SUPPLEMENTARY MATERIAL

Non-adiabatic quantum dynamics of polycyclic aromatic hydrocarbons exhibiting anti-Kasha emission from the S_2 state

Nikita A. Shekhovtsov [a)] and Mark B. Bushuev [a)]

AFFILIATIONS

[a)] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia*

Authors to whom correspondence should be addressed: nikita.shekhovtsov.niic@gmail.com (N. A. Shekhovtsov), bushuev@niic.nsc.ru (M. B. Bushuev).

TABLE OF CONTENTS

TABLE S1. Comparison between the energies of vertical $S_0 \rightarrow S_n$ (n = 1-3) excitations computed at the B3LYP/TZP and ADC(2)/def2TZVP levels of theory for studied PAHs in the gas phase.

Compound	Transition	ADC(2)/def2TZVP		B3LYP/TZP	
		Energy, eV	Energy, eV	Energy, eV	Osc. strength
3,4-benzopyrene	$S_0 \rightarrow S_1$	3.59	0.0320	3.44	0.0736
	$S_0 \rightarrow S_2$	3.70	0.3834	3.35	0.2649
	$S_0 \rightarrow S_3$	4.54	0.0439	4.06	0.0257
1,12-benzoperylene	$S_0 \rightarrow S_1$	3.55	0.0001	3.38	0.0005
	$S_0 \rightarrow S_2$	3.73	0.3364	3.37	0.2791
	$S_0 \rightarrow S_3$	4.30	0.0069	4.29	0.0087
2'-methyl-1,2-benzanthracene	$S_0 \rightarrow S_1$	3.78	0.0047	3.59	0.0466
	$S_0 \rightarrow S_2$	4.03	0.0968	3.46	0.0352
	$S_0 \rightarrow S_3$	4.75	0.0145	4.33	0.3087
3,4-benzotetraphene	$S_0 \rightarrow S_1$	3.73	0.0335	3.50	0.0036
	$S_0 \rightarrow S_2$	3.82	0.0837	3.28	0.0922
	$S_0 \rightarrow S_3$	4.34	0.0019	3.76	0.0012

TABLE S2. Frontier molecular orbitals of 3,4-benzopyrene at the ADC(2)/def2TZVP level of theory.

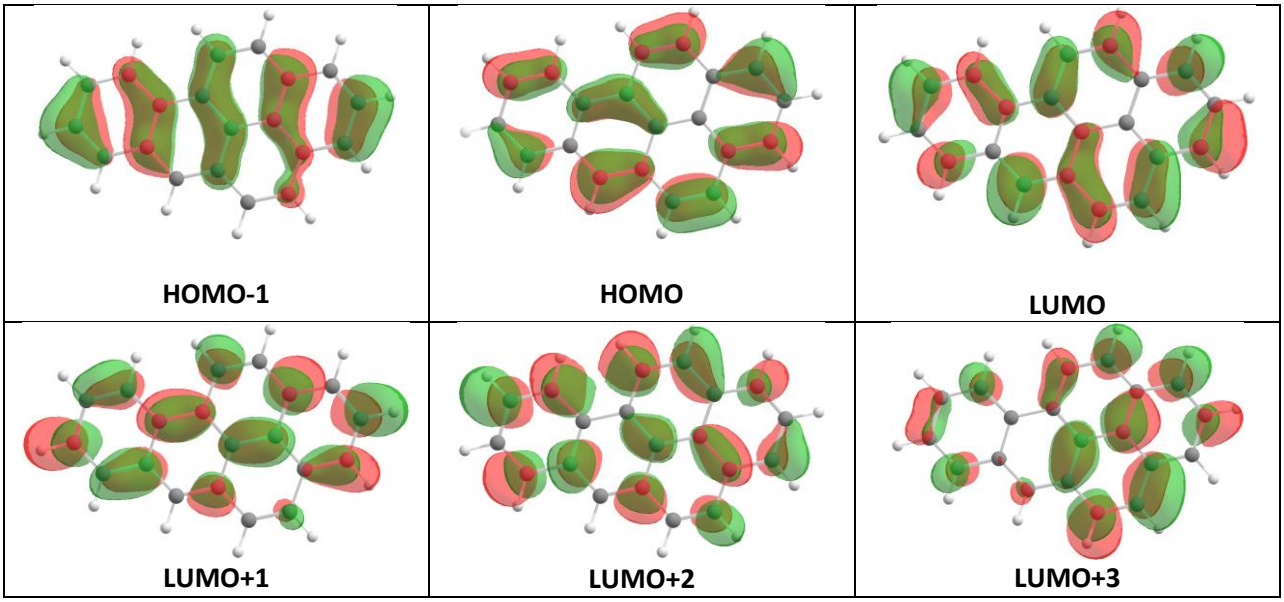
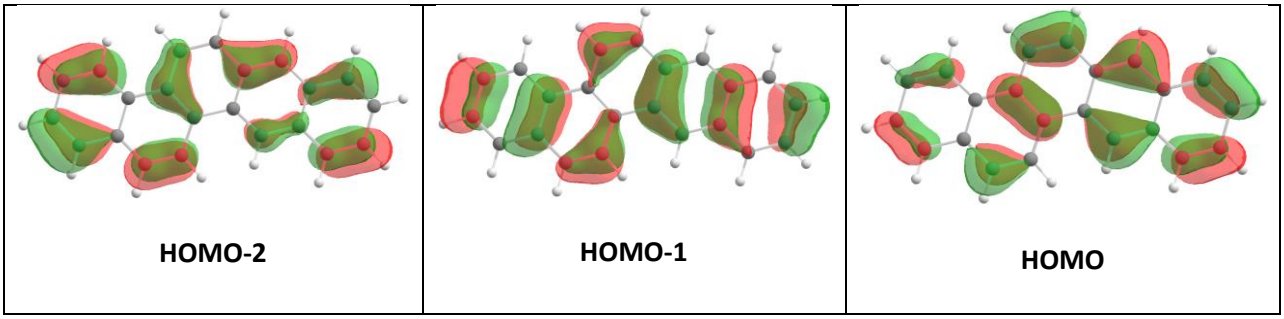


TABLE S3. Frontier molecular orbitals of 3,4-benzotetraphene at the ADC(2)/def2TZVP level of theory.



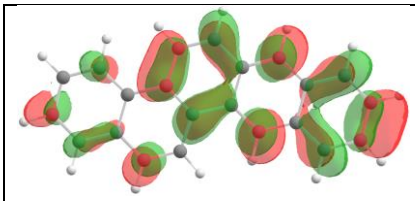
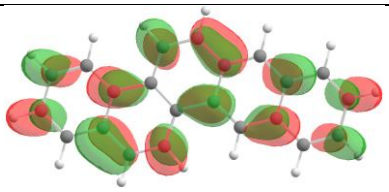
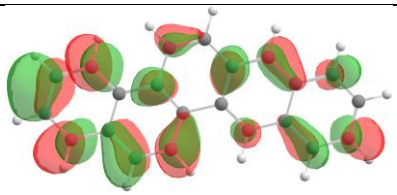
		
LUMO	**LUMO+1**	**LUMO+2**

TABLE S4. Frontier molecular orbitals of 1,12-benzoperylene at the ADC(2)/def2TZVP level of theory.

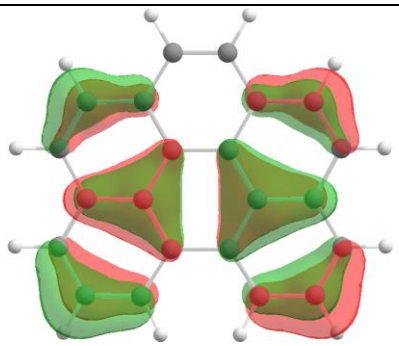
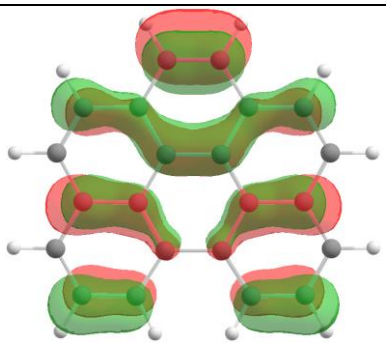
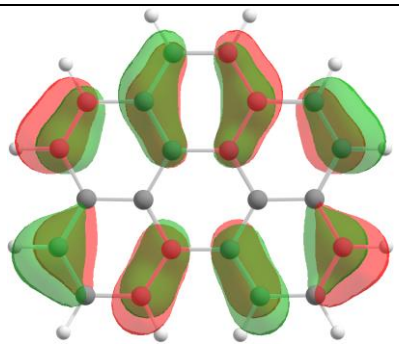
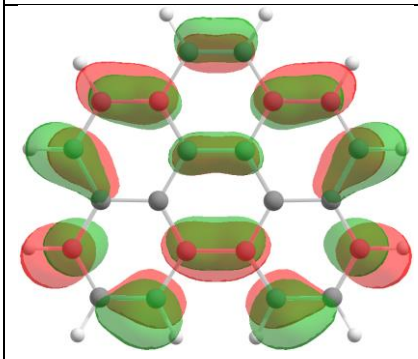
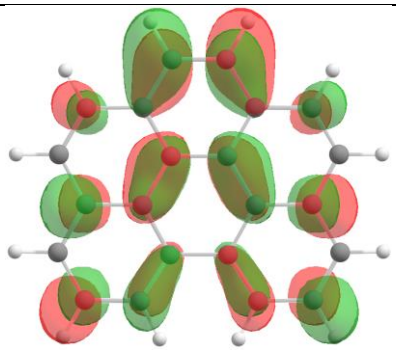
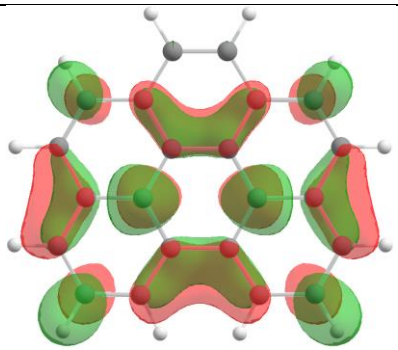
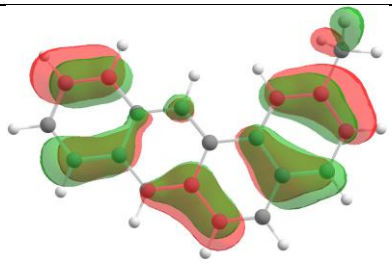
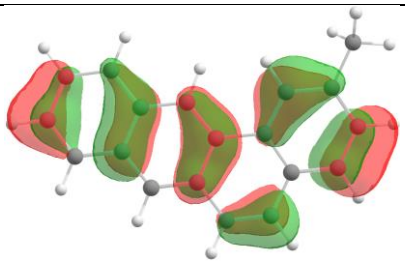
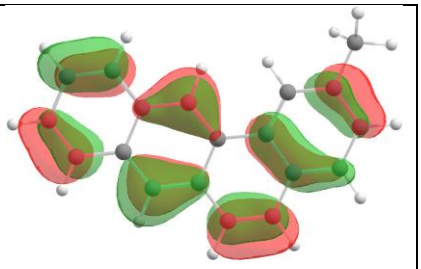
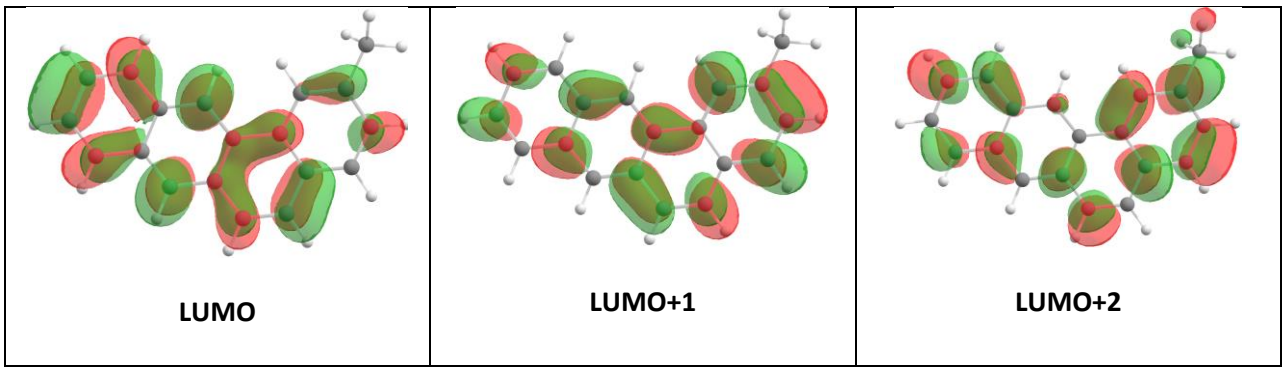
		
HOMO-2	**HOMO-1**	**HOMO**
		
LUMO	**LUMO+1**	**LUMO+2**

TABLE S5. Frontier molecular orbitals of 2'-methyl-1,2-benzanthracene at the ADC(2)/def2TZVP level of theory.

		
HOMO-2	**HOMO-1**	**HOMO**



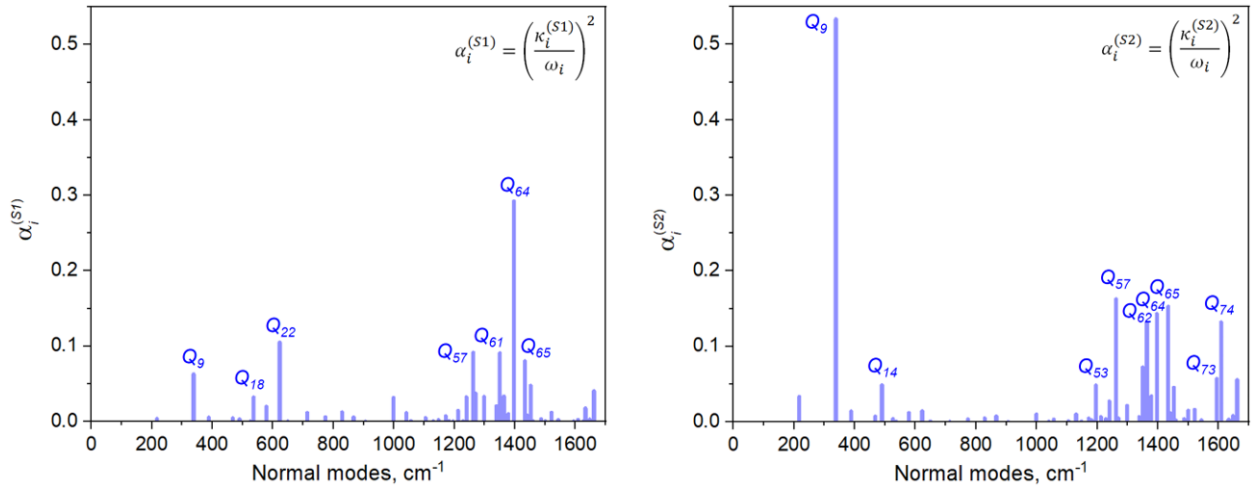


FIG. S1. The computed Poisson parameters $\alpha_i^{(S1)} = (\kappa_i^{(S1)}/\omega_i)^2$ and $\alpha_i^{(S2)} = (\kappa_i^{(S2)}/\omega_i)^2$ *versus* normal modes for 3,4-benzopyrene.

TABLE S6. Calculated frequencies (in cm^{-1}) at the optimized ground state geometry of 3,4-benzopyrene.

Gas phase							
Q_1	56.49	Q_{25}	704.85	Q_{49}	1130.29	Q_{73}	1594.22
Q_2	80.87	Q_{26}	713.61	Q_{50}	1148.02	Q_{74}	1608.62
Q_3	150.34	Q_{27}	753.91	Q_{51}	1171.4	Q_{75}	1629.43
Q_4	182.02	Q_{28}	762.45	Q_{52}	1182.11	Q_{76}	1633.51
Q_5	210.14	Q_{29}	772.86	Q_{53}	1195.48	Q_{77}	1647.26
Q_6	217.3	Q_{30}	773.42	Q_{54}	1212.03	Q_{78}	1661.37
Q_7	282.79	Q_{31}	814.07	Q_{55}	1228.33	Q_{79}	3152.59
Q_8	302.55	Q_{32}	828.79	Q_{56}	1239.9	Q_{80}	3154.52
Q_9	337.95	Q_{33}	841.33	Q_{57}	1262.61	Q_{81}	3155.91
Q_{10}	388.24	Q_{34}	851.01	Q_{58}	1269.83	Q_{82}	3158.24
Q_{11}	395.01	Q_{35}	866.21	Q_{59}	1298.28	Q_{83}	3161.3
Q_{12}	464.64	Q_{36}	866.83	Q_{60}	1338.88	Q_{84}	3164.59
Q_{13}	467.56	Q_{37}	903.74	Q_{61}	1350.12	Q_{85}	3169.31
Q_{14}	489.73	Q_{38}	905.99	Q_{62}	1363.86	Q_{86}	3172.12
Q_{15}	511.29	Q_{39}	917.6	Q_{63}	1378.4	Q_{87}	3180.27
Q_{16}	524.98	Q_{40}	969.7	Q_{64}	1396.63	Q_{88}	3181.4
Q_{17}	525.73	Q_{41}	980.77	Q_{65}	1433.41	Q_{89}	3191.84
Q_{18}	536.1	Q_{42}	986.29	Q_{66}	1440.5	Q_{90}	3208.27
Q_{19}	546.1	Q_{43}	991.49	Q_{67}	1452.15		
Q_{20}	570.04	Q_{44}	996.12	Q_{68}	1459.87		
Q_{21}	578.64	Q_{45}	999.35	Q_{69}	1486.71		

Q_{22}	622.56	Q_{46}	1041.41	Q_{70}	1500.47		
Q_{23}	649.52	Q_{47}	1056.71	Q_{71}	1521.12		
Q_{24}	686.27	Q_{48}	1105	Q_{72}	1543.57		
MeCN							
Q_1	53.41	Q_{25}	708.2	Q_{49}	1124.16	Q_{73}	1588.2
Q_2	78.89	Q_{26}	709.84	Q_{50}	1140.73	Q_{74}	1603.96
Q_3	151.09	Q_{27}	759.14	Q_{51}	1167.6	Q_{75}	1623.21
Q_4	179.93	Q_{28}	766.85	Q_{52}	1168.78	Q_{76}	1630.59
Q_5	205.69	Q_{29}	770.33	Q_{53}	1181.75	Q_{77}	1637.93
Q_6	212.32	Q_{30}	779.68	Q_{54}	1197.25	Q_{78}	1656.61
Q_7	280.92	Q_{31}	822.62	Q_{55}	1218.15	Q_{79}	3161.82
Q_8	300.16	Q_{32}	823.6	Q_{56}	1237.02	Q_{80}	3163.33
Q_9	335.59	Q_{33}	850.46	Q_{57}	1260.83	Q_{81}	3164.97
Q_{10}	381.9	Q_{34}	860.54	Q_{58}	1267.58	Q_{82}	3165.59
Q_{11}	396.65	Q_{35}	872.57	Q_{59}	1290.26	Q_{83}	3168.66
Q_{12}	458.87	Q_{36}	882.04	Q_{60}	1330.34	Q_{84}	3172.07
Q_{13}	465.2	Q_{37}	899.53	Q_{61}	1343.45	Q_{85}	3174.64
Q_{14}	481.38	Q_{38}	916.1	Q_{62}	1364.51	Q_{86}	3178.96
Q_{15}	513.25	Q_{39}	923.65	Q_{63}	1369.52	Q_{87}	3186.67
Q_{16}	516.64	Q_{40}	964.14	Q_{64}	1385.55	Q_{88}	3187.18
Q_{17}	529.05	Q_{41}	977.46	Q_{65}	1422.37	Q_{89}	3196.21
Q_{18}	531.4	Q_{42}	983.88	Q_{66}	1437.84	Q_{90}	3211.1
Q_{19}	551.3	Q_{43}	991.02	Q_{67}	1445.87		
Q_{20}	567.19	Q_{44}	992.57	Q_{68}	1456.32		
Q_{21}	567.71	Q_{45}	995.31	Q_{69}	1484.55		
Q_{22}	617.83	Q_{46}	1038.81	Q_{70}	1497.06		
Q_{23}	644.56	Q_{47}	1051.6	Q_{71}	1519.96		
Q_{24}	686.9	Q_{48}	1095.86	Q_{72}	1541.28		

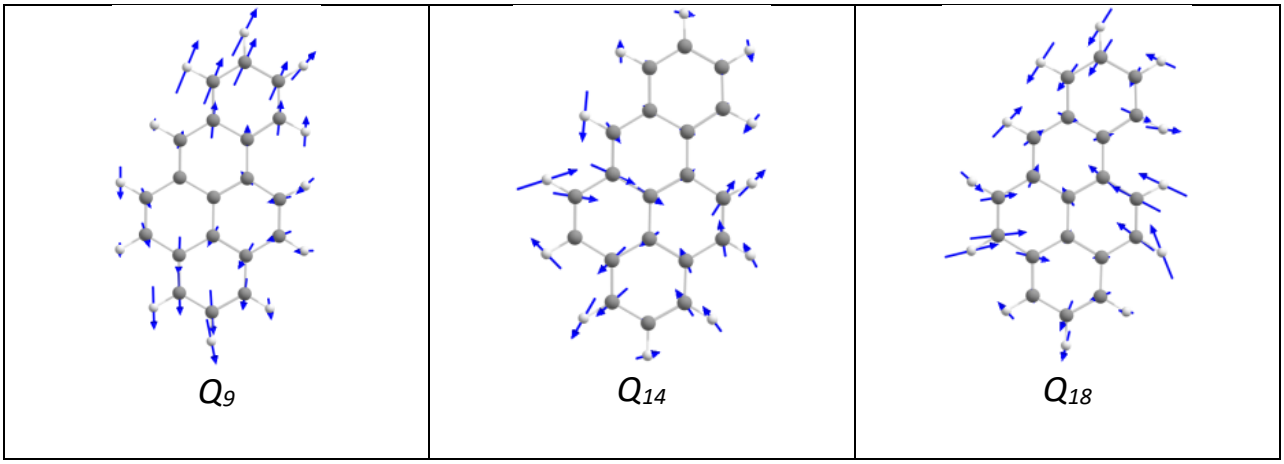
TABLE S7. Intrastate and interstate linear vibronic coupling constants (in eV) for 3,4-benzopyrene entering the model linear vibronic coupling Hamiltonian.

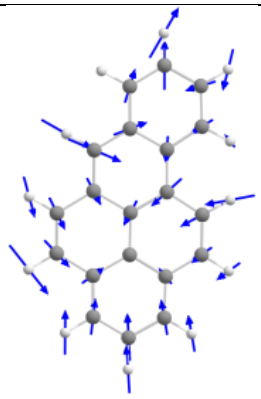
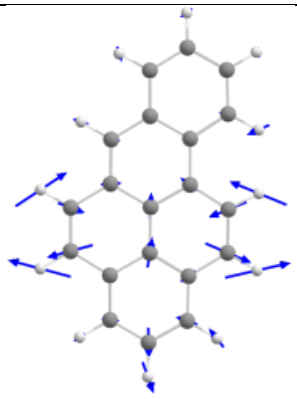
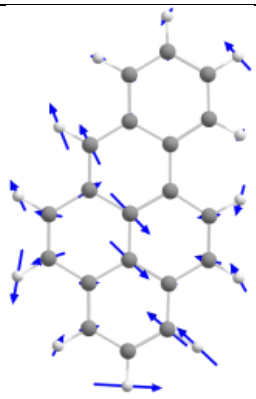
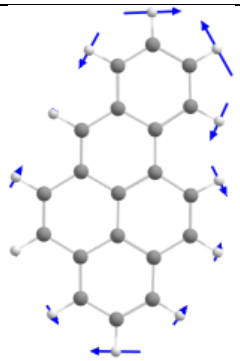
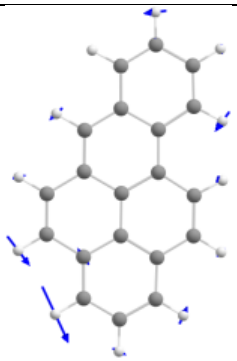
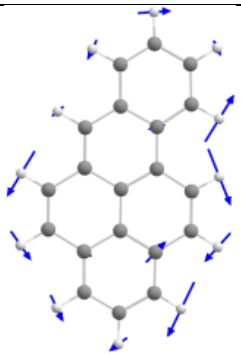
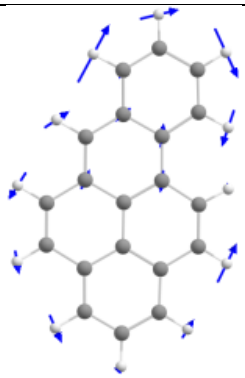
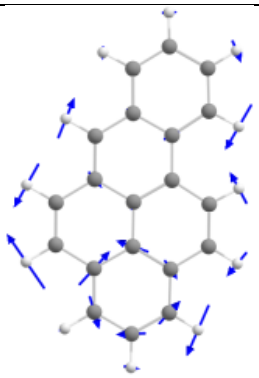
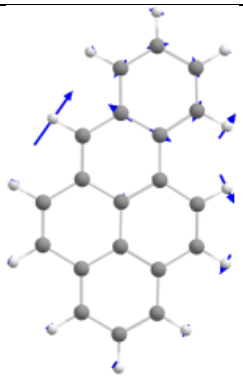
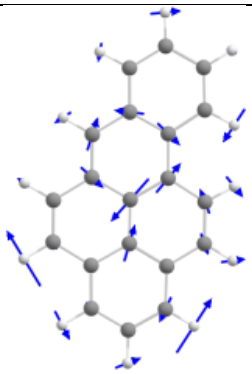
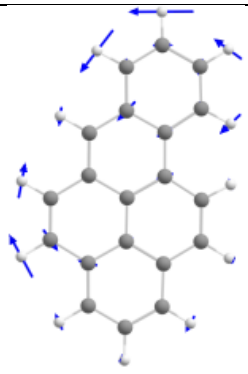
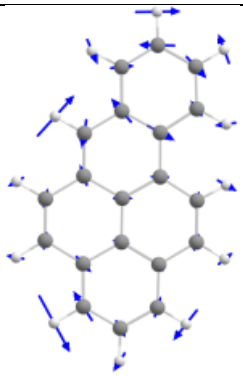
18-mode model in the gas phase Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_9	0.0306	0.0105	0.0103	0.0093	0.0058	0.0054
Q_{14}	0.0134	0.0033	0.0127	0.0055	-	-
Q_{18}	-0.0019	0.0119	8E-4	0.0069	-	0.0051
Q_{22}	-0.0092	0.025	0.0116	0.0175	0.0191	0.013
Q_{32}	0.0071	-0.0114	-0.0122	0.0109	-	-
Q_{45}	0.0123	0.0221	-7E-4	-	-	0.0161
Q_{53}	-0.0325	-0.0026	-0.0127	0.0171	0.014	-
Q_{57}	-0.0631	-0.0473	-0.041	0.0101	0.0191	-
Q_{58}	0.0105	0.0304	-0.03	0.0098	-	-
Q_{60}	0.0133	0.0238	0.0163	0.0047	0.0059	0.0087
Q_{62}	0.0612	0.0309	0.051	0.0194	-	-
Q_{63}	0.0314	0.0171	-0.0042	0.0156	0.045	0.0188
Q_{64}	0.0655	0.0936	0.003	0.0153	-	0.029
Q_{70}	-0.0226	-0.0031	0.0249	0.013	0.0472	0.034
Q_{73}	-0.0472	-0.0029	-0.0049	0.0229	-	-
Q_{74}	0.0724	0.0099	0.0329	0.034	-	-

Q_{77}	-0.018	0.0105	-0.1173	0.03	0.0668	0.0363
Q_{78}	-0.0485	-0.0414	-0.1552	-	-	-
Additional coupling constants for **21-mode model in the gas phase** Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_{30}	-0.0056	0.0074	-0.0037	0.0087	0.0058	-
Q_{46}	0.002	-0.0137	-0.0089	0.0087	-	-
Q_{65}	0.0694	0.0503	0.0265	0.0173	0.0337	-
Additional coupling constants for **24-mode model in the gas phase** Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_6	-0.0049	0.0016	-0.0092	0.0023	-	0.0076
Q_{26}	-0.0013	0.0095	-0.0081	-	-	-
Q_{49}	-0.014	0.0016	0.0102	0.008	-	-
Additional coupling constants for **28-mode model in the gas phase** Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_{17}	0.0041	-0.0008	-0.0073	0.0049	0.0066	-
Q_{50}	0.0034	-0.0066	0.0056	0.0067	-	-
Q_{75}	-0.0035	0.007	0.0034	-	-	0.0171
Q_{76}	0.011	0.0267	-0.0143	0.0106	-	-
18-mode model in the gas phase "Classical" selection methodology (modes are chosen based on the largest Poisson parameters)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_9	0.0306	0.0105	0.0103	0.0093	0.0058	0.0054
Q_{14}	0.0134	0.0033	0.0127	0.0055	-	-
Q_{22}	-0.0092	0.025	0.0116	0.0175	0.0191	0.013
Q_{45}	0.0123	0.0221	-0.0007	-	-	0.0161
Q_{53}	-0.0325	-0.0026	-0.0127	0.0171	0.014	-
Q_{56}	0.0254	0.0276	0.0494	0.0094	0.0191	-
Q_{57}	-0.0631	-0.0473	-0.041	0.0101	0.0191	-
Q_{58}	0.0105	0.0304	-0.03	0.0098	-	-
Q_{59}	-0.0233	-0.0291	0.0077	-	-	-
Q_{61}	-0.045	-0.0504	-0.0524	0.0091	-	-
Q_{62}	0.0612	0.0309	0.051	0.0194	-	-
Q_{63}	0.0314	0.0171	-0.0042	0.0156	0.045	0.0188
Q_{64}	0.0655	0.0936	0.003	0.0153	-	0.029
Q_{65}	0.0694	0.0503	0.0265	0.0173	0.0337	-
Q_{67}	0.0384	0.0392	0.0017	-	0.0394	0.0427
Q_{73}	-0.0472	-0.0029	-0.0049	0.0229	-	-
Q_{74}	0.0724	0.0099	0.0329	0.034	-	-
Q_{78}	-0.0485	-0.0414	-0.1552	-	-	-
Additional coupling constants for **21-mode model in the gas phase** "Classical" selection methodology (modes are chosen based on the largest Poisson parameters)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_6	-0.0049	0.0016	-0.0092	0.0023	-	0.0076
Q_{21}	0.0078	0.0101	0.0246	0.0025	0.0108	0.0077
Q_{60}	0.0133	0.0238	0.0163	0.0047	0.0059	0.0087
Additional coupling constants for **24-mode model in the gas phase** "Classical" selection methodology (modes are chosen based on the largest Poisson parameters)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$

Q_{70}	-0.0226	-0.0031	0.0249	0.013	0.0472	0.034
Q_{71}	-0.0238	-0.0204	0.0066	0.0069	0.0337	0.026
Q_{76}	0.011	0.0267	-0.0143	0.0106	-	-
Additional coupling constants for **28-mode model in the gas phase** "Classical" selection methodology (modes are chosen based on the largest Poisson parameters)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_{10}	-0.0057	-0.0035	0.0142	0.0044	0.017	0.011
Q_{18}	-0.0019	0.0119	0.0008	0.0069	-	0.0051
Q_{26}	-0.0013	0.0095	-0.0081	-	-	-
Q_{32}	0.0071	-0.0114	-0.0122	0.0109	-	-
18-mode model in MeCN Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)						
Mode	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_9	-0.0375	-0.0111	-0.0044	0.0139	0.0108	-
Q_{14}	0.0149	0.0026	0.0114	0.0049	-	-
Q_{18}	-0.0071	0.0053	0.0014	0.0059	0.0112	0.0095
Q_{22}	-0.0089	0.0168	0.0162	0.0121	0.02	0.0113
Q_{31}	0.0037	-0.0081	-0.0097	0.0018	-	-
Q_{45}	-0.0122	-0.0192	-0.0125	0.0069	0.0171	0.0253
Q_{53}	-0.0326	0.0006	-0.0126	0.0144	0.0099	-
Q_{57}	-0.0763	-0.0359	-0.0378	0.019	0.0252	-
Q_{58}	0.0212	0.0531	0.0047	0.0154	-	0.0065
Q_{60}	0.006	0.0361	0.0176	0.0143	0.0176	0.014
Q_{62}	-0.0839	-0.0339	-0.0451	0.0211	-	-
Q_{63}	-0.0022	0.0288	0.0003	0.0123	0.0339	0.0276
Q_{64}	0.065	0.1013	0.0257	0.0127	0.0269	0.0204
Q_{70}	-0.0251	0.0038	0.0236	0.0131	0.0504	0.0449
Q_{73}	-0.0956	0.0089	-0.0179	0.0486	0.0237	-
Q_{74}	0.0418	0.0008	0.008	0.0167	-	-
Q_{77}	-0.0999	0.0198	-0.0819	0.0525	0.0521	-
Q_{78}	-0.0755	-0.0499	-0.1121	0.0234	-	-

TABLE S8. The visualization of some normal modes of 3,4-benzopyrene entering the model linear vibronic coupling Hamiltonian.



 Q_{22}	 Q_{32}	 Q_{45}
 Q_{53}	 Q_{57}	 Q_{58}
 Q_{60}	 Q_{62}	 Q_{63}
 Q_{64}	 Q_{70}	 Q_{73}

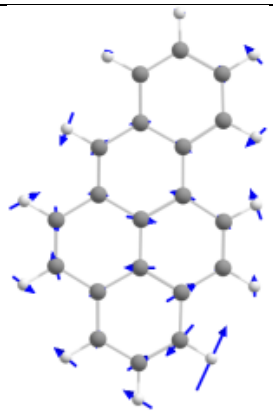
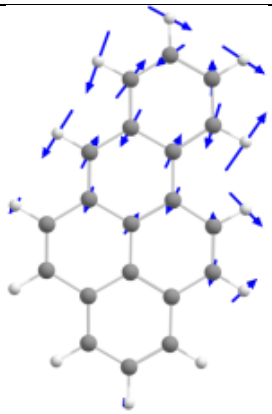
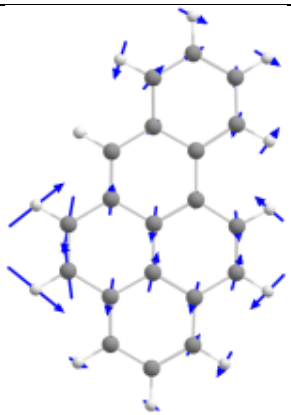
 Q_{74}	 Q_{77}	 Q_{78}

TABLE S9. Number of primitive basis and SPF for different mode combination used in the MCTDH calculation for two lowest excited singlet states of 3,4-benzopyrene.

18-mode model in the gas phase Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)		
Modes	Primitive basis	SPF basis
(Q_9, Q_{14}, Q_{18})	(13, 13, 13)	(7, 7, 7)
(Q_{22}, Q_{32}, Q_{45})	(13, 13, 13)	(7, 7, 7)
(Q_{53}, Q_{57}, Q_{58})	(13, 13, 13)	(7, 7, 7)
(Q_{60}, Q_{62}, Q_{63})	(13, 13, 13)	(7, 7, 7)
(Q_{64}, Q_{70}, Q_{73})	(13, 13, 13)	(7, 7, 7)
(Q_{74}, Q_{77}, Q_{78})	(13, 13, 13)	(7, 7, 7)
21-mode model in the gas phase Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)		
Modes	Primitive basis	SPF basis
(Q_9, Q_{14}, Q_{18})	(13, 13, 13)	(7, 7, 7)
(Q_{22}, Q_{30}, Q_{32})	(13, 13, 13)	(7, 7, 7)
(Q_{45}, Q_{46}, Q_{53})	(13, 13, 13)	(7, 7, 7)
(Q_{57}, Q_{58}, Q_{60})	(13, 13, 13)	(7, 7, 7)
(Q_{62}, Q_{63}, Q_{64})	(13, 13, 13)	(7, 7, 7)
(Q_{65}, Q_{70}, Q_{73})	(13, 13, 13)	(7, 7, 7)
(Q_{74}, Q_{77}, Q_{78})	(13, 13, 13)	(7, 7, 7)
24-mode model in the gas phase Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)		
Modes	Primitive basis	SPF basis
(Q_6, Q_9, Q_{14}, Q_{18})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{22}, Q_{26}, Q_{30}, Q_{32})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{45}, Q_{46}, Q_{49}, Q_{53})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{57}, Q_{58}, Q_{60}, Q_{62})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{63}, Q_{64}, Q_{65}, Q_{70})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{73}, Q_{74}, Q_{77}, Q_{78})	(13, 13, 13, 13)	(7, 7, 7)
28-mode model in the gas phase Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)		
Modes	Primitive basis	SPF basis
(Q_6, Q_9, Q_{14}, Q_{17})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{18}, Q_{22}, Q_{26}, Q_{30})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{32}, Q_{45}, Q_{46}, Q_{49})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{50}, Q_{53}, Q_{57}, Q_{58})	(13, 13, 13, 13)	(7, 7, 7)

(Q_{60}, Q_{62}, Q_{63}, Q_{64})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{65}, Q_{70}, Q_{73}, Q_{74})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{75}, Q_{76}, Q_{77}, Q_{78})	(13, 13, 13, 13)	(7, 7, 7)
18-mode model in the gas phase "Classical" selection methodology (modes are chosen based on the largest Poisson parameters)		
Modes	Primitive basis	SPF basis
(Q_9, Q_{14}, Q_{22})	(13, 13, 13)	(7, 7, 7)
(Q_{45}, Q_{53}, Q_{56})	(13, 13, 13)	(7, 7, 7)
(Q_{57}, Q_{58}, Q_{59})	(13, 13, 13)	(7, 7, 7)
(Q_{61}, Q_{62}, Q_{63})	(13, 13, 13)	(7, 7, 7)
(Q_{64}, Q_{65}, Q_{67})	(13, 13, 13)	(7, 7, 7)
(Q_{73}, Q_{74}, Q_{78})	(13, 13, 13)	(7, 7, 7)
21-mode model in the gas phase "Classical" selection methodology (modes are chosen based on the largest Poisson parameters)		
Modes	Primitive basis	SPF basis
(Q_6, Q_9, Q_{14})	(13, 13, 13)	(7, 7, 7)
(Q_{21}, Q_{22}, Q_{45})	(13, 13, 13)	(7, 7, 7)
(Q_{53}, Q_{56}, Q_{57})	(13, 13, 13)	(7, 7, 7)
(Q_{58}, Q_{59}, Q_{60})	(13, 13, 13)	(7, 7, 7)
(Q_{61}, Q_{62}, Q_{63})	(13, 13, 13)	(7, 7, 7)
(Q_{64}, Q_{65}, Q_{67})	(13, 13, 13)	(7, 7, 7)
(Q_{73}, Q_{74}, Q_{78})	(13, 13, 13)	(7, 7, 7)
24-mode model in the gas phase "Classical" selection methodology (modes are chosen based on the largest Poisson parameters)		
Modes	Primitive basis	SPF basis
(Q_6, Q_9, Q_{14}, Q_{21})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{22}, Q_{45}, Q_{53}, Q_{56})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{57}, Q_{58}, Q_{59}, Q_{60})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{61}, Q_{62}, Q_{63}, Q_{64})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{65}, Q_{67}, Q_{70}, Q_{71})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{73}, Q_{74}, Q_{76}, Q_{78})	(13, 13, 13, 13)	(7, 7, 7)
28-mode model in the gas phase "Classical" selection methodology (modes are chosen based on the largest Poisson parameters)		
Modes	Primitive basis	SPF basis
(Q_6, Q_9, Q_{10}, Q_{14})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{18}, Q_{21}, Q_{22}, Q_{26})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{32}, Q_{45}, Q_{53}, Q_{56})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{57}, Q_{58}, Q_{59}, Q_{60})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{61}, Q_{62}, Q_{63}, Q_{64})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{65}, Q_{67}, Q_{70}, Q_{71})	(13, 13, 13, 13)	(7, 7, 7)
(Q_{73}, Q_{74}, Q_{76}, Q_{78})	(13, 13, 13, 13)	(7, 7, 7)
18-mode model in MeCN Novel selection methodology (modes are chosen based on small $K_i^{(S1,S2)}$ and large $\beta_i^{(S1,S2)}$)		
Modes	Primitive basis	SPF basis
(Q_9, Q_{14}, Q_{18})	(13, 13, 13)	(7, 7, 7)
(Q_{22}, Q_{31}, Q_{45})	(13, 13, 13)	(7, 7, 7)
(Q_{53}, Q_{57}, Q_{58})	(13, 13, 13)	(7, 7, 7)
(Q_{60}, Q_{62}, Q_{63})	(13, 13, 13)	(7, 7, 7)
(Q_{64}, Q_{70}, Q_{73})	(13, 13, 13)	(7, 7, 7)
(Q_{74}, Q_{77}, Q_{78})	(13, 13, 13)	(7, 7, 7)

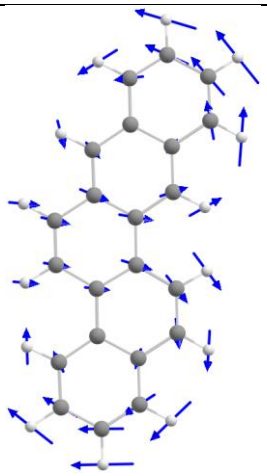
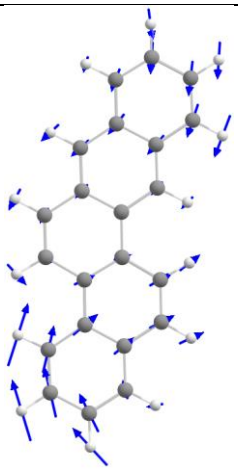
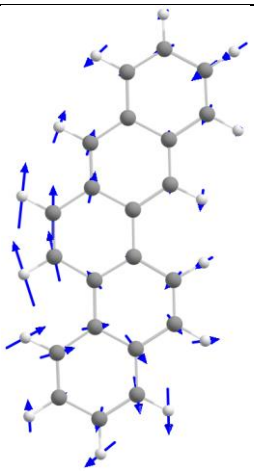
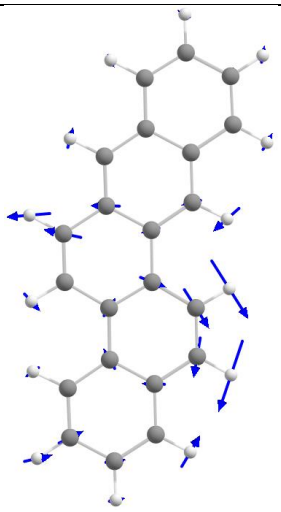
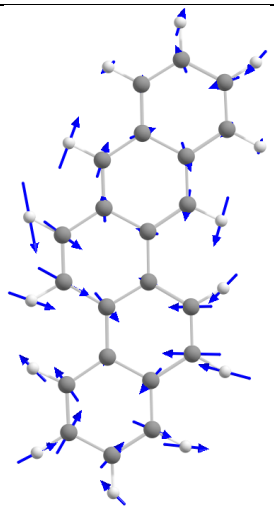
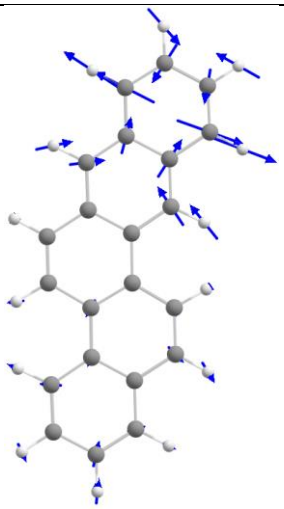
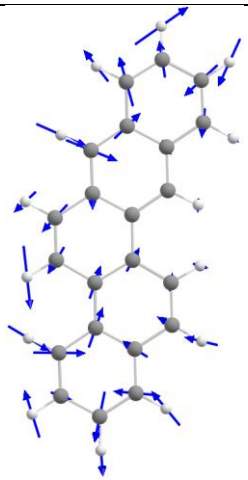
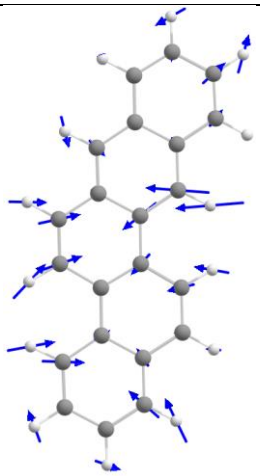
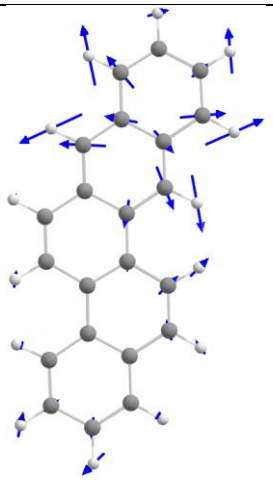
TABLE S10. Calculated frequencies (in cm^{-1}) at the optimized ground state geometry of 3,4-benzotetraphene.

Q_1	29.96	Q_{27}	661.97	Q_{53}	1031.61	Q_{79}	1507.98
Q_2	50.17	Q_{28}	705.1	Q_{54}	1056.35	Q_{80}	1516.35
Q_3	103.78	Q_{29}	726.85	Q_{55}	1097.19	Q_{81}	1548.81
Q_4	111.95	Q_{30}	737.05	Q_{56}	1157.18	Q_{82}	1578.42
Q_5	130.59	Q_{31}	751.05	Q_{57}	1167.9	Q_{83}	1588.29
Q_6	193.82	Q_{32}	761.85	Q_{58}	1173.82	Q_{84}	1620.35
Q_7	214.96	Q_{33}	770.57	Q_{59}	1187.98	Q_{85}	1632.54
Q_8	247.74	Q_{34}	790.88	Q_{60}	1203.23	Q_{86}	1647.65
Q_9	264.99	Q_{35}	797.17	Q_{61}	1205.31	Q_{87}	1651.2
Q_{10}	288.41	Q_{36}	823.03	Q_{62}	1220.14	Q_{88}	1659.77
Q_{11}	318.02	Q_{37}	823.61	Q_{63}	1239.53	Q_{89}	3155.3
Q_{12}	389.54	Q_{38}	838.36	Q_{64}	1252.79	Q_{90}	3157.25
Q_{13}	411.73	Q_{39}	855.25	Q_{65}	1287.12	Q_{91}	3159.07
Q_{14}	428.94	Q_{40}	877.2	Q_{66}	1290.1	Q_{92}	3160.99
Q_{15}	454.29	Q_{41}	880.44	Q_{67}	1295.02	Q_{93}	3161.98
Q_{16}	473.33	Q_{42}	900.04	Q_{68}	1318.62	Q_{94}	3162.63
Q_{17}	488.35	Q_{43}	900.55	Q_{69}	1353.61	Q_{95}	3171.9
Q_{18}	500.26	Q_{44}	908.15	Q_{70}	1354.5	Q_{96}	3174.82
Q_{19}	514.77	Q_{45}	940.67	Q_{71}	1377.2	Q_{97}	3184.29
Q_{20}	524.7	Q_{46}	965.45	Q_{72}	1383.3	Q_{98}	3184.49
Q_{21}	549.57	Q_{47}	975.67	Q_{73}	1393.87	Q_{99}	3187.68
Q_{22}	558.13	Q_{48}	980.01	Q_{74}	1410.05	Q_{100}	3195.16
Q_{23}	580.17	Q_{49}	984.05	Q_{75}	1450.86	Q_{101}	3204.09
Q_{24}	586.86	Q_{50}	995.42	Q_{76}	1456.7	Q_{102}	3213.45
Q_{25}	633.75	Q_{51}	997.17	Q_{77}	1463.96		
Q_{26}	649.66	Q_{52}	1024.34	Q_{78}	1482.37		

TABLE S11. Intrastate and interstate linear vibronic coupling constants (in eV) for 3,4-benzotetraphene entering the model linear vibronic coupling Hamiltonian.

	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_5	0.0019	-0.0028	0.0025	0.0065	0.0058	0.0171
Q_8	-0.0294	-0.0083	-0.0127	0.0108	-	-
Q_{15}	-0.0207	-0.0027	-0.0197	0.0085	-	-
Q_{19}	0.0197	-0.0029	0.015	0.0101	0.0121	0.0086
Q_{23}	0.0072	-0.0071	-0.0066	-0.0071	0.0113	-
Q_{25}	0.0143	2E-4	0.0128	-0.0057	0.0083	-
Q_{26}	0.0072	-0.0145	0.0162	0.0115	-	0.0101
Q_{29}	0.0089	-0.0152	-0.0127	0.0121	0.0162	0.0133
Q_{35}	0.0033	-0.0166	-0.0064	0.0103	0.0069	0.0099
Q_{53}	0.0084	-0.0122	0.0038	0.0101	0.0108	0.013
Q_{57}	0.0142	-0.0095	0.0108	0.0141	-	-
Q_{59}	0.0366	-0.0042	0.0382	0.0198	0.0116	0.021
Q_{63}	0.027	-5E-4	0.0311	0.0119	0.0103	0.0076
Q_{71}	0.0291	0.0319	0.0744	-	0.0405	0.0151
Q_{73}	-0.1159	-0.1294	-0.0653	0.0103	0.0367	0.0476
Q_{74}	0.0635	0.0311	0.0517	0.0131	-	-
Q_{83}	0.1109	0.009	0.1082	0.0507	-	0.0095
Q_{86}	0.0209	0.0102	-0.021	0.0263	0.0429	0.0796

TABLE S12. The visualization of the normal modes of 3,4-benzotetraphene entering the model linear vibronic coupling Hamiltonian.

 Q_5	 Q_8	 Q_{15}
 Q_{19}	 Q_{23}	 Q_{25}
 Q_{26}	 Q_{29}	 Q_{35}

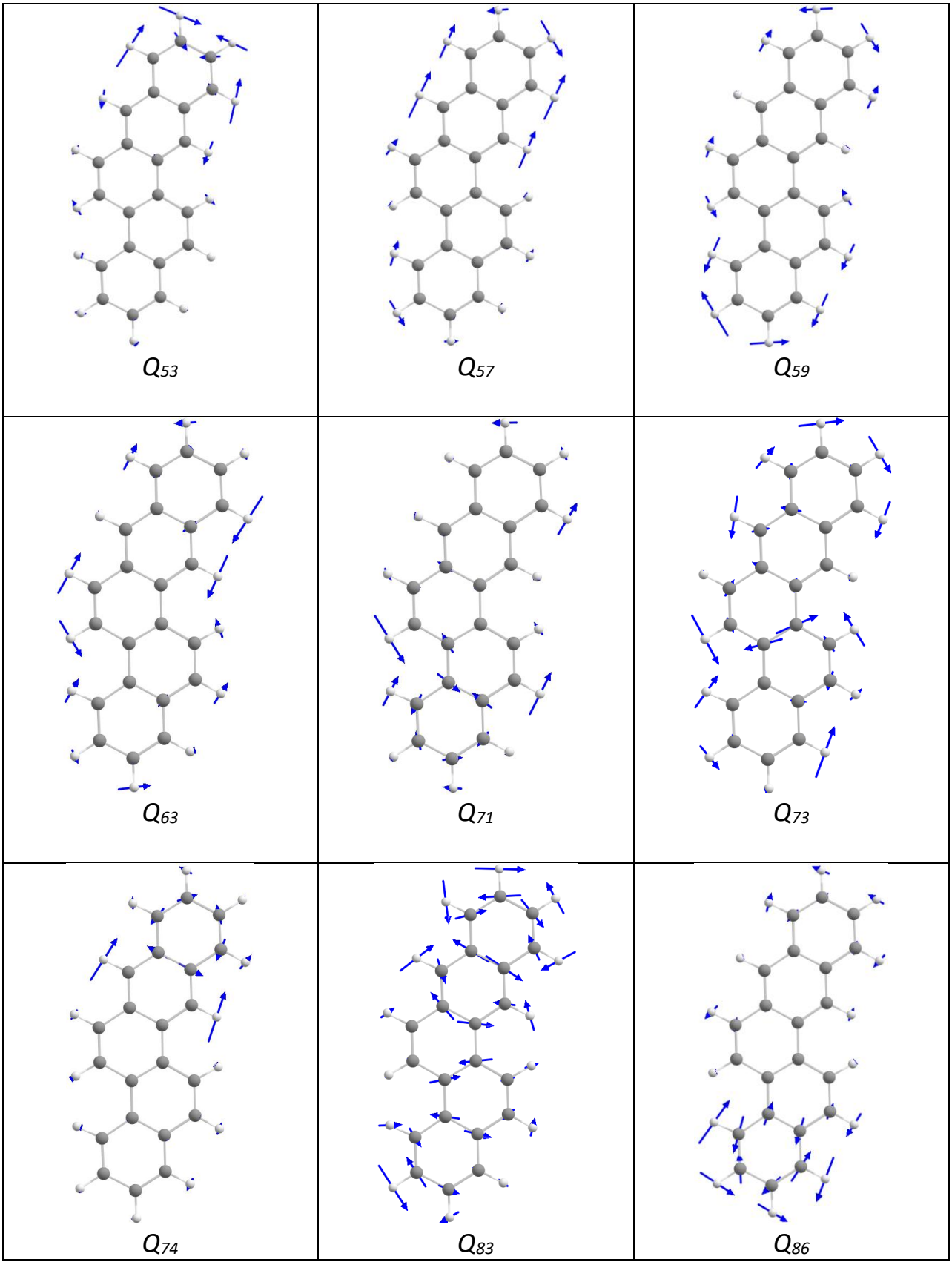


TABLE S13. Number of primitive basis and SPF for different mode combination used in the MCTDH calculation for two lowest excited singlet states of 3,4-benzotetraphene.

Modes	Primitive basis	SPF basis
(Q_5, Q_8, Q_{15})	(13, 13, 13)	(7, 7)

(Q_{19}, Q_{23}, Q_{25})	(13, 13, 13)	(7, 7)
(Q_{26}, Q_{29}, Q_{35})	(13, 13, 13)	(7, 7)
(Q_{53}, Q_{57}, Q_{59})	(13, 13, 13)	(7, 7)
(Q_{63}, Q_{71}, Q_{73})	(13, 13, 13)	(7, 7)
(Q_{74}, Q_{83}, Q_{86})	(13, 13, 13)	(7, 7)

TABLE S14. Calculated frequencies (in cm^{-1}) at the optimized ground state geometry of 1,12-benzoperylene.

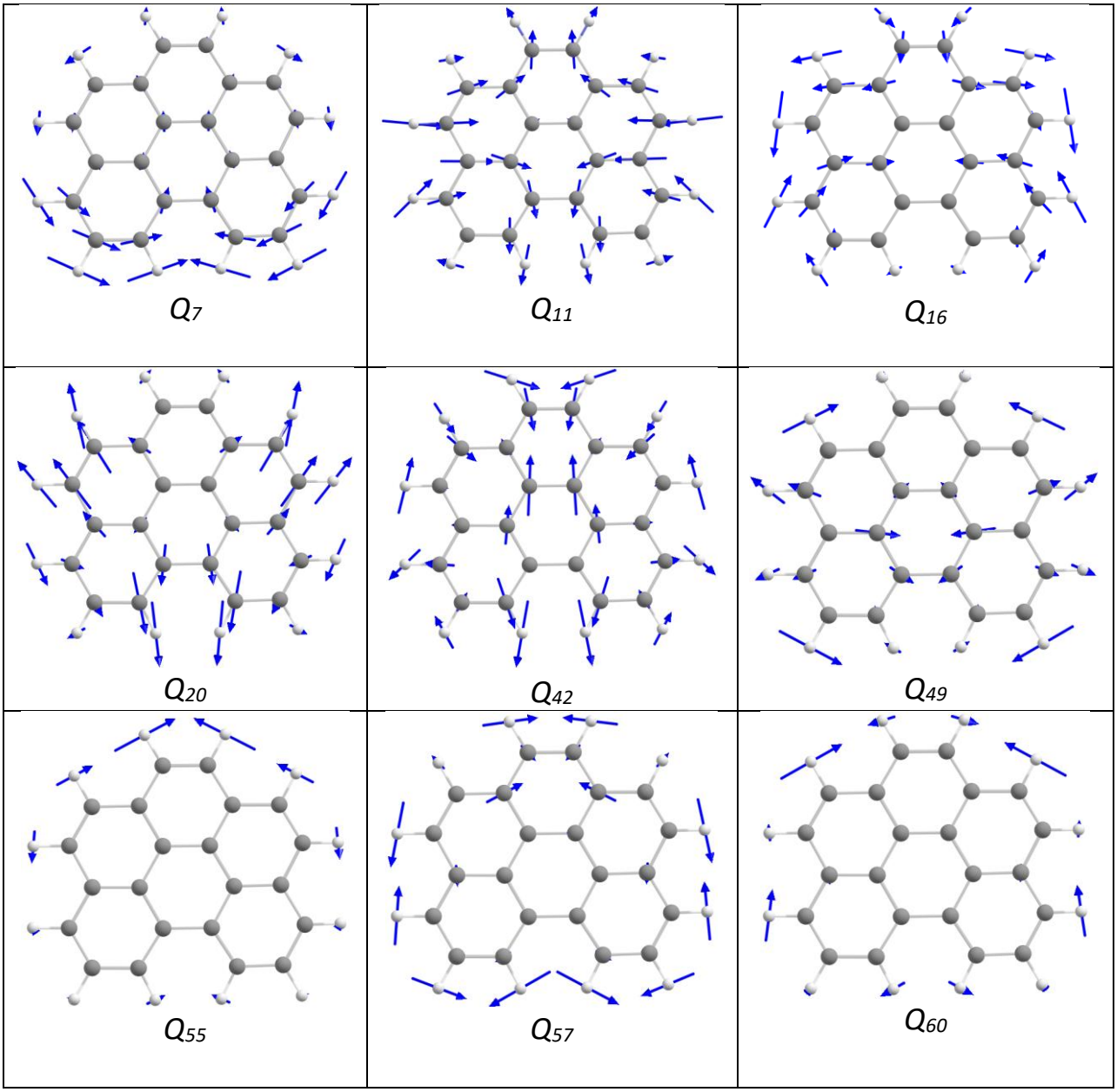
Q_1	59.01	Q_{25}	664.07	Q_{49}	1004.15	Q_{73}	1467.29
Q_2	92.11	Q_{26}	664.43	Q_{50}	1061.47	Q_{74}	1473.01
Q_3	133.18	Q_{27}	691.43	Q_{51}	1109.98	Q_{75}	1507.94
Q_4	180.33	Q_{28}	726.52	Q_{52}	1116.68	Q_{76}	1526.84
Q_5	201.91	Q_{29}	735.16	Q_{53}	1160.87	Q_{77}	1536.82
Q_6	276.99	Q_{30}	767.07	Q_{54}	1176.46	Q_{78}	1549.45
Q_7	293.2	Q_{31}	783.08	Q_{55}	1176.64	Q_{79}	1606.41
Q_8	294.1	Q_{32}	784.23	Q_{56}	1187.27	Q_{80}	1617.48
Q_9	297.8	Q_{33}	788.81	Q_{57}	1215.02	Q_{81}	1629.11
Q_{10}	368.53	Q_{34}	791.96	Q_{58}	1224.82	Q_{82}	1630.81
Q_{11}	390.47	Q_{35}	820.82	Q_{59}	1231.99	Q_{83}	1651.1
Q_{12}	420.38	Q_{36}	829.98	Q_{60}	1241.55	Q_{84}	1658.84
Q_{13}	434.75	Q_{37}	841.68	Q_{61}	1245.75	Q_{85}	3150.89
Q_{14}	462.03	Q_{38}	862.7	Q_{62}	1265.82	Q_{86}	3152.97
Q_{15}	462.33	Q_{39}	862.83	Q_{63}	1278.69	Q_{87}	3153.89
Q_{16}	493.29	Q_{40}	913.79	Q_{64}	1316.22	Q_{88}	3157.59
Q_{17}	525.01	Q_{41}	919.22	Q_{65}	1331.19	Q_{89}	3158.19
Q_{18}	539.86	Q_{42}	942.56	Q_{66}	1359.82	Q_{90}	3168.52
Q_{19}	543.86	Q_{43}	961.3	Q_{67}	1364.99	Q_{91}	3170.74
Q_{20}	548.15	Q_{44}	972.72	Q_{68}	1395.15	Q_{92}	3171.48
Q_{21}	558.75	Q_{45}	983.19	Q_{69}	1406.78	Q_{93}	3172.53
Q_{22}	579.63	Q_{46}	984.11	Q_{70}	1427.18	Q_{94}	3174.41
Q_{23}	589.14	Q_{47}	990.57	Q_{71}	1430.66	Q_{95}	3188.67
Q_{24}	640.01	Q_{48}	992.29	Q_{72}	1453.92	Q_{96}	3203.51

TABLE S15. Intrastate and interstate linear vibronic coupling constants (in eV) for 1,12-benzoperylene entering the model linear vibronic coupling Hamiltonian.

	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_7	-0.0207	-0.0041	-0.0048	0.0078	0.0198	0.0199
Q_{11}	-0.0263	0.0058	-0.027	0.0147	-	-
Q_{16}	0.0203	0.0048	0.0183	-	-	-
Q_{20}	0.0147	0.0144	0.0093	-	0.0226	-
Q_{42}	-0.0113	-0.0017	-0.0225	0.0161	-	0.0218
Q_{49}	-0.0037	1E-4	0.0272	-	0.0245	0.0138
Q_{55}	-0.0399	-8E-4	-0.0258	0.0151	-	--
Q_{57}	-0.0182	-0.0383	0.003	0.0025	-	-
Q_{60}	-6E-4	0.0147	0.0032	-	-	-
Q_{63}	-0.0809	-0.049	-0.0346	0.0107	0.0356	0.0199
Q_{64}	0.0488	0.071	0.0701	-	0.0418	0.0299
Q_{65}	-0.0574	-0.0293	-0.0276	0.0177	0.0301	0.0372
Q_{68}	0.0562	0.1185	0.0121	0.0274	0.0295	0.0489

Q_{69}	-0.0076	0.0079	-0.0539	-	-	-
Q_{75}	-0.0332	0.0156	-0.0068	0.0202	0.0486	0.0465
Q_{77}	0.0544	0.0159	0.0253	0.0016	0.0593	0.0522
Q_{80}	-0.0639	0.0117	-4E-4	0.0421	0.0411	0.0493
Q_{82}	0.1111	-0.0133	0.1252	0.0586	-	-

TABLE S16. The visualization of the normal modes of 1,12-benzoperylene entering the model linear vibronic coupling Hamiltonian.



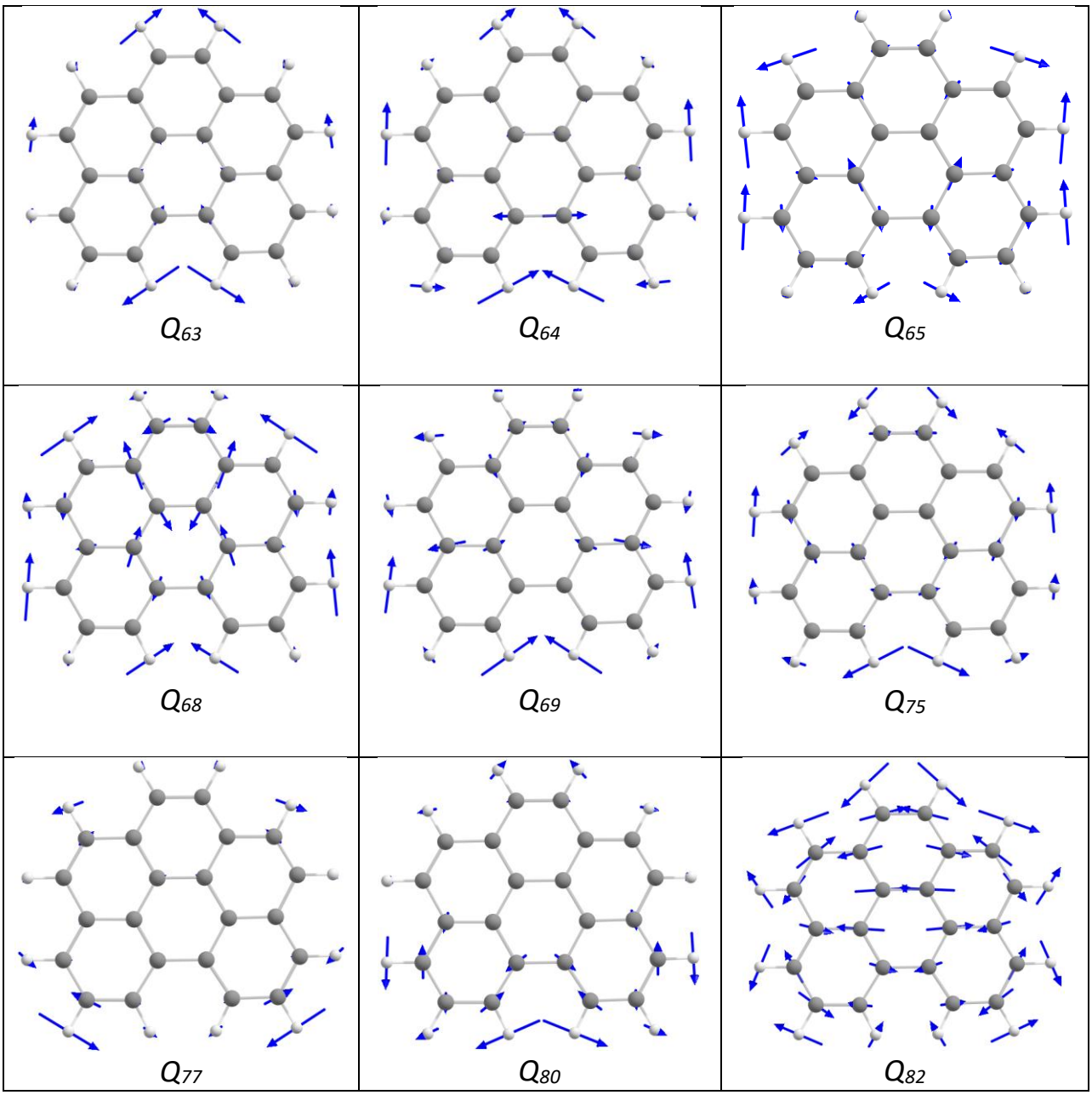


TABLE S17. Number of primitive basis and SPF for different mode combination used in the MCTDH calculation for two lowest excited singlet states of 1,12-benzoperylene.

Modes	Primitive basis	SPF basis
(Q_7, Q_{11}, Q_{16})	(13, 13, 13)	(7, 7)
(Q_{20}, Q_{42}, Q_{49})	(13, 13, 13)	(7, 7)
(Q_{55}, Q_{57}, Q_{60})	(13, 13, 13)	(7, 7)
(Q_{63}, Q_{64}, Q_{65})	(13, 13, 13)	(7, 7)
(Q_{68}, Q_{69}, Q_{75})	(13, 13, 13)	(7, 7)
(Q_{77}, Q_{80}, Q_{82})	(13, 13, 13)	(7, 7)

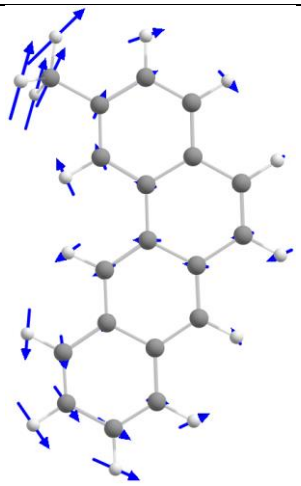
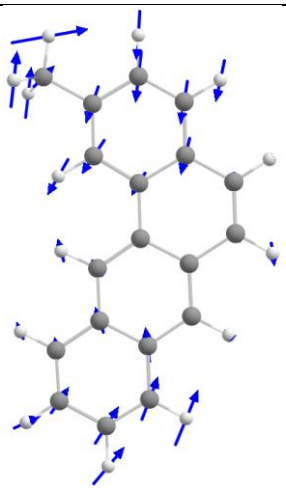
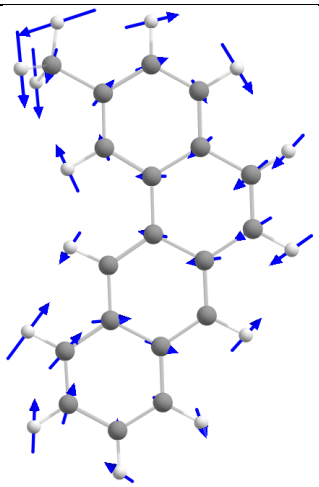
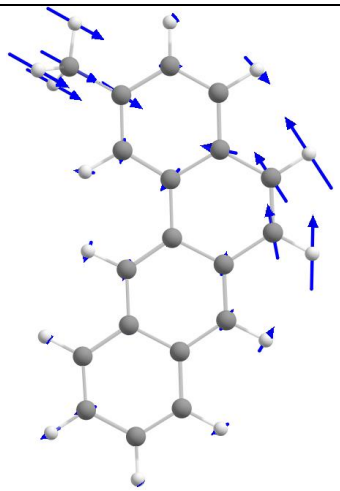
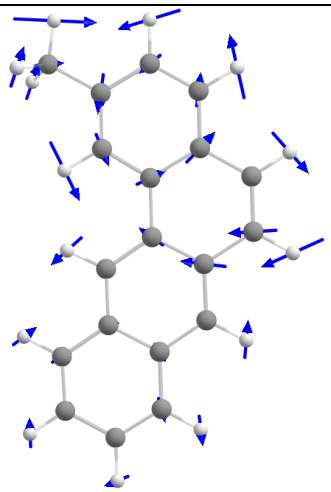
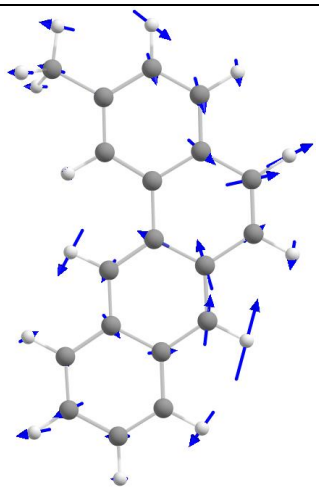
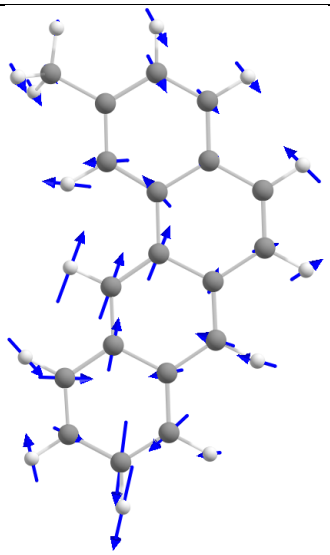
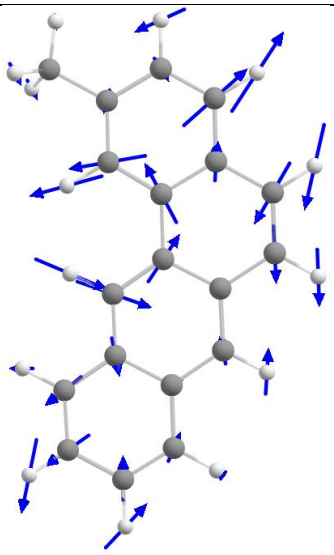
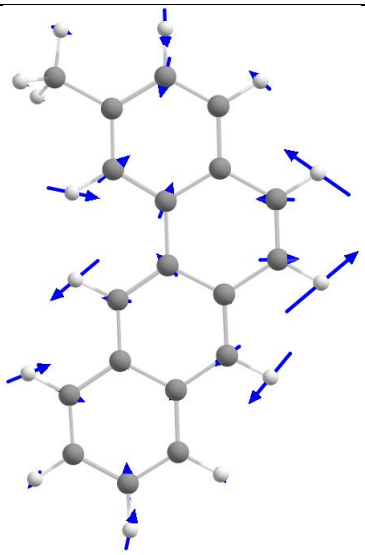
TABLE S18. Calculated frequencies (in cm^{-1}) at the optimized ground state geometry of 2'-methyl-1,2-benzanthracene.

Q_1	14.47	Q_{25}	699.34	Q_{49}	1127.6	Q_{73}	1542.38
Q_2	49.96	Q_{26}	708.93	Q_{50}	1164.82	Q_{74}	1573.95
Q_3	61.66	Q_{27}	751.93	Q_{51}	1169.29	Q_{75}	1588.96
Q_4	133.94	Q_{28}	752.7	Q_{52}	1187.88	Q_{76}	1626.99
Q_5	137.87	Q_{29}	770.59	Q_{53}	1200.12	Q_{77}	1646.11
Q_6	152.58	Q_{30}	792.4	Q_{54}	1211.39	Q_{78}	1654.98
Q_7	228.09	Q_{31}	796.32	Q_{55}	1227.17	Q_{79}	1660.64
Q_8	269.52	Q_{32}	798.14	Q_{56}	1246.2	Q_{80}	3018.22
Q_9	286.41	Q_{33}	845.8	Q_{57}	1266.4	Q_{81}	3067.52
Q_{10}	307.7	Q_{34}	847.06	Q_{58}	1284.6	Q_{82}	3094.25
Q_{11}	325.54	Q_{35}	856.41	Q_{59}	1311.62	Q_{83}	3150.11
Q_{12}	398.84	Q_{36}	898.14	Q_{60}	1319.58	Q_{84}	3152.61
Q_{13}	409.56	Q_{37}	900.32	Q_{61}	1340.06	Q_{85}	3155.61
Q_{14}	431.99	Q_{38}	904.73	Q_{62}	1366.25	Q_{86}	3156.36
Q_{15}	443.71	Q_{39}	909.71	Q_{63}	1380.02	Q_{87}	3160.05
Q_{16}	474.76	Q_{40}	934.93	Q_{64}	1405.78	Q_{88}	3165.45
Q_{17}	484.01	Q_{41}	971.78	Q_{65}	1416.98	Q_{89}	3168.42
Q_{18}	529.54	Q_{42}	975.03	Q_{66}	1431.34	Q_{90}	3173.6
Q_{19}	530.49	Q_{43}	988.79	Q_{67}	1449.75	Q_{91}	3173.86
Q_{20}	564.77	Q_{44}	995.03	Q_{68}	1457.68	Q_{92}	3186.57
Q_{21}	588.74	Q_{45}	1009.28	Q_{69}	1481.49	Q_{93}	3188.63
Q_{22}	589.1	Q_{46}	1031.04	Q_{70}	1488.82		
Q_{23}	638.28	Q_{47}	1050.67	Q_{71}	1496.63		
Q_{24}	670.03	Q_{48}	1059.95	Q_{72}	1510.53		

TABLE S19. Intrastate and interstate linear vibronic coupling constants (in eV) for 2'-methyl-1,2-benzanthracene entering the model linear vibronic coupling Hamiltonian.

	κ_i^{S1}	κ_i^{S2}	κ_i^{S3}	$\lambda_i^{S1,S2}$	$\lambda_i^{S1,S3}$	$\lambda_i^{S2,S3}$
Q_5	0.0073	-0.0092	-0.002	0.0071	-	0.0089
Q_{11}	0.0246	0.0083	0.0309	0.0066	-	-
Q_{12}	1E-4	-0.0269	-0.0205	0.0173	0.0273	-
Q_{15}	0.0146	0.0011	0.0147	0.01	-	-
Q_{17}	0.0172	-7E-4	0.0124	0.0084	-	-
Q_{18}	-0.0154	0.0161	8E-4	0.0191	0.0254	-
Q_{22}	0.0117	0.001	0.0087	0.0063	-	-
Q_{24}	-0.0011	0.0131	-0.0297	0.0057	-	-
Q_{37}	-0.0261	-0.0058	-0.0303	0.0119	-	-
Q_{47}	0.018	-0.0105	0.0219	0.0198	0.0218	-
Q_{55}	0.0317	0.0171	0.0388	0.0031	-	0.0042
Q_{66}	0.0052	0.0233	-0.0089	0.0073	-	-
Q_{67}	-0.0283	-0.0446	0.0077	0.0148	-	-
Q_{68}	-0.0696	-0.0814	-0.0239	0.0096	-	0.0036
Q_{76}	-0.0514	-0.0341	-0.0392	0.0075	-	-
Q_{77}	0.0181	0.0395	0.0438	0.0322	0.0885	0.0389
Q_{78}	0.063	0.0491	0.0183	0.0092	-	-
Q_{79}	-0.0311	-0.0017	-0.0067	0.0149	-	-

TABLE S20. The visualization of the normal modes of 2'-methyl-1,2-benzanthracene entering the model linear vibronic coupling Hamiltonian.

 Q_5	 Q_{11}	 Q_{12}
 Q_{15}	 Q_{17}	 Q_{18}
 Q_{22}	 Q_{24}	 Q_{37}

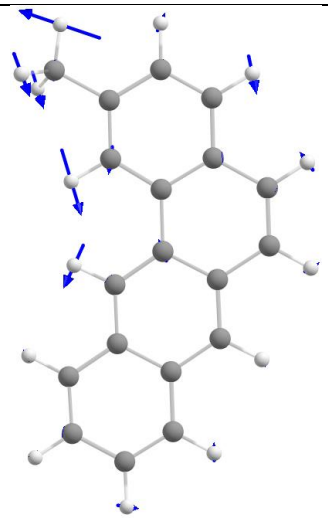
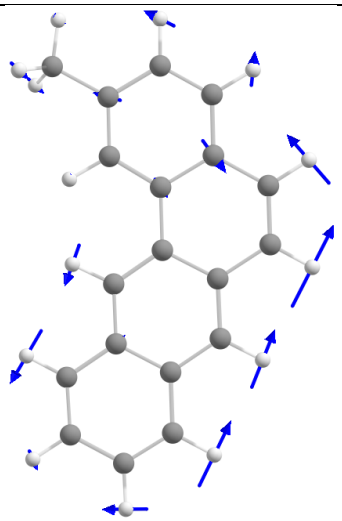
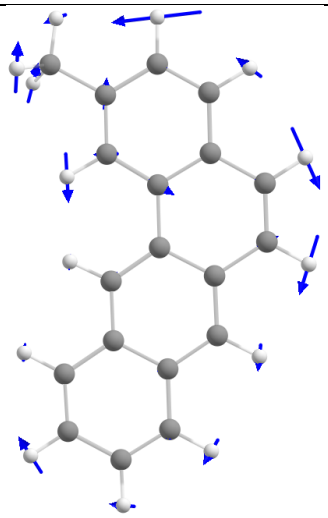
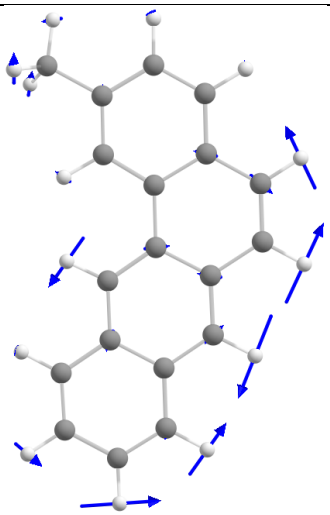
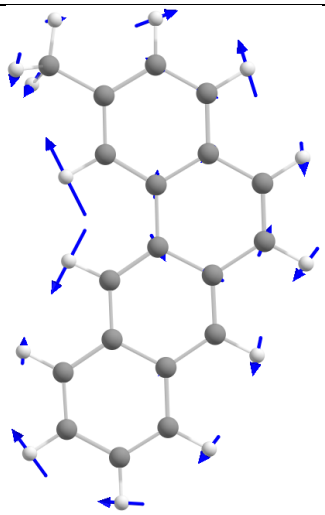
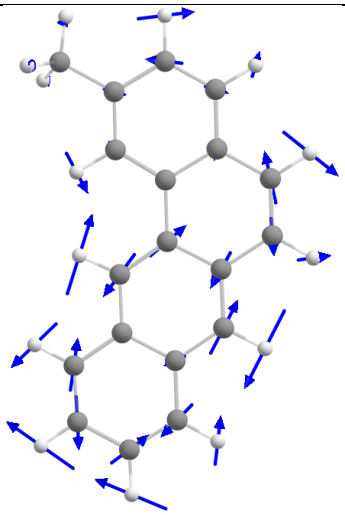
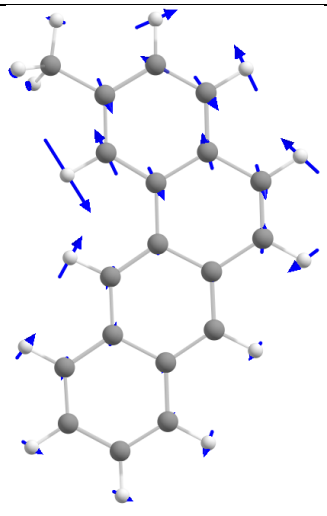
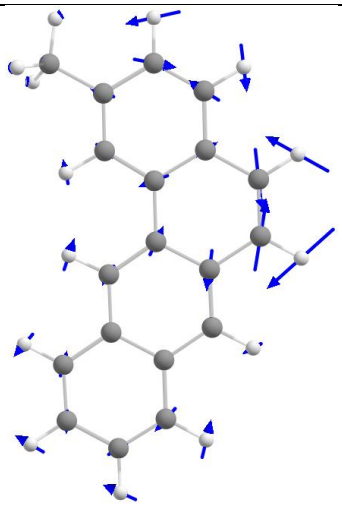
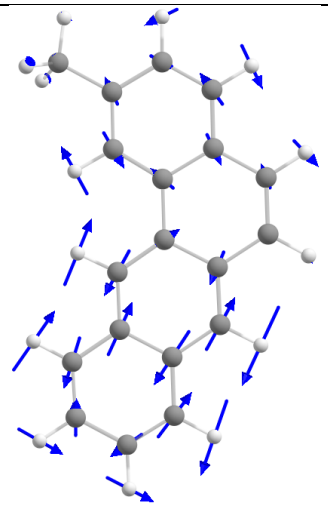
 Q_{47}	 Q_{55}	 Q_{66}
 Q_{67}	 Q_{68}	 Q_{76}
 Q_{77}	 Q_{78}	 Q_{79}

TABLE S21. Number of primitive basis and SPF for different mode combination used in the MCTDH calculation for two lowest excited singlet states of 2'-methyl-1,2-benzanthracene.

Modes	Primitive basis	SPF basis
(Q_5, Q_{11}, Q_{12})	(13, 13, 13)	(7, 7)
(Q_{15}, Q_{17}, Q_{18})	(13, 13, 13)	(7, 7)
(Q_{22}, Q_{24}, Q_{37})	(13, 13, 13)	(7, 7)
(Q_{47}, Q_{55}, Q_{66})	(13, 13, 13)	(7, 7)
(Q_{67}, Q_{68}, Q_{76})	(13, 13, 13)	(7, 7)
(Q_{77}, Q_{78}, Q_{79})	(13, 13, 13)	(7, 7)

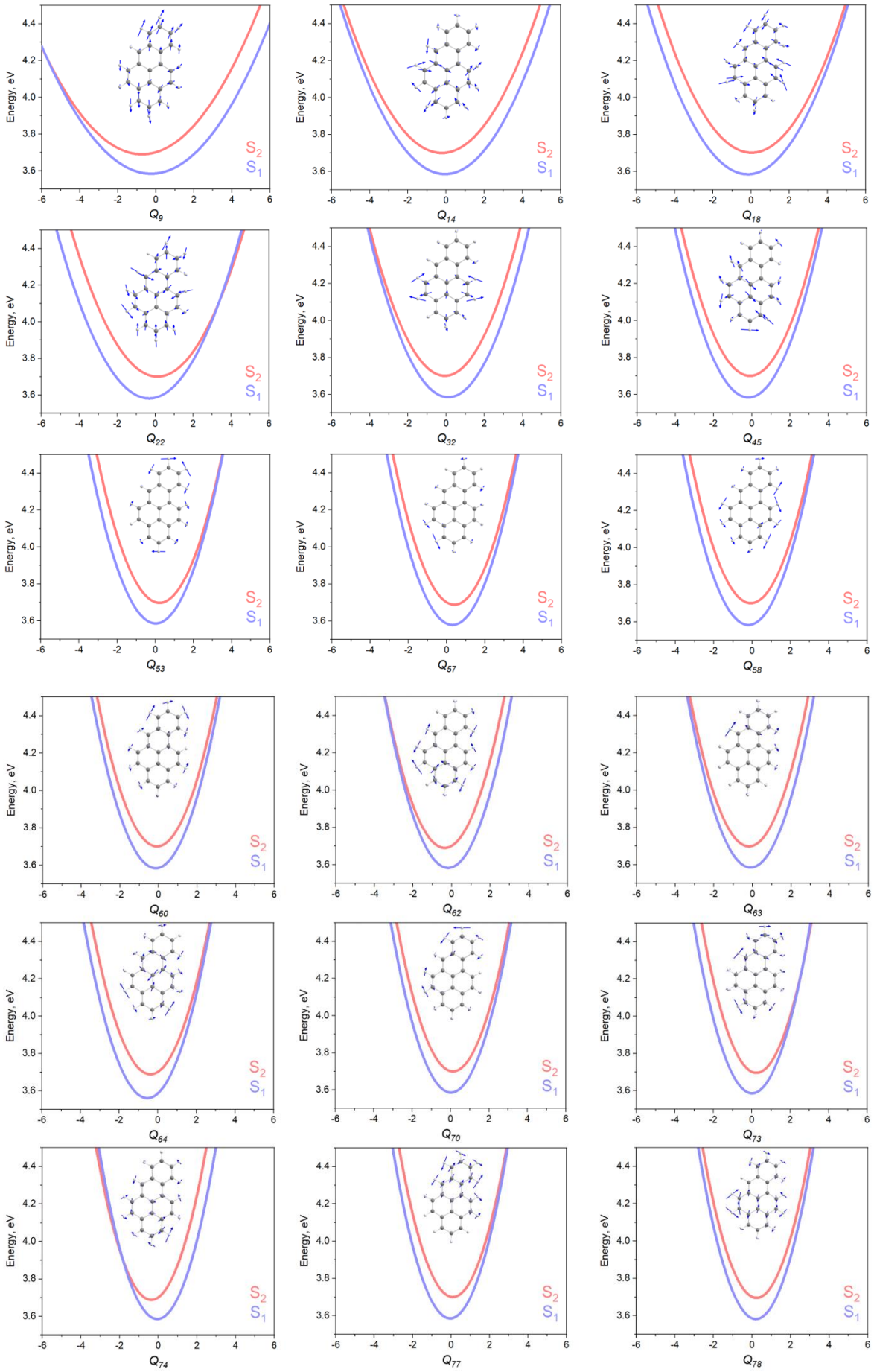


FIG. S2. **1D cuts of the diabatic potentials associated with the S_1 and S_2 states for 3,4-benzopyrene along the most relevant normal modes that enter a model Hamiltonian.**

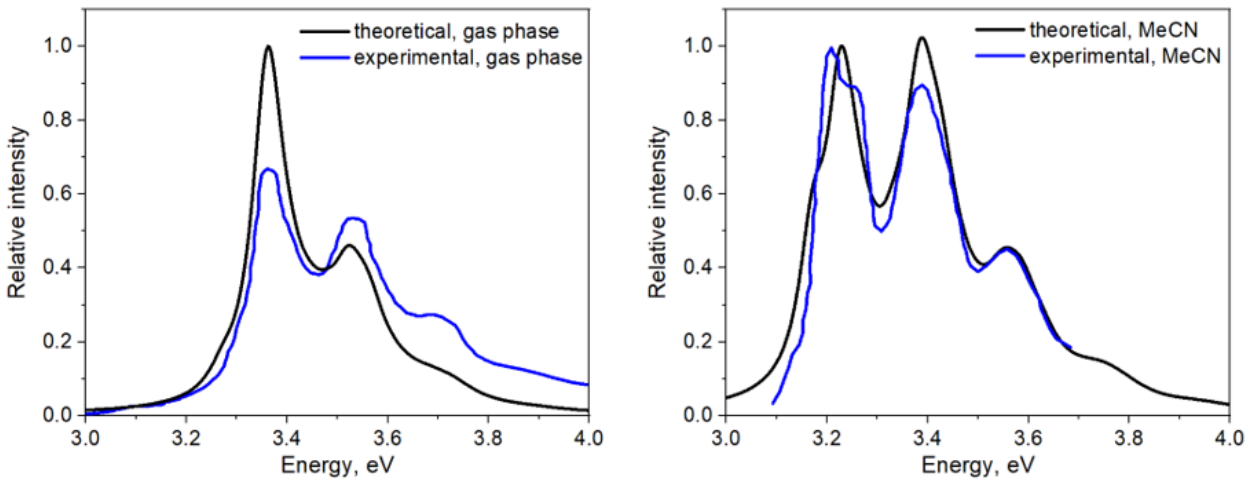


FIG. S3. Comparison of the experimental $S_0 \rightarrow S_2$ absorption spectra of 3,4-benzopyrene in the gas phase[1] (left) and in MeCN solution[2-3] (right) with theoretical spectra generated by MCTDH.

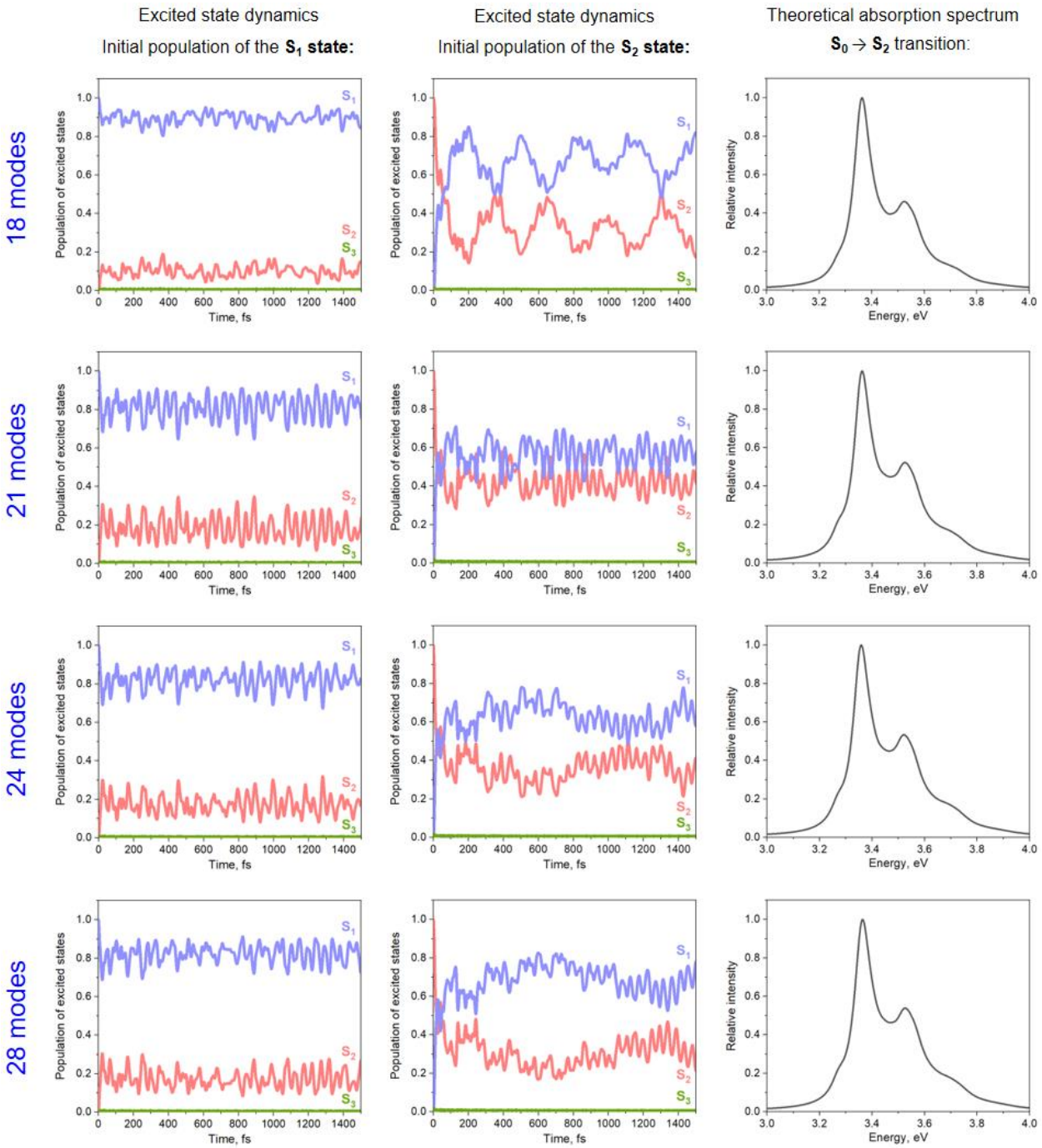


FIG. S4. Population kinetics of the S_1 and S_2 states of 3,4-benzopyrene for the first 1.5 ps after excitation into the S_1 state (left) or into the S_2 state (middle) for different sets of normal modes included in the model Hamiltonian (18, 21, 24 or 28 modes). The corresponding $S_0 \rightarrow S_2$ absorption spectra simulated by MCTDH (right). The normal modes were selected using **the novel methodology based on the new parameters $\mathbb{K}_i^{(S1,S2)}$ and $\beta_i^{(S1,S2)}$**.

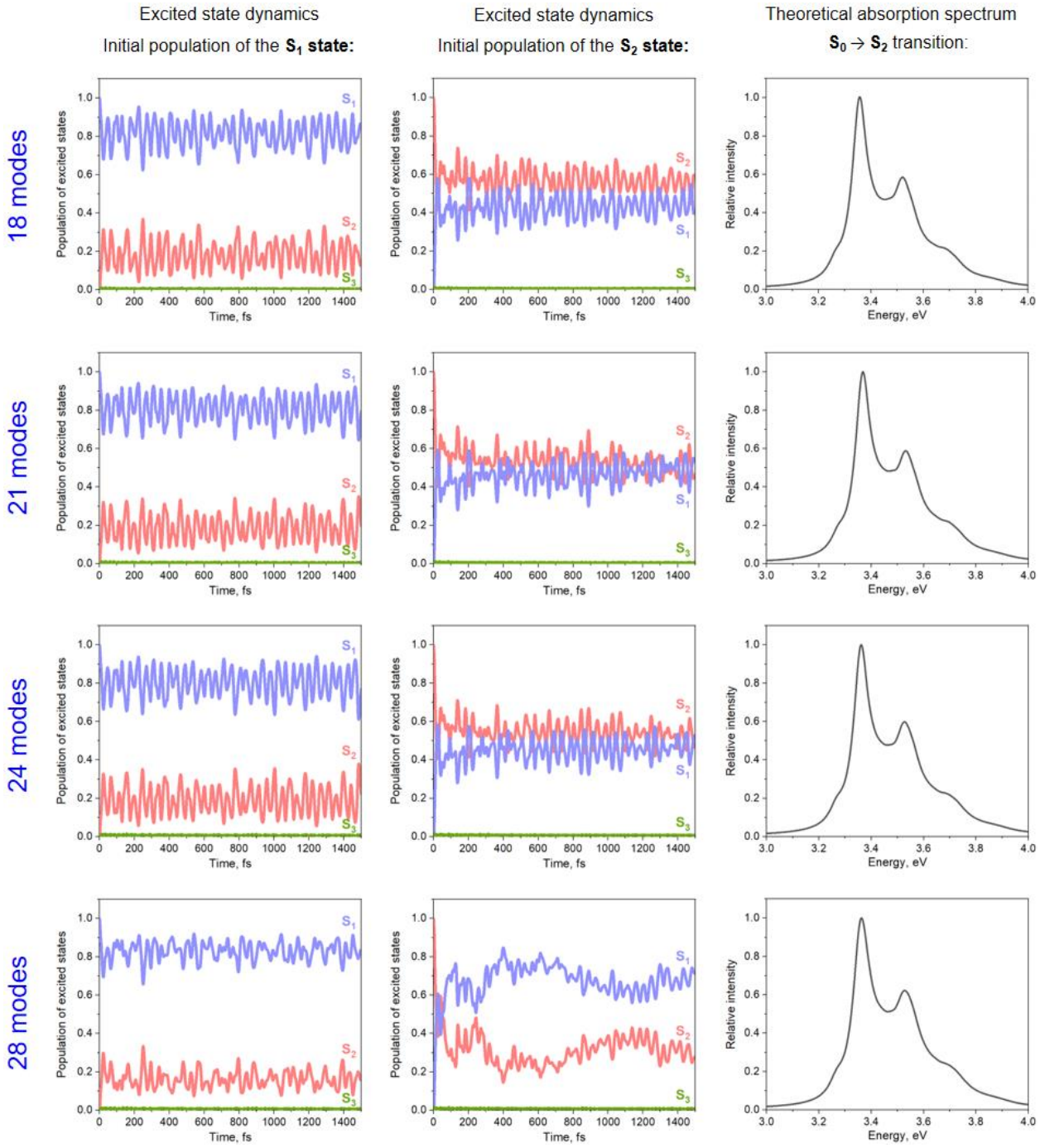


FIG. S5. Population kinetics of the S_1 and S_2 states of 3,4-benzopyrene for the first 1.5 ps after excitation into the S_1 state (left) or into the S_2 state (middle) for different sets of normal modes included in the model Hamiltonian (18, 21, 24 or 28 modes). The corresponding $S_0 \rightarrow S_2$ absorption spectra simulated by MCTDH (right). The normal modes were selected using **the "classical" methodology based on the Poisson parameters** $\alpha_i^{(S1)} = (\kappa_i^{(S1)}/\omega_i)^2$ **and** $\alpha_i^{(S2)} = (\kappa_i^{(S2)}/\omega_i)^2$.

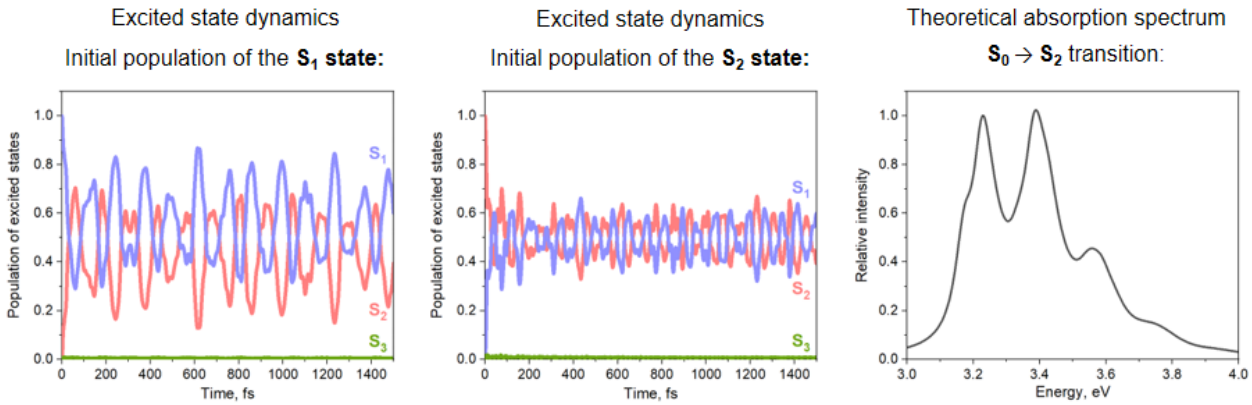


FIG. S6. Population kinetics of the S_1 and S_2 states of 3,4-benzopyrene for the first 1.5 ps after excitation into the S_1 state (left) or into the S_2 state (middle) **including the solvation effects of MeCN.**

References:

[1] P. A. Geldof, R. P. H. Rettschnick, and G. J. Hoytink, Chem. Phys. Lett. **4**, 59–61 (1969).

[2] Y. Han, X. Wang, X. He, M. Jia, H. Pan, and J. Chen, Molecules **28**, 5269 (2023).

[3] A. A. Elbashir, A. A. Alfadil, F. O. Suliman, and A. O. Alnajjar, Molecules **28**, 1136 (2023).