Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information
Electron scattering data and potential energy landscapes for plasma modelling of perfluoroalkyl substances

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PFBA

	ADC(2) d-aug-cc-pVTZ	CCSD aug-cc-pVDZ	B3LYP def2-TZVPD	ωB97X-D def2-TZVPD	CASSCF aug-cc-pVDZ	CASPT2 aug-cc-pVDZ
S_1	5.33	5.62	5.41	5.51	5.50	5.51
S_2	7.57	7.96	7.43	8.04	7.55	7.86
S_3	8.02	8.54	7.62	8.21	8.89	9.90
S_4	8.49	8.86	8.18	8.69	x	x
S_5	8.81	8.96	8.42	9.00	7.96	9.20
S_6	8.82	9.48	8.50	9.18	9.49	8.71
S_7	9.04	9.81	8.58	9.25	9.73	10.13
S_8	9.29	10.05	8.71	9.71		
S_9	9.49	10.17	8.92	9.88		
S_{10}	9.65	10.34	9.18	10.01		

PFBS

	ADC(2) d-aug-cc-pVTZ	CCSD aug-cc-pVDZ	B3LYP def2-TZVPD	ωB97X-D def2-TZVPD	CASSCF aug-cc-pVDZ
S_1	7.74	8.22	7.53	8.08	8.33
S_2	7.90	8.39	7.64	8.22	8.74
S_3	8.09	8.62	7.94	8.43	9.07
S_4	8.29	8.78	8.07	8.65	9.22
S_5	8.44	8.90	8.15	8.67	9.59
S_6	8.50	9.00	8.33	8.73	10.13
S_7	8.71	9.09	8.35	8.95	10.24
S_8	8.74	9.31	8.42	9.03	
S_9	8.87	-	8.51	9.17	
S_{10}	9.02	-	8.66	9.32	

Table S1: Additional electronic structure results for PFBA and PFBS.

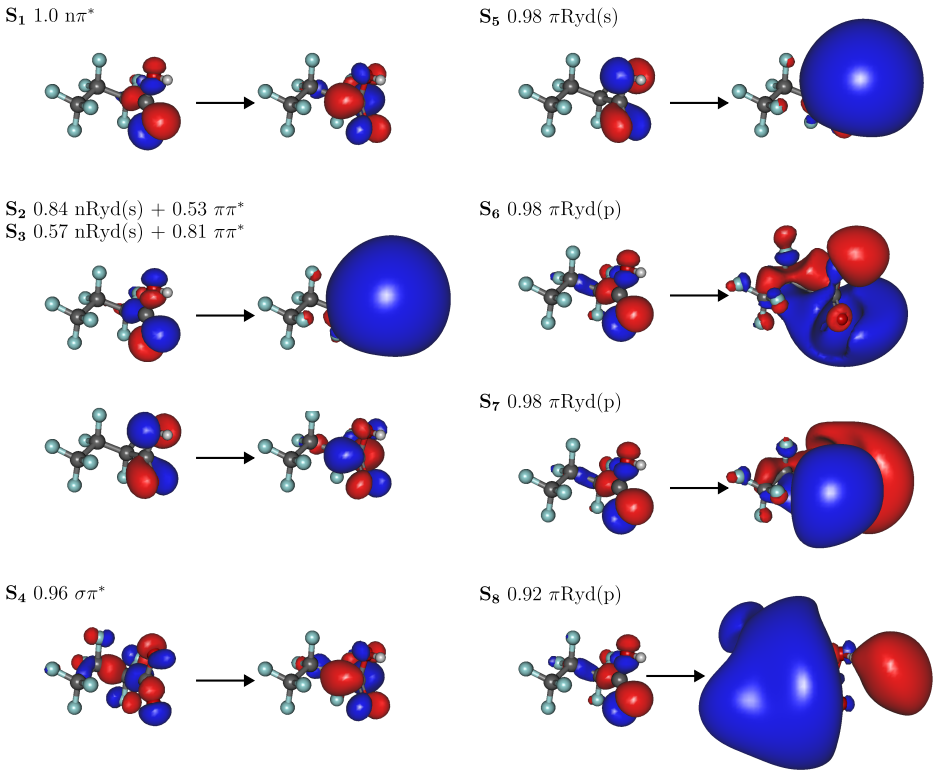

Figure S1: Dominant natural transition orbitals for the 8 lowest singlet excited states of PFBA calculated at the ADC(2)/aug-cc-pVDZ level. In the case of S_2 and S_3 the NTOs for the two states are almost identical due to the two states being a mixture of the same two dominant contributions so only the NTOs of S_2 are shown. Rydberg-like orbitals are shown with an isovalue 0.02, while other orbitals are shown with an isovalue of 0.05.

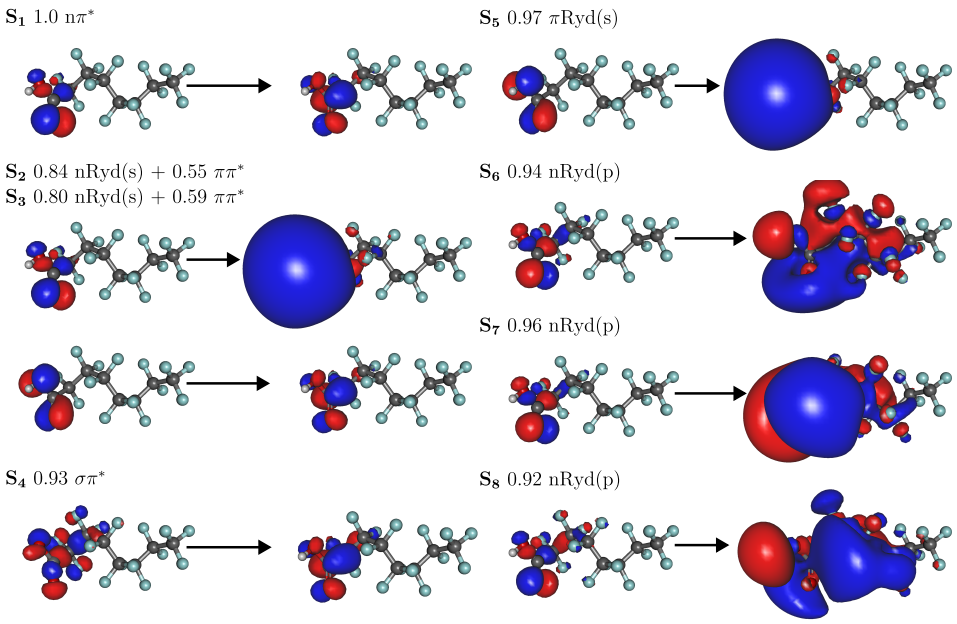

Figure S2: Dominant natural transition orbitals for the 8 lowest singlet excited states of PFOA calculated at the ADC(2)/aug-cc-pVDZ level. In the case of S_2 and S_3 the NTOs for the two states are almost identical due to the two states being a mixture of the same two dominant contributions so only the NTOs of S_2 are shown. Rydberg-like orbitals are shown with an isovalue 0.015, while other orbitals are shown with an isovalue of 0.05.

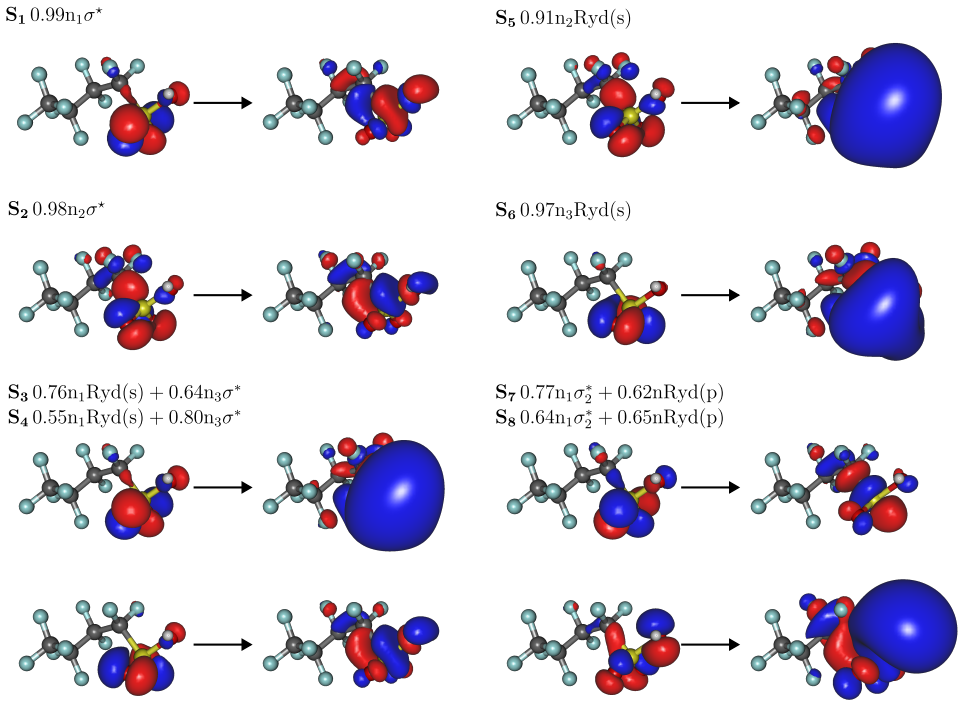

Figure S3: Dominant natural transition orbitals for the 8 lowest singlet excited states of PFBS calculated at the ADC(2)/aug-cc-pVDZ level. In the case of S_3/S_4 and S_7/S_8 the NTOs for the two states are almost identical due to the two states being a mixture of the same two dominant contributions so only the NTOs of S_3 and S_7 are shown. Rydberg-like orbitals are shown with an isovalue 0.02, while other orbitals are shown with an isovalue of 0.05.

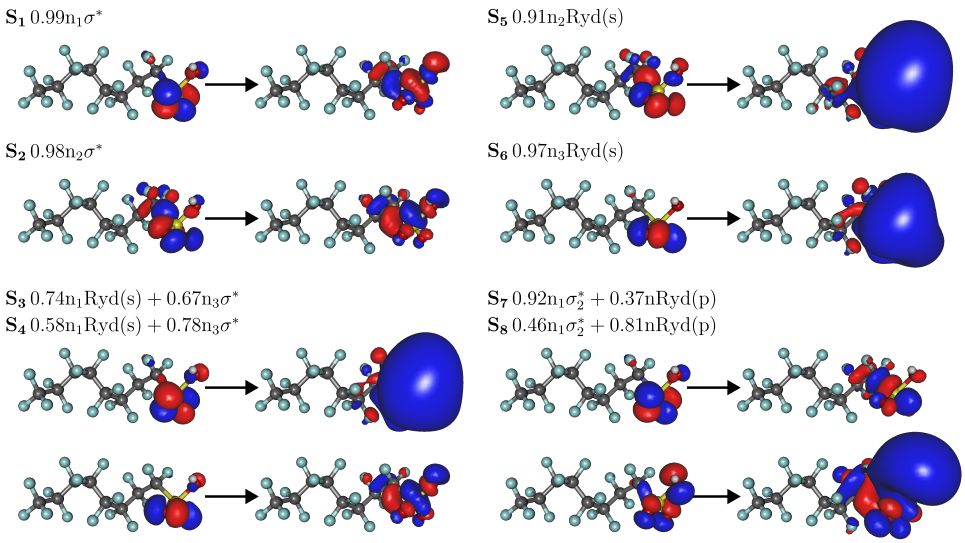

Figure S4: Dominant natural transition orbitals for the 8 lowest singlet excited states of PFOS calculated at the ADC(2)/aug-cc-pVDZ level. In the case of S_3/S_4 and S_7/S_8 the NTOs for the two states are almost identical due to the two states being a mixture of the same two dominant contributions so only the NTOs of S_3 and S_7 are shown. Rydberg-like orbitals are shown with an isovalue 0.015, while other orbitals are shown with an isovalue of 0.05.

PFBA		PFBS	
State	Transition	State	Transition
S_1	0.98 $n\pi^*$	S_1	0.81 $n_2\sigma_1^*$
S_2	0.66 $\pi_1\pi^*$ + 0.56 nRyd(s)	S_2	0.54 n_3Ryd + 0.52 n_2Ryd
S_3	0.92 π_1Ryd(s)	S_3	0.52 $n_1\sigma_1^*$ + 0.45 n_1Ryd
S_4	0.60 $\pi_1\pi^*$ + 0.72 nRyd(s)	S_4	0.68 $n_2\sigma_2^*$ + 0.35 $n_1\sigma_1^*$
S_5	0.98 $\sigma\pi^*$	S_5	0.89 $n_1\sigma_2^*$
S_6	0.82 π_2Ryd(s)	S_6	0.57 $n_2\sigma_1^*$ + 0.48 n_1Ryd
S_7	0.87 $\pi_2\pi^*$	S_7	0.60 $n_3\sigma_1^*$+ 0.32 $n_1\sigma_1^*$

Table S2: Dominant transitions for the seven lowest excited singlet states of PFBA and PFBS at the CASSCF/cc-pVDZ level. The active space orbitals are shown in Fig. S5.

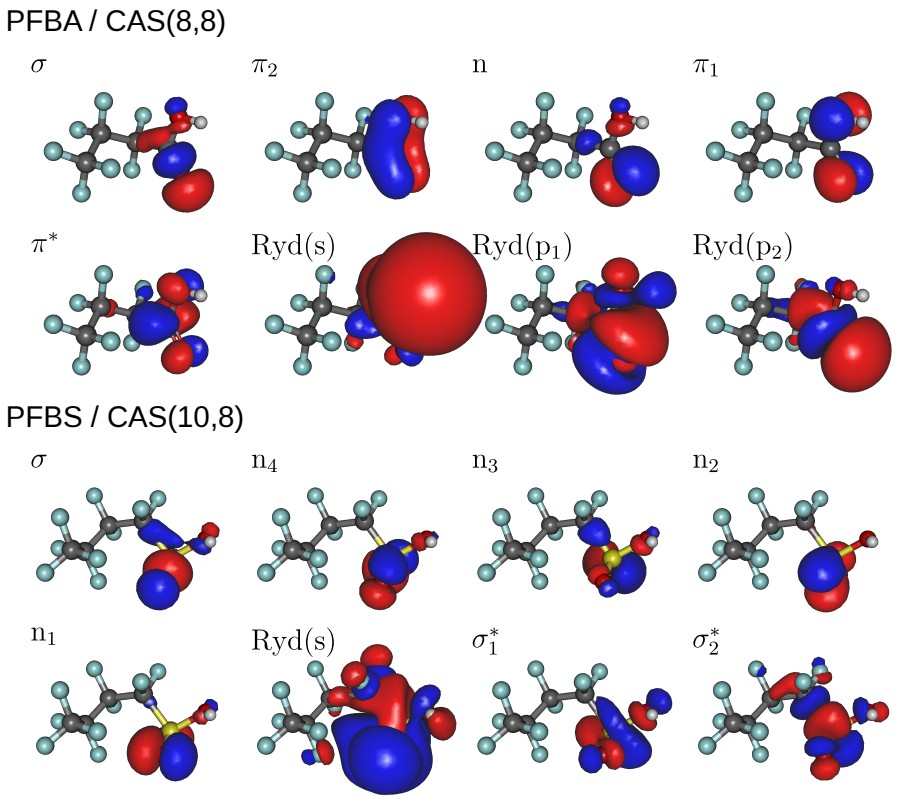

Figure S5: Active space orbitals of PFBA and PFBS at the CASSCF/cc-pVDZ level. Rydberg-like orbitals are shown with an isovalue 0.015, while other orbitals are shown with an isovalue of 0.05.

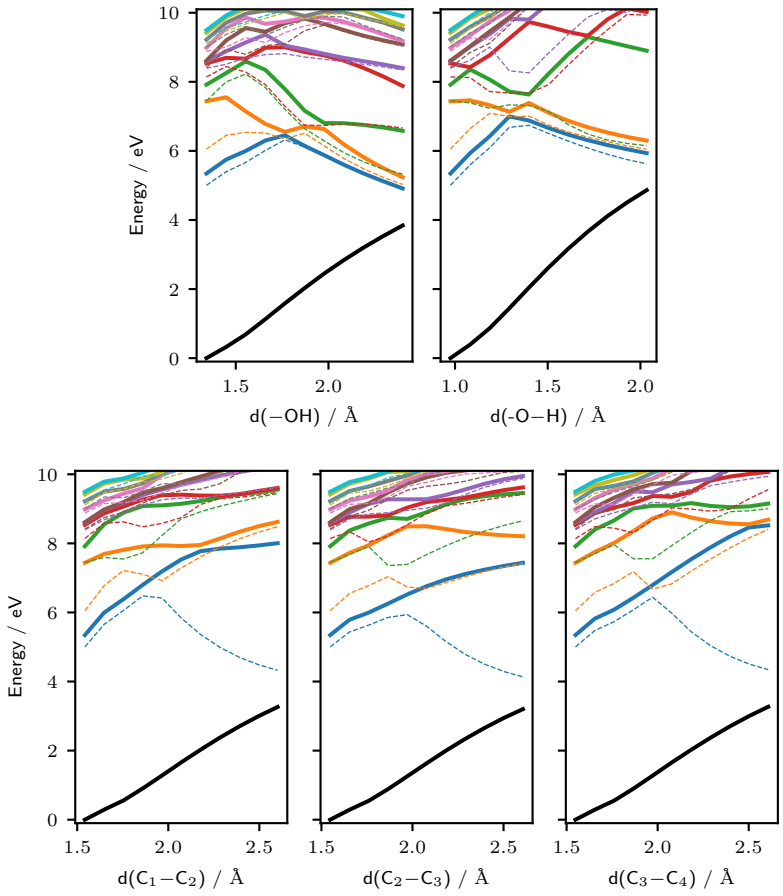

Figure S6: Scan of the PES of PFOA along the H, OH, C_1-C_2, C_2-C_3 and C_3-C_4 dissociation coordinates at the RI-ADC(2)/aug-cc-pVDZ level relaxed on the S_0 surface. The ten lowest singlet (full lines) and triplet (dashed lines) excited states are shown.

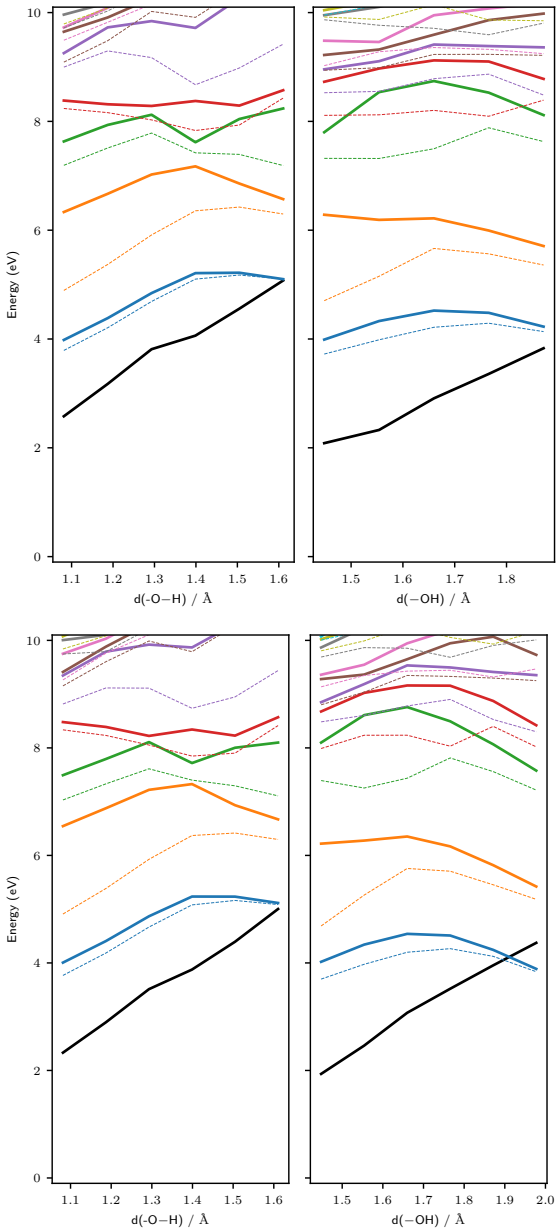

Figure S7: Scan of the PES of PFBA along the OH and H dissociation coordinates at the RI-ADC(2)/aug-cc-pVDZ level relaxed on the S_1 (upper panels) and T_1 (lower panels) surfaces. The ten lowest singlet (full lines) and triplet (dashed lines) excited states are shown.

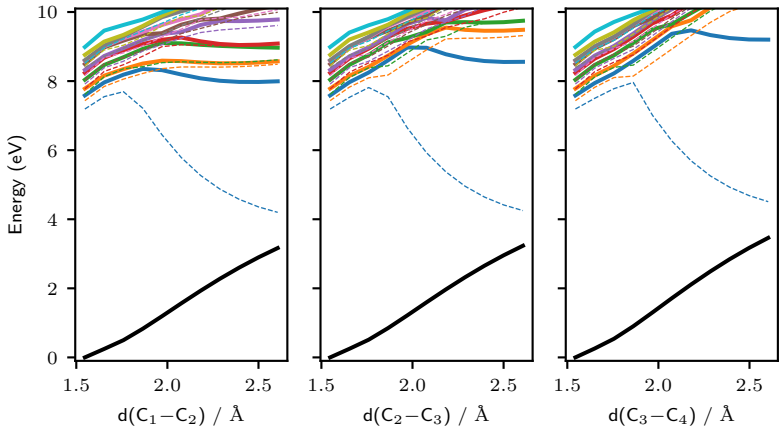

Figure S8: Scan of the PES of PFBS along the C_1-C_2, C_2-C_3 and C_3-C_4 dissociation coordinates at the RI-ADC(2)/aug-cc-pVDZ level relaxed on the S_0 surface. The ten lowest singlet (full lines) and triplet (dashed lines) excited states are shown.

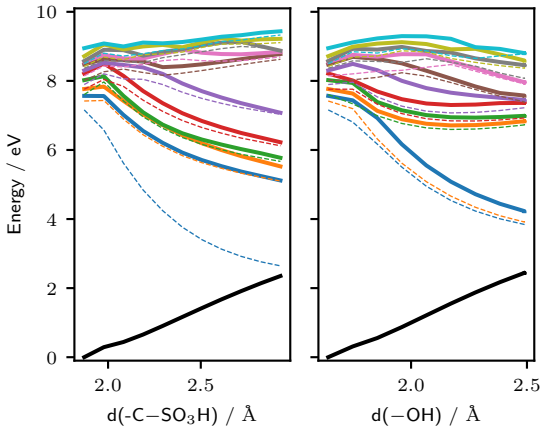

Figure S9: Scan of the PES of PFOS along the sulfo and OH dissociation coordinates at the RI-ADC(2)/aug-cc-pVDZ level relaxed on the S_0 surface. The ten lowest singlet (full lines) and triplet (dashed lines) excited states are shown.

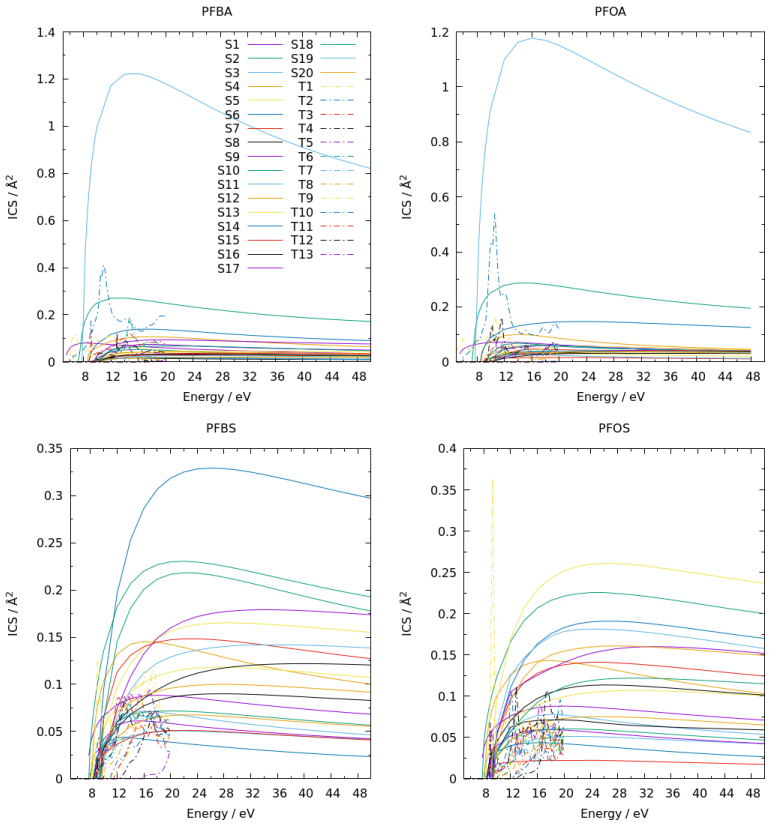

Figure S10: Recommended cross sections for impact excitation of singlet and triplet states of PFBA, PFOA, PFBS and PFOS calculated using the Born approximation and the R-matrix approach.

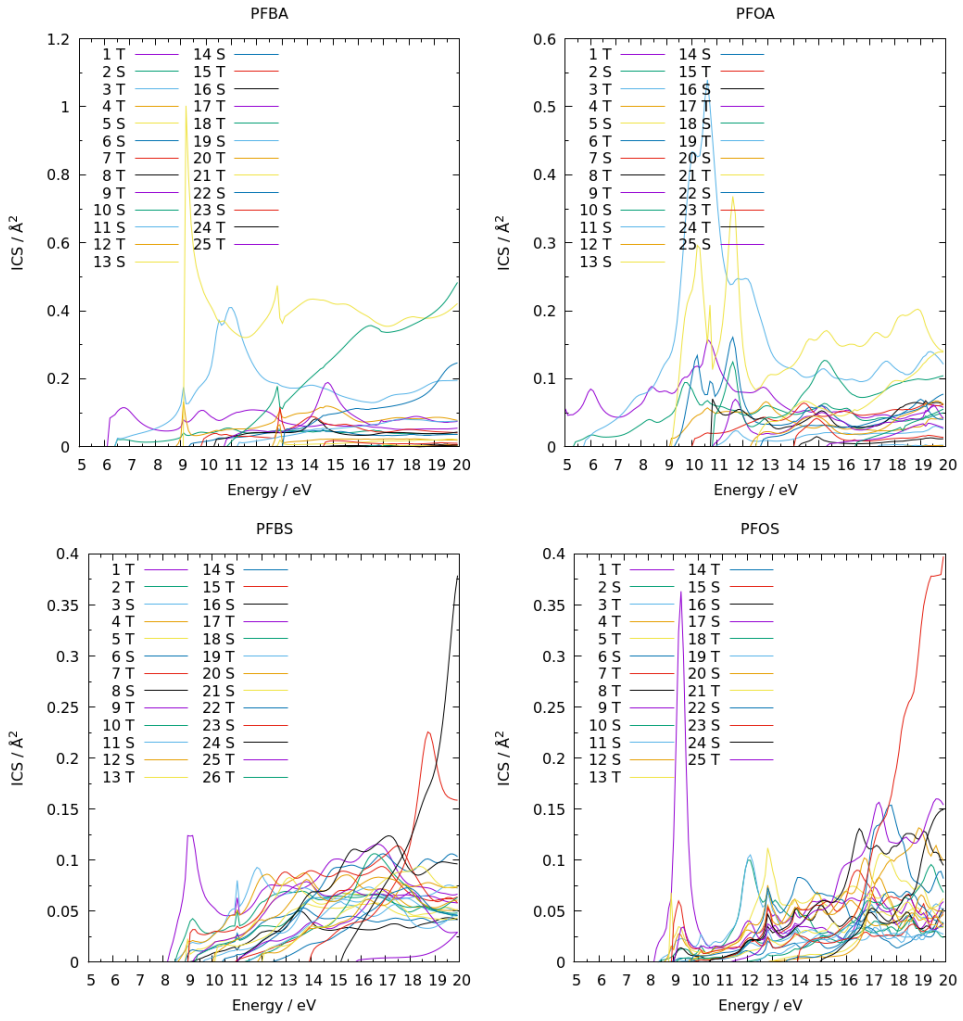

Figure S11: Complete set of R-matrix CAS inelastic cross sections for PFBA, PFOA (top row), PFBS, PFOS (bottom row) calculated on the CAS level.