1.057228	-1.128211
F	0.016024	-1.129525	1.030743
C	-1.099458	0.577773	-0.180434
F	-1.085192	1.098448	-1.421532
S	-2.735286	-0.299209	0.073062
F	-1.025328	1.598285	0.699446
O	-3.686045	0.686030	-0.431995
O	-2.800756	-0.526285	1.511872
O	-2.607282	-1.504501	-0.740041

Table 28 Cartesians coordinates of 1^1A PFBS optimized at the M06-2X/aug-cc-pVTZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	2.755901	-0.302377	-0.074971
F	2.913237	-0.501508	-1.374693
F	3.800785	0.378471	0.377852
C	1.464983	0.507808	0.206766
F	2.709271	-1.476283	0.542985
F	1.472653	1.571642	-0.609168
C	0.161061	-0.310863	-0.003988
F	1.517527	0.930573	1.474953
F	0.321301	-1.075701	-1.095468
F	0.002410	-1.108771	1.060910
C	-1.091611	0.579437	-0.185939
F	-1.065600	1.079880	-1.432584
S	-2.715831	-0.297325	0.069076
F	-1.014787	1.608675	0.680639
O	-3.668102	0.663292	-0.474793
O	-2.797532	-0.486181	1.511443
O	-2.559352	-1.520817	-0.709807

Table 29 Cartesians coordinates of 1^1A PFBS optimized at the CAM-B3LYP/aug-cc-pVDZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	2.766585	-0.301963	-0.065682
F	2.934169	-0.520375	-1.363196
F	3.802799	0.400309	0.381452
C	1.467774	0.501410	0.196811
F	2.734513	-1.467895	0.571284
F	1.487438	1.566985	-0.620433
C	0.161148	-0.310390	-0.023166
F	1.507697	0.927157	1.467463
F	0.310095	-1.054020	-1.133348
F	0.017605	-1.134051	1.026806
C	-1.098890	0.575425	-0.178597
F	-1.079769	1.099558	-1.419190
S	-2.726504	-0.298850	0.073411
F	-1.018720	1.594910	0.703534
O	-3.674320	0.681737	-0.430297
O	-2.785764	-0.523030	1.507249
O	-2.592175	-1.498519	-0.736967

Table 30 Cartesians coordinates of 1^1A PFBS optimized at the M06-2X/aug-cc-pVDZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	2.755532	-0.302111	-0.076249
F	2.913319	-0.494776	-1.383491
F	3.807044	0.376000	0.382888
C	1.467449	0.506867	0.208782
F	2.705487	-1.485617	0.537208
F	1.471838	1.576013	-0.611724
C	0.164475	-0.309640	-0.000613
F	1.522499	0.933014	1.482202
F	0.325760	-1.080305	-1.095023
F	0.001592	-1.108337	1.070586
C	-1.083385	0.582522	-0.187663
F	-1.059457	1.080507	-1.440123
S	-2.719290	-0.297921	0.068926
F	-1.011222	1.616789	0.681015
O	-3.685572	0.662455	-0.528394
O	-2.821544	-0.447759	1.543896
O	-2.543824	-1.567033	-0.688026

Table 31 Cartesians coordinates of 1^1A PFOS optimized at the CAM-B3LYP/aug-cc-pVTZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-5.384226	0.180866	-0.204256
F	-5.523968	-0.353861	-1.409430
F	-6.401142	-0.210809	0.554420
C	-4.058158	-0.285962	0.459568
F	-5.411345	1.505317	-0.309115
F	-4.003658	-1.623012	0.359919
C	-2.779413	0.336354	-0.175583
F	-4.108295	0.053640	1.753443
F	-2.919944	0.344227	-1.509305
F	-2.670236	1.601620	0.255752
C	-1.475491	-0.442057	0.183582
F	-1.423841	-1.548277	-0.572467
C	-0.178776	0.395135	-0.049620
F	-1.528245	-0.798358	1.475320
F	-0.309375	1.078092	-1.197052
F	-0.051233	1.264659	0.963129
C	1.108930	-0.483277	-0.136565
F	1.143332	-1.054394	-1.350202
C	2.425071	0.326127	0.089640
F	1.032921	-1.448058	0.794264
F	2.309331	1.504369	-0.546978
F	2.542104	0.557598	1.405866
C	3.695535	-0.399109	-0.429797
F	3.721747	-0.280821	-1.770048
S	5.320635	0.241615	0.248784
F	3.599913	-1.711166	-0.129183
O	6.288421	-0.404426	-0.632042
O	5.345041	-0.229059	1.628583
O	5.212341	1.688334	0.088792

Table 32 Cartesians coordinates of 1^1A PFOS optimized at the M06-2X/aug-cc-pVTZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-5.349666	0.172343	-0.189898
F	-5.500594	-0.407916	-1.369434
F	-6.360700	-0.179152	0.591003
C	-4.024004	-0.274140	0.478274
F	-5.361538	1.489833	-0.345644
F	-3.963768	-1.611020	0.416127
C	-2.759965	0.331450	-0.189937
F	-4.062002	0.106084	1.758511
F	-2.920151	0.308804	-1.518983
F	-2.635179	1.602817	0.212500
C	-1.462906	-0.444774	0.176129
F	-1.403940	-1.556313	-0.567337
C	-0.177819	0.394929	-0.071427
F	-1.516942	-0.782765	1.470559
F	-0.318586	1.055435	-1.228547
F	-0.047010	1.277146	0.926887
C	1.103408	-0.483724	-0.144813
F	1.143185	-1.072316	-1.347871
C	2.408701	0.335818	0.065617
F	1.025699	-1.428552	0.803183
F	2.287692	1.488333	-0.611448
F	2.520118	0.608559	1.372110
C	3.674972	-0.409227	-0.425741
F	3.716692	-0.317336	-1.765189
S	5.277380	0.242900	0.268387
F	3.563432	-1.711690	-0.098934
O	6.264611	-0.386143	-0.601159
O	5.288624	-0.232422	1.645647
O	5.145258	1.687065	0.110406

Table 33 Cartesians coordinates of 1^1A PFOS optimized at the CAM-B3LYP/aug-cc-pVDZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-5.388733	0.179326	-0.198615
F	-5.532185	-0.357266	-1.410239
F	-6.408527	-0.216747	0.565946
C	-4.061416	-0.284560	0.459704
F	-5.419990	1.510883	-0.302963
F	-4.007664	-1.629337	0.361765
C	-2.783198	0.333553	-0.176348
F	-4.108169	0.057687	1.760523
F	-2.924699	0.336787	-1.517526
F	-2.675520	1.608352	0.250962
C	-1.477803	-0.438345	0.182859
F	-1.427101	-1.555243	-0.570989
C	-0.181764	0.394502	-0.055962
F	-1.527174	-0.791408	1.483410
F	-0.313955	1.076217	-1.212596
F	-0.053007	1.275294	0.956777
C	1.106444	-0.479877	-0.140394
F	1.140368	-1.059475	-1.358333
C	2.422891	0.326499	0.079772
F	1.032633	-1.447764	0.797974
F	2.309920	1.506310	-0.569417
F	2.540680	0.570301	1.401032
C	3.692919	-0.402328	-0.431430
F	3.731888	-0.288166	-1.776823
S	5.328813	0.240999	0.256521
F	3.600585	-1.718499	-0.123036
O	6.319554	-0.411696	-0.647540
O	5.355306	-0.250328	1.663215
O	5.217665	1.720784	0.103070

Table 34 Cartesians coordinates of 1^1A PFOS optimized at the M06-2X/aug-cc-pVDZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	-5.340926	0.152346	-0.198461
F	-5.484546	-0.467627	-1.366120
F	-6.358677	-0.182530	0.592144
C	-4.016877	-0.265346	0.485476
F	-5.359806	1.471151	-0.395995
F	-3.940020	-1.608856	0.447536
C	-2.757311	0.340909	-0.185446
F	-4.067086	0.138421	1.764608
F	-2.920658	0.314253	-1.520774
F	-2.632013	1.619560	0.214270
C	-1.462576	-0.432416	0.181409
F	-1.405328	-1.552541	-0.561335
C	-0.179493	0.403372	-0.070568
F	-1.518297	-0.766580	1.483312
F	-0.323325	1.064544	-1.234234
F	-0.043972	1.292706	0.929719
C	1.096982	-0.477058	-0.143520
F	1.134092	-1.071237	-1.350722
C	2.403081	0.336769	0.063937
F	1.015018	-1.424713	0.810190
F	2.282929	1.495627	-0.614698
F	2.520834	0.609192	1.376237
C	3.662169	-0.412374	-0.432459
F	3.708019	-0.314996	-1.775824
S	5.277701	0.233395	0.267816
F	3.548441	-1.719821	-0.106768
O	6.281377	-0.386835	-0.638006
O	5.298604	-0.282268	1.661897
O	5.135777	1.709040	0.137212

Table 35 Cartesians coordinates of 1^1A PFOA optimized at the CAM-B3LYP/aug-cc-pVTZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.272885	-0.206644	-0.232906
F	4.361512	-0.217070	-1.555825
F	5.301587	0.476703	0.255631
C	2.955118	0.475645	0.230992
F	4.334130	-1.455333	0.217729
F	2.861203	1.651968	-0.407939
C	1.675471	-0.370797	-0.038412
F	3.055981	0.701442	1.546955
F	1.778949	-0.933152	-1.252072
F	1.617096	-1.342666	0.884539
C	0.361096	0.468355	0.013957
F	0.260498	1.157843	-1.132236
C	-0.918713	-0.404868	0.203137
F	0.447595	1.333877	1.036095
F	-0.793203	-1.506964	-0.555140
F	-0.983324	-0.771232	1.493017
C	-2.236437	0.330273	-0.186223
F	-2.311330	0.352405	-1.532347
C	-3.529685	-0.324348	0.362983
F	-2.151555	1.598146	0.255028
F	-3.366467	-1.667748	0.295583
F	-3.635570	-0.007379	1.678437
C	-4.810905	0.146451	-0.415829
O	-5.092909	1.337178	-0.222117
O	-5.357953	-0.714926	-1.112046

Table 36 Cartesians coordinates of 1^1A PFOA optimized at the M06-2X/aug-cc-pVTZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.240997	-0.196455	-0.253238
F	4.310817	-0.161200	-1.574361
F	5.277241	0.461876	0.245931
C	2.934518	0.471673	0.247138
F	4.293676	-1.458541	0.153256
F	2.823141	1.659826	-0.361646
C	1.663574	-0.376792	-0.031467
F	3.050091	0.662149	1.564778
F	1.771119	-0.926288	-1.248136
F	1.599883	-1.352615	0.884149
C	0.358565	0.464941	0.028418
F	0.254062	1.162336	-1.110426
C	-0.913271	-0.412143	0.208357
F	0.450493	1.316626	1.058979
F	-0.776609	-1.508033	-0.553428
F	-0.988923	-0.780798	1.494534
C	-2.218984	0.329444	-0.189589
F	-2.293389	0.340938	-1.533039
C	-3.508002	-0.318303	0.367199
F	-2.120582	1.596848	0.244471
F	-3.337305	-1.659143	0.314345
F	-3.613380	0.018047	1.674252
C	-4.779802	0.147551	-0.428297
O	-5.043290	1.346428	-0.259412
O	-5.327785	-0.722398	-1.112347

Table 37 Cartesians coordinates of 1^1A PFOA optimized at the CAM-B3LYP/aug-cc-pVDZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.274440	-0.207200	-0.229924
F	4.363994	-0.231490	-1.559630
F	5.306813	0.487798	0.253047
C	2.956246	0.474032	0.226826
F	4.341416	-1.457555	0.236137
F	2.863950	1.654415	-0.420596
C	1.675577	-0.368826	-0.039210
F	3.055339	0.708060	1.548925
F	1.776982	-0.936005	-1.259053
F	1.619318	-1.346750	0.888428
C	0.361005	0.466467	0.014073
F	0.261239	1.161921	-1.137414
C	-0.919386	-0.402879	0.201938
F	0.447291	1.337172	1.041680
F	-0.793718	-1.511467	-0.560251
F	-0.982780	-0.773064	1.498641
C	-2.237373	0.329045	-0.185625
F	-2.309589	0.354301	-1.539528
C	-3.532800	-0.323594	0.359483
F	-2.152190	1.603924	0.258881
F	-3.366452	-1.675111	0.291498
F	-3.635920	-0.008750	1.683879
C	-4.815124	0.146658	-0.413183
O	-5.095740	1.344425	-0.219257
O	-5.371352	-0.718026	-1.109251

Table 38 Cartesians coordinates of 1^1A PFOA optimized at the M06-2X/aug-cc-pVDZ level of theory in water (IEF-PCM). Values are given in Å

Atom	X	Y	Z
C	4.232966	-0.189660	-0.261873
F	4.296132	-0.124246	-1.588768
F	5.276111	0.461196	0.248982
C	2.929317	0.462344	0.258280
F	4.291387	-1.466939	0.117645
F	2.809908	1.667699	-0.329853
C	1.660313	-0.381536	-0.030423
F	3.050707	0.629599	1.584479
F	1.768046	-0.920140	-1.259272
F	1.593621	-1.373322	0.876821
C	0.359161	0.460675	0.037012
F	0.259240	1.175205	-1.099240
C	-0.913027	-0.413207	0.204342
F	0.452162	1.304913	1.082002
F	-0.775440	-1.508449	-0.568820
F	-0.995416	-0.794347	1.493133
C	-2.213125	0.334390	-0.192089
F	-2.282776	0.351419	-1.542166
C	-3.502800	-0.311592	0.362374
F	-2.106984	1.605913	0.248730
F	-3.322580	-1.659093	0.317080
F	-3.608017	0.031148	1.674919
C	-4.778012	0.145076	-0.430054
O	-5.026321	1.356728	-0.287724
O	-5.349137	-0.739721	-1.085582

Table 39 S^2 operator values for the open-shell H, F, PFES, PFBS, PFOS, and PFOA as obtained using the UCAM-B3LYP/6-311+G(2d,2p) and UM06-2X/6-311+G(2d,2p) in water (IEF-PCM). For the PFES, values obtained using the UMP2-2X/6-311+G(2d,2p), UCCSD/6-311+G(2d,2p), and UCCSD(T)/6-311+G(2d,2p) approaches are given in parentheses, square brackets, and angle brackets, respectively.

Radical	UCAM-B3LYP/ 6-311+G(2d,2p)	UM06-2X/ 6-311+G(2d,2p)
H	0.75	0.75
F	0.751	0.751
PFES		
C_1	0.754	0.755
	(0.761)	[0.760] <0.763>
C_2	0.753	0.754
	(0.757)	[0.757] <0.757>
PFBS		
C_1	0.754	0.755
C_2	0.754	0.755
C_3	0.753	0.754
C_4	0.752	0.753
PFOS		
C_1	0.754	0.755
C_2	0.754	0.755
C_3	0.754	0.755
C_4	0.754	0.755
C_5	0.754	0.755
C_6	0.753	0.754
C_7	0.754	0.755
C_8	0.752	0.753
PFOA		
C_2	0.755	0.756
C_3	0.754	0.755
C_4	0.754	0.755
C_5	0.754	0.755
C_6	0.754	0.755
C_7	0.754	0.755
C_8	0.752	0.753
PHBS		
C_1	0.754	0.755
C_2	0.754	0.755
C_3	0.754	0.755
C_4	0.754	0.755

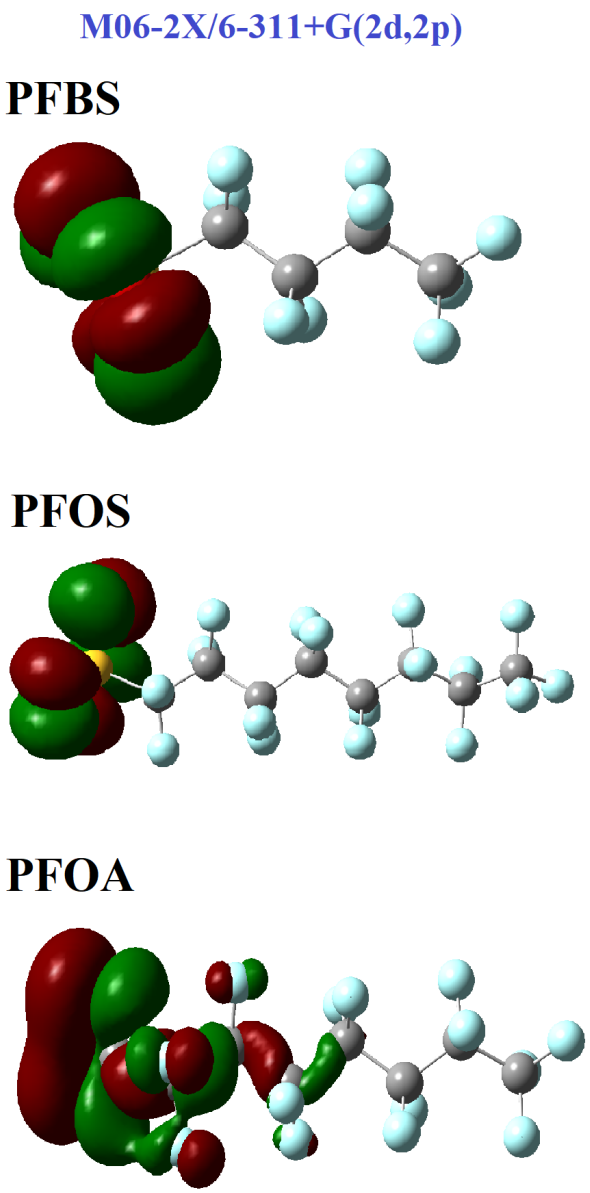

Fig. 1 Highest occupied molecular orbital (HOMO) for PFBS, PFOS, and PFOA as determined in water (IEF-PCM). All plots generated with the same (default) isovalue.

Table 40 Vertical excitation energies (in eV) and GOS (values in parentheses) for PFBS, PFOS, and PFOA in water (IEF-PCM).

	PFBS	
	CAM-B3LYP/aug-cc-pVDZ	M06-2X/aug-cc-pVDZ
2^1A	7.18 (0.0006)	7.26 (0.0005)
3^1A	7.64 (0.0069)	7.67 (0.0108)
4^1A	7.83 (0.0170)	7.86 (0.2003)
5^1A	7.94 (0.2318)	7.92 (0.0223)
	PFOS	
	CAM-B3LYP/aug-cc-pVDZ	M06-2X/aug-cc-pVDZ
2^1A	6.97 (0.0019)	7.24 (0.0009)
3^1A	7.26 (0.0044)	7.56 (0.0371)
4^1A	7.53 (0.3642)	7.69 (0.3292)
5^1A	7.70 (0.0154)	7.87 (0.0105)
	PFOA	
	CAM-B3LYP/aug-cc-pVDZ	M06-2X/aug-cc-pVDZ
2^1A	5.75 (0.0001)	5.78 (0.0004)
3^1A	5.90 (0.0171)	5.82 (0.0121)
4^1A	6.79 (0.0010)	7.00 (0.0121)
5^1A	6.96 (0.1048)	7.05 (0.0705)

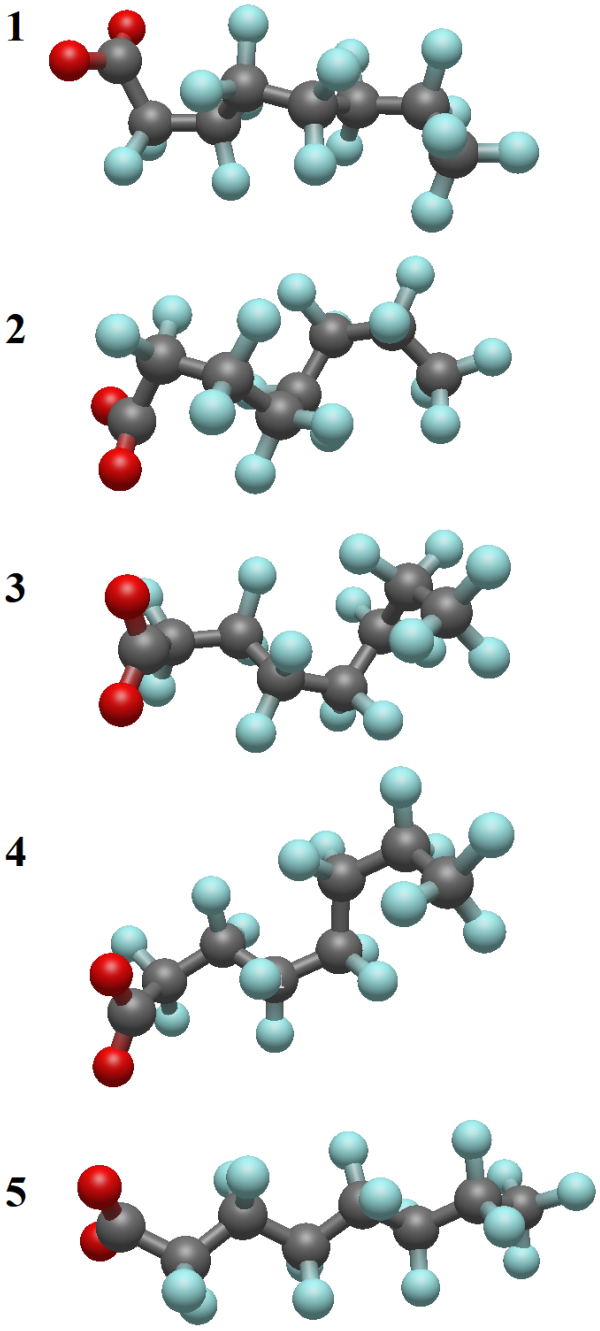

Fig. 2 The most likely conformations for PFOA as suggested by the molecular dynamics simulation.

Table 41 Vertical excitation energies (in eV) and GOS (values in parentheses) for the lowest four transitions of the most likely conformations of PFOA in water (IEF-PCM).

	Conformation 1	
	CAM-B3LYP/6-311+G(2d,2p)	M06-2X/6-311+G(2d,2p)
2^1A	5.09 (0.0002)	5.03 (0.0002)
3^1A	5.73 (0.0036)	5.60 (0.00.35)
4^1A	6.53 (0.0427)	6.54 (0.0691)
5^1A	6.71 (0.0498)	6.93 (0.0282)
	Conformation 2	
	CAM-B3LYP/6-311+G(2d,2p)	M06-2X/6-311+G(2d,2p)
2^1A	5.63 (0.0007)	5.53 (0.0015)
3^1A	5.75 (0.0027)	5.65 (0.0015)
4^1A	6.46 (0.0025)	6.60 (0.0060)
5^1A	6.79 (0.0507)	6.91 (0.0374)
	Conformation 3	
	CAM-B3LYP/6-311+G(2d,2p)	M06-2X/6-311+G(2d,2p)
2^1A	5.08 (0.0001)	5.02 (0.0001)
3^1A	5.88 (0.0006)	5.76 (0.0008)
4^1A	6.44 (0.0271)	6.56 (0.0723)
5^1A	6.52 (0.0361)	6.81 (0.0141)
	Conformation 4	
	CAM-B3LYP/6-311+G(2d,2p)	M06-2X/6-311+G(2d,2p)
2^1A	5.18 (0.0006)	5.13 (0.0004)
3^1A	5.46 (0.0005)	5.35 (0.0006)
4^1A	6.56 (0.0788)	6.58 (0.0931)
5^1A	6.97 (0.0230)	7.18 (0.0127)
	Conformation 5	
	CAM-B3LYP/6-311+G(2d,2p)	M06-2X/6-311+G(2d,2p)
2^1A	5.84 (0.0001)	5.86 (0.0005)
3^1A	5.97 (0.0193)	5.89 (0.0136)
4^1A	6.92 (0.0035)	7.12 (0.0319)
5^1A	7.09 (0.0969)	7.21 (0.0559)

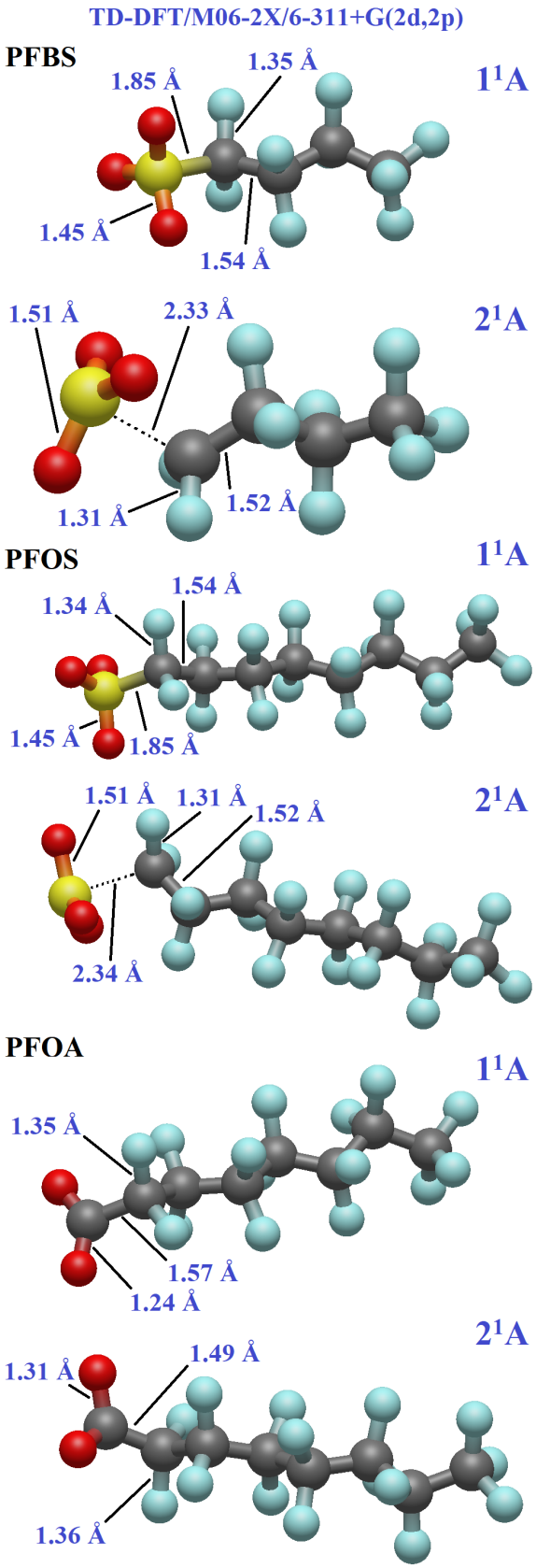

Fig. 3 Optimized structures of ground (1^1A) and excited (2^1A) states of PFBS, PFOS, and PFOA. Results determined in water (IEF-PCM).

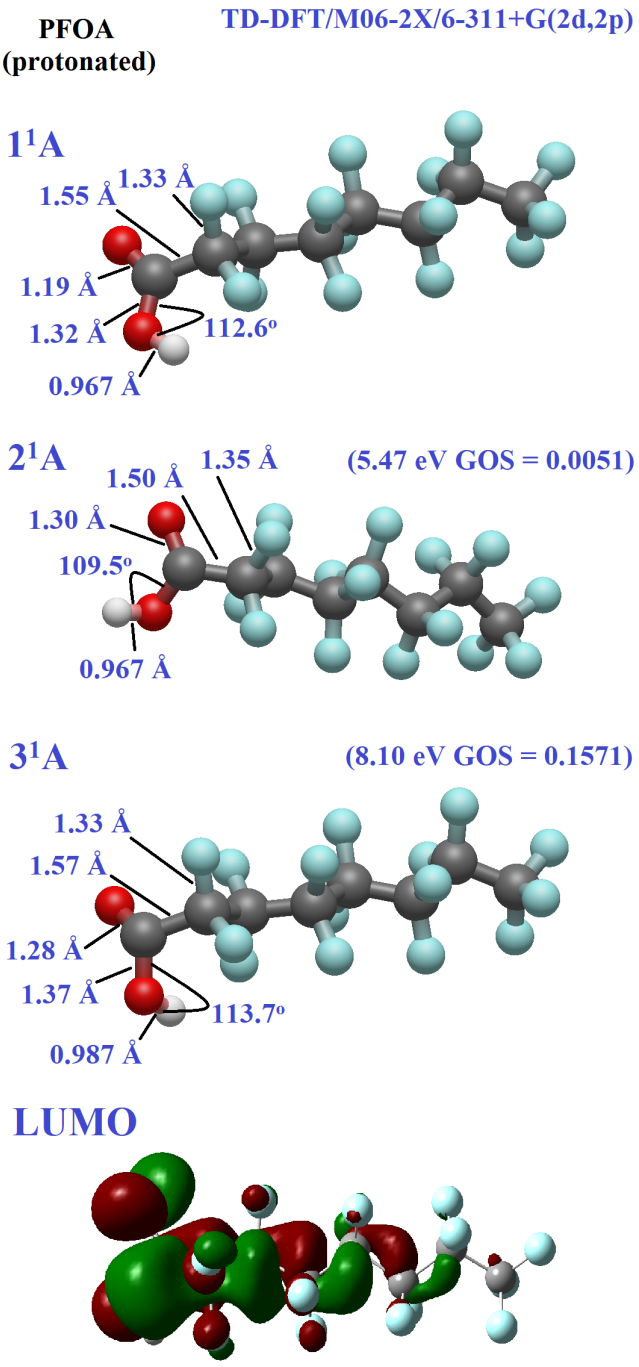

Fig. 4 Optimized structures of ground (1^1A) and excited (2^1A and 3^1A) states, and lowest unoccupied molecular orbital (LUMO) for protonated PFOA. Results determined in water (IEF-PCM).