Electronic Supplementary Information for “Ultrafast relaxation from the S_3 state of pyrene”

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Triply charged Pyrene

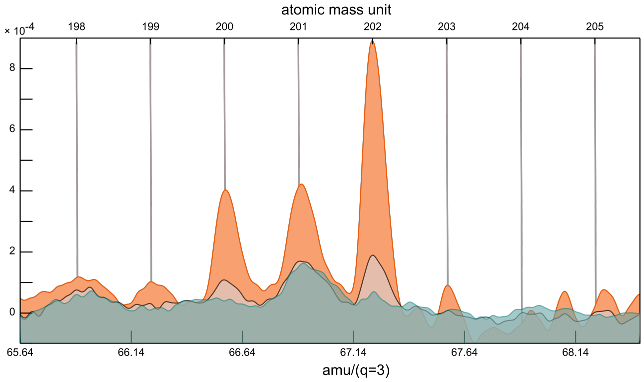


Figure S 1: A magnification of the signal from the triply charged ion, with the ions produced at dt=0fs traced in orange, at -250 fs in green, and at +250 fs in red.

Photoelectron images at three different pump probe delays

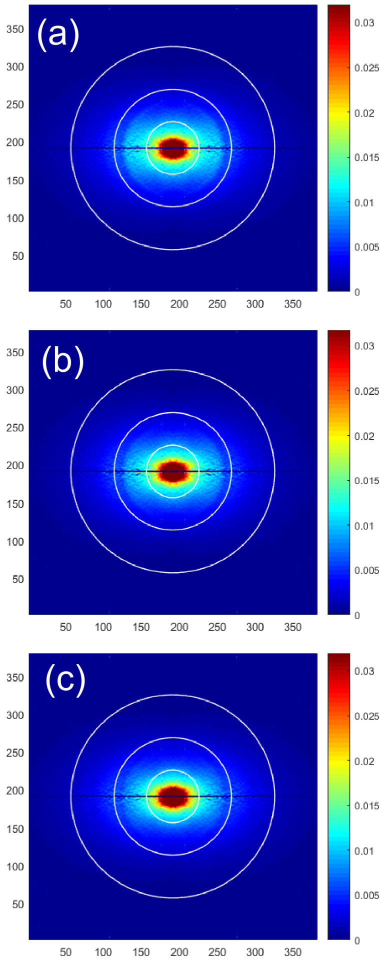
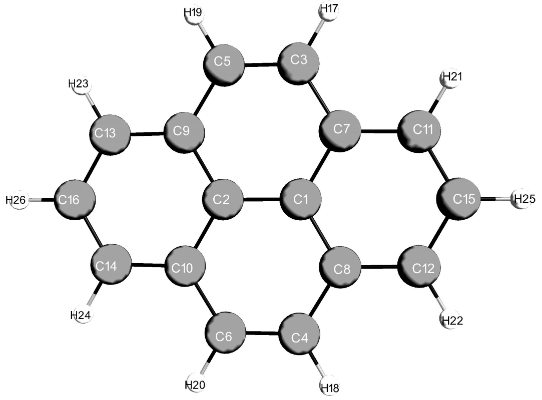


Figure S 2: Pump-probe photoelectron images at (a) 216 fs, (b) 405 fs, and (c) 5 ps delays. The contour plots has been normalised by the pixel of maximal intensity at 216 fs, *(i.e.)* 3.2×10^8. The anisotropies at 0.13 eV (D$_2\nu_{CC}$), 0.52 (D$_1\nu_{CC}+\nu_{CH}$), 0.9 eV (D$_1\nu_{CC}$), and 1.5 eV (D$_0$) are listed in Table 3.

Optimised B3LYP geometries

Table S 1: Calculated B3LYP/6-31+G* geometries of the ground state (GS), the bB$_{2u}$ (S$_3$) and the bB$_{3g}$ excited states (x,y,z coordinates in Angströms). The optimisations were performed without symmetry constraints but the final geometries have D$_{2h}$ point group symmetry. The Q-Chem code was used for all the geometry optimisations.



	GS			bB$_{3g}$			bB$_{2u}$		
C1	0.000000	0.000000	0.713999	0.000000	0.000000	0.744529	0.000000	0.000000	0.710124
C2	0.000000	0.000000	-0.713999	0.000000	0.000000	-0.744529	0.000000	0.000000	-0.710124
C3	0.000000	2.465754	0.681718	0.000000	2.438593	0.703583	0.000000	2.469369	0.690641
C4	0.000000	-2.465754	0.681718	0.000000	-2.438593	0.703583	0.000000	-2.469369	0.690641
C5	0.000000	2.465754	-0.681718	0.000000	2.438593	-0.703583	0.000000	2.469369	-0.690641
C6	0.000000	-2.465754	-0.681718	0.000000	-2.438593	-0.703583	0.000000	-2.469369	-0.690641
C7	0.000000	1.236993	1.430286	0.000000	1.244622	1.455074	0.000000	1.245796	1.438041
C8	0.000000	-1.236993	1.430286	0.000000	-1.244622	1.455074	0.000000	-1.245796	1.438041
C9	0.000000	1.236993	-1.430286	0.000000	1.244622	-1.455074	0.000000	1.245796	-1.438041
C10	0.000000	-1.236993	-1.430286	0.000000	-1.244622	-1.455074	0.000000	-1.245796	-1.438041
C11	0.000000	1.211911	2.835690	0.000000	1.216191	2.882655	0.000000	1.219867	2.849741
C12	0.000000	-1.211911	2.835690	0.000000	-1.216191	2.882655	0.000000	-1.219867	2.849741
C13	0.000000	1.211911	-2.835690	0.000000	1.216191	-2.882655	0.000000	1.219867	-2.849741
C14	0.000000	-1.211911	-2.835690	0.000000	-1.216191	-2.882655	0.000000	-1.219867	-2.849741
C15	0.000000	0.000000	3.527735	0.000000	0.000000	3.563382	0.000000	0.000000	3.550174
C16	0.000000	0.000000	-3.527735	0.000000	0.000000	-3.563382	0.000000	0.000000	-3.550174
H17	0.000000	3.404988	1.230563	0.000000	3.388961	1.232041	0.000000	3.411090	1.234511
H18	0.000000	-3.404988	1.230563	0.000000	-3.388961	1.232041	0.000000	-3.411090	1.234511
H19	0.000000	3.404988	-1.230563	0.000000	3.388961	-1.232041	0.000000	3.411090	-1.234511
H20	0.000000	-3.404988	-1.230563	0.000000	-3.388961	-1.232041	0.000000	-3.411090	-1.234511
H21	0.000000	2.151913	3.383084	0.000000	2.155260	3.429109	0.000000	2.159645	3.396456
H22	0.000000	-2.151913	3.383084	0.000000	-2.155260	3.429109	0.000000	-2.159645	3.396456
H23	0.000000	2.151913	-3.383084	0.000000	2.155260	-3.429109	0.000000	2.159645	-3.396456
H24	0.000000	-2.151913	-3.383084	0.000000	-2.155260	-3.429109	0.000000	-2.159645	-3.396456
H25	0.000000	0.000000	4.614772	0.000000	0.000000	4.650830	0.000000	0.000000	4.636343
H26	0.000000	0.000000	-4.614772	0.000000	0.000000	-4.650830	0.000000	0.000000	-4.636343

Table S 1: Continued. Calculated B3LYP/6-31+G* geometry of the aB_{2u} (x,y,z coordinates in Angströms).

	aB_{2u}		
C1	0.00000	0.00000	0.69817
C2	0.00000	0.00000	-0.69817
C3	0.00000	2.46907	0.69040
C4	0.00000	-2.46907	0.69040
C5	0.00000	2.46907	-0.69040
C6	0.00000	-2.46907	-0.69040
C7	0.00000	1.25182	1.43632
C8	0.00000	-1.25182	1.43632
C9	0.00000	1.25182	-1.43632
C10	0.00000	-1.25182	-1.43632
C11	0.00000	1.22052	2.84516
C12	0.00000	-1.22052	2.84516
C13	0.00000	1.22052	-2.84516
C14	0.00000	-1.22052	-2.84516
C15	0.00000	0.00000	3.54814
C16	0.00000	0.00000	-3.54814
H17	0.00000	3.41211	1.23225
H18	0.00000	-3.41211	1.23225
H19	0.00000	3.41211	-1.23225
H20	0.00000	-3.41211	-1.23225
H21	0.00000	2.15979	3.39315
H22	0.00000	-2.15979	3.39315
H23	0.00000	2.15979	-3.39315
H24	0.00000	-2.15979	-3.39315
H25	0.00000	0.00000	4.63387
H26	0.00000	0.00000	-4.63387

Table S 2: C-C distances (in Angströms) in the B3LYP geometries of the ground state (GS), the aB_{2u} (S_1), the bB_{2u} (S_3) and the bB_{3g} excited states. Only the relevant distances in the D_{2h} symmetry point group are given. Numbers in parenthesis indicate the percentage deviation from the ground state.

Distances	GS	bB3g (%/GS)	bB2u (%/GS)	aB2u (%/GS)
C1-C2	1.4280	1.4891 (-4.3)	1.4202 (0.5)	1.3964 (2.2)
C1-C7	1.4294	1.4332 (-0.3)	1.4429 (-0.9)	1.3808 (-1.3)
C3-C5	1.3634	1.4072 (-3.2)	1.3813 (-1.3)	1.4532 (-1.7)
C3-C7	1.4388	1.4108 (1.9)	1.4338 (0.3)	1.4276 (0.8)
C7-C11	1.4056	1.4279 (-1.6)	1.4119 (-0.4)	1.4092 (-0.2)
C11-C15	1.3956	1.3937 (0.1)	1.4067 (-0.8)	1.4085 (-0.9)

Non adiabatic coupling

The minimum-energy crossing point (MECP) connecting the two bB_{2u} and bB_{3g} excited states was determined, using 6-31G* Pople basis sets and B3LYP method. It was calculated with the MECP direct optimisation algorithm implemented in Q-Chem code. At this point (energy difference of 0.00005 a.u.), the CIS derivative coupling was calculated and is given in Table S 3.

Table S 3: CIS derivative coupling

Atom	X	Y	Z
C1	272.053339	-0.000005	-0.000000
C2	272.053334	0.000061	0.000000
C3	-86.529000	36.901616	-0.000000
C4	-86.529104	-36.901705	0.000000
C5	-86.529094	-36.901646	-0.000000
C6	-86.529022	36.901587	0.000000
C7	-205.579560	-329.255328	0.000000
C8	-205.579453	329.255408	0.000000
C9	-205.579447	329.255374	-0.000000
C10	-205.579592	-329.255406	-0.000000
C11	171.972348	-46.321275	-0.000000
C12	171.972314	46.321338	0.000000
C13	171.972270	46.321353	-0.000000
C14	171.972342	-46.321303	0.000000
C15	-37.489717	-0.000040	-0.000000
C16	-37.489749	-0.000026	0.000000
H17	-1.142997	5.954161	0.000000
H18	-1.143001	-5.954160	0.000000
H19	-1.143002	-5.954150	-0.000000
H20	-1.142999	5.954152	-0.000000
H21	3.372856	-0.443988	-0.000000
H22	3.372856	0.443987	0.000000
H23	3.372851	0.443993	-0.000000
H24	3.372851	-0.443995	0.000000
H25	1.242010	-0.000001	-0.000000
H26	1.242003	-0.000001	-0.000000

CASSCF Molecular Orbitals

The HOMO (H) / LUMO (L) denomination corresponds to the DFT orbital energies

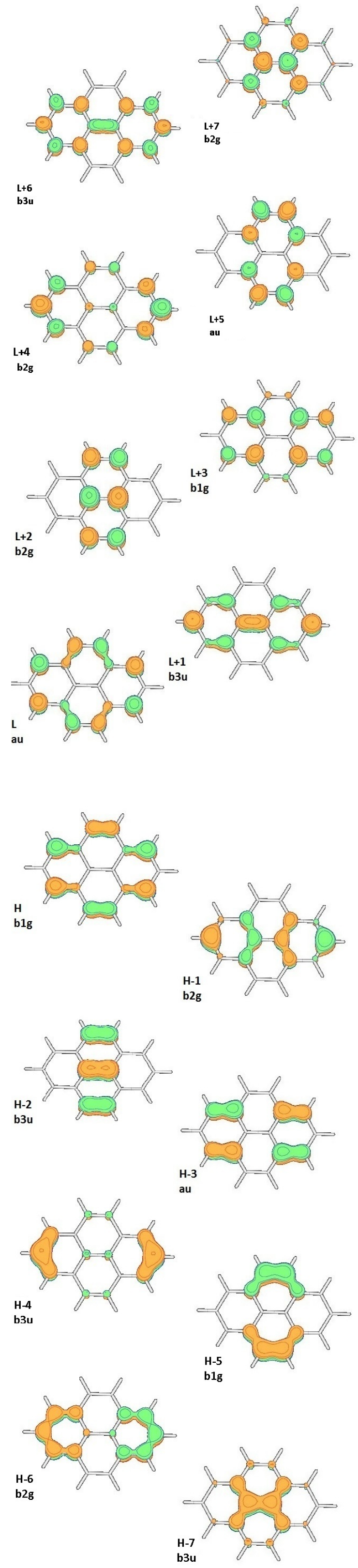


Figure S 3

Excitation energies and oscillator strengths between excited states

Table S 4: Excitation energies (eV) for excited states from the ground electronic state and oscillator strength between initial and final excited states.

Initial State (Energy from S_0)	Final State (Energy from S_0)	Oscillator strength (≥ 0.01)
bA_g (4.47)	fB_{2u} (6.63)	0.02
bA_g (4.47)	eB_{1u} (6.75)	0.02
bA_g (4.47)	fB_{1u} (6.94)	0.09
cA_g (4.94)	eB_{1u} (6.75)	0.03
cA_g (4.94)	hB_{1u} (7.92)	0.01
dA_g (5.09)	hB_{2u} (7.19)	0.02
dA_g (5.09)	iB_{2u} (8.02)	0.01
dA_g (5.09)	gB_{1u} (7.61)	0.02
dA_g (5.09)	hB_{1u} (7.92)	0.03
eA_g (5.41)	hB_{1u} (7.92)	0.01
aB_{2u} (3.43)	dA_g (5.09)	0.03
aB_{2u} (3.43)	eB_{3g} (5.85)	0.07
aB_{2u} (3.43)	fB_{3g} (6.72)	0.13
aB_{2u} (3.43)	hB_{3g} (7.25)	0.02
bB_{2u} (4.44)	hA_g (6.69)	0.02
bB_{2u} (4.44)	iA_g (7.14)	0.03
bB_{2u} (4.44)	dB_{3g} (5.52)	0.03
bB_{2u} (4.44)	gB_{3g} (7.04)	0.05
aB_{1u} (3.82)	fA_g (6.04)	0.01
aB_{1u} (3.82)	gA_g (6.36)	0.15
aB_{1u} (3.82)	iA_g (7.14)	0.02
aB_{1u} (3.82)	cB_{3g} (5.07)	0.03
aB_{1u} (3.82)	gB_{3g} (7.04)	0.05
aB_{1u} (3.82)	hB_{3g} (7.25)	0.01
bB_{1u} (5.28)	fA_g (6.04)	0.02
bB_{1u} (5.28)	iA_g (7.14)	0.02
cB_{1u} (6.05)	hB_{3g} (7.25)	0.02
aB_{3g} (4.15)	gB_{2u} (7.15)	0.05
aB_{3g} (4.15)	hB_{2u} (7.19)	0.02
aB_{3g} (4.15)	cB_{1u} (6.05)	0.01
aB_{3g} (4.15)	eB_{1u} (6.75)	0.01
aB_{3g} (4.15)	gB_{1u} (7.61)	0.01
aB_{3g} (4.15)	hB_{1u} (7.92)	0.02
bB_{3g} (4.53)	gB_{2u} (7.15)	0.06
bB_{3g} (4.53)	hB_{2u} (7.19)	0.02
bB_{3g} (4.53)	cB_{1u} (6.05)	0.02
bB_{3g} (4.53)	fB_{1u} (6.94)	0.01
eB_{3g} (5.85)	iB_{2u} (8.02)	0.03

Dyson orbitals

The transition probability to form an ionic state from the ground or excited state of the neutral is proportional to the norm of the Dyson orbital between the two electronic states. The norm of the Dyson orbital quantifies the extent of differential electron correlation in the neutral and ionised states. In the present case, with multireference excited states, this norm is different from one, reflecting the weights of the Slater determinants.[1] Koopmans' theorem is valid when there are neither orbital relaxations nor electron dynamical correlation. As mentioned by Oana and Krylov,[1] a Koopmans-type picture also applies to the ionisation of multiconfigurational wave functions.

Dyson orbitals were determined with the Q-chem code, using equation of motion single and double coupled cluster (EOM-CCSD) formalism. The $\hat{R}$ is the general excitation operator in the EOM-CC ansatz and $\hat{R}_1$ describes the singlet excited part of the wave function.

In Table S 5, the magnitude $\|\mathrm{R}_1\|^2$ close to one reflects the predominantly mono-excited character of the excited state. The low value of $\|\mathrm{R}_2\|^2$ means that the dynamical correlation plays the same role in the two states and that uncorrelated Koopmans can be used in a first approximation. D_0 and D_1 ionic states coming from the aB_{2u} state have similar Dyson norms (0.4850 and 0.4711) whose sum is 0.96. The weights of the Slater determinants are 0.44 (H → L+1) / 0.41 (H-1 → L) for aB_{2u}, very similar to the Dyson norms. The same observation occurs for the bB_{2u}. Concerning the aB_{1u} and bB_{1u} states, the weights of the Slater determinants, 0.79/0.11 and 0.09/0.76, respectively, are also close to the Dyson norms (0.64/0.24 and 0.22/0.63, see Table S 5). The sum is now about ~ 0.86. Finally, the aB_{3g} and bB_{3g} states are developed on three main Slater determinants with a corresponding hole in H, H-1, and H-2 with weights of the same order of magnitude as the Dyson norms presented in Table S 5. The D_2 ionic state mainly comes from the bB_{3g} state with a Dyson norm of 0.55.

Table S 5: Dyson orbital norms were calculated for the three D_0, D_1, and D_2 cations and the two lowest excited states of B_{3g}, B_{1u}, B_{2u} symmetries by EOM-IP-CCSD/6-31G* calculations with Q-Chem code.

Excited state	ΔE (eV) from the GS	$\|\mathrm{R}_1\|^2$	$\|\mathrm{R}_2\|^2$	Dyson norm D_0	Dyson norm D_1	Dyson norm D_2
$\mathbf{aB}_{2u}$	3.85	0.887	0.113	0.4850	0.4711	0.0332
aB_{1u}	4.56	0.919	0.081	0.6360	0.2404	0.0498
aB_{3g}	5.10	0.889	0.111	0.5439	0.1839	0.2801
$\mathbf{bB}_{3g}$	5.43	0.915	0.055	0.3682	0.1205	0.5527
$\mathbf{bB}_{2u}$	5.51	0.900	0.100	0.4666	0.4770	0.1217
bB_{1u}	6.17	0.916	0.084	0.2246	0.6281	0.1338

References

(1) Melania Oana, C.; Krylov, A. I. Dyson orbitals for ionization from the ground and electronically excited states within equation-of-motion coupled-cluster formalism: Theory, implementation, and examples. *The Journal of Chemical Physics* **2007**, *127*, 234106.