Supplementary Material (ESI) for PCCP

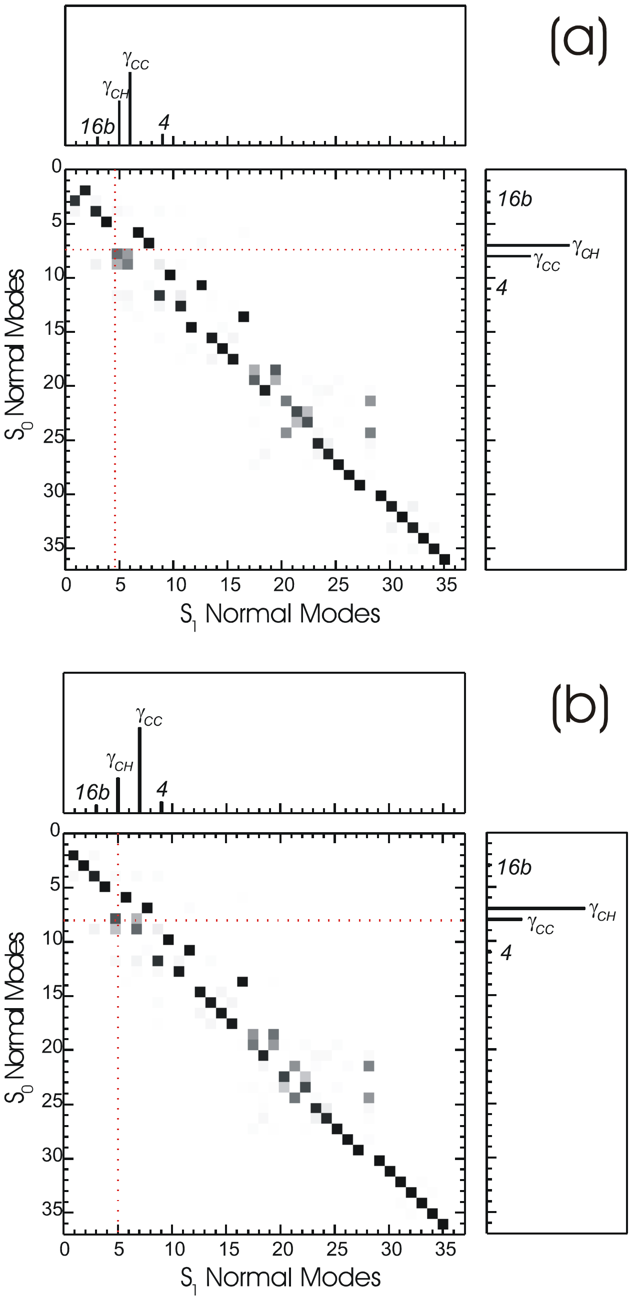
Supplementary Table 1: The (10,10)-CASSCF vibrational frequencies and assignments found at the (10,10)-CASSCF optimized geometries. # = Vibrational mode number, V = Varsanyi notation, S = symmetry, M = Mulliken notation.

#	Assignment									(10,10)-CASSCF Freq @ (10,10)-CASSCF geometry		
	S_0			S_1			D_0					
	V	S	M	V	S	M	V	S	M	S_0	S_1	D_0
1	$\gamma_{C\equiv C}$	b_1	24^1	$\gamma_{C\equiv C}$	b_1	24^1	$\gamma_{C\equiv C}$	b_1	24^1	141.5	113.2	121.7
2	$\beta_{C\equiv C}$	b_2	36^1	$\beta_{C\equiv C}$	b_2	36^1	$\beta_{C\equiv C}$	b_2	36^1	145.9	142.8	132.6
3	*16b*	b_1	23^1	*16b*	b_1	23^1	*16b*	b_1	23^1	354.5	293.2	311.7
4	*16a*	a_2	16^1	*16a*	a_2	16^1	*16a*	a_2	16^1	428.2	294.0	379.4
5	*6a*	a_1	13^1	γ_{CC}	b_1	22^1	β_{CC}	b_2	35^1	492.5	418.5	487.3
6	β_{CC}	b_2	35^1	*6a*	a_1	13^1	*6a*	a_1	13^1	504.7	451.5	488.3
7	γ_{CH}	b_1	22^1	γ_{CH}	b_1	21^1	γ_{CC}	b_1	22^1	523.0	455.4	492.4
8	γ_{CC}	b_1	21^1	β_{CC}	b_2	35^1	*6b*	b_2	34^1	547.0	492.9	578.4
9	β_{CH}	b_2	34^1	*4*	b_1	20^1	β_{CH}	b_2	33^1	566.2	519.2	608.2
10	*6b*	b_2	33^1	β_{CH}	b_2	34^1	*4*	b_1	21^1	665.7	551.5	669.1
11	*4*	b_1	20^1	*11*	b_1	19^1	γ_{CH}	b_1	20^1	716.7	579.2	685.0
12	*11*	b_1	19^1	*6b*	b_2	33^1	*1*	a_1	12^1	778.0	600.9	794.8
13	*1*	a_1	12^1	*10a*	a_2	15^1	*11*	b_1	19^1	804.9	609.3	841.0
14	*10a*	a_2	15^1	*17b*	b_1	18^1	*10a*	a_2	15^1	864.1	652.5	857.9
15	*17b*	b_1	18^1	*17a*	a_2	14^1	*17b*	b_1	18^1	936.6	695.8	1015.9
16	*17a*	a_2	14^1	*5*	b_1	17^1	*18a*	a_1	11^1	988.6	733.4	1035.7
17	*5*	b_1	17^1	*1*	a_1	12^1	*17a*	a_2	14^1	1010.9	753.7	1041.5
18	*12*	a_1	11^1	*18a*	a_1	11^1	*5*	b_1	17^1	1062.5	979.8	1049.9
19	*18a*	a_1	10^1	*18b*	b_2	32^1	*12*	a_1	10^1	1098.4	1011.7	1064.4
20	*18b*	b_2	32^1	*12*	a_1	10^1	*18b*	b_2	32^1	1147.2	1023.7	1151.0
21	*9b*	b_2	31^1	*9a*	a_1	9^1	*14*	b_2	31^1	1194.6	1229.0	1224.6
22	*9a*	a_1	9^1	*14*	b_2	31^1	*9a*	a_1	9^1	1261.1	1235.9	1277.1
23	*13*	a_1	8^1	*13*	a_1	8^1	*13*	a_1	8^1	1275.6	1250.4	1321.0
24	*14*	b_1	30^1	*3*	b_2	30^1	*3*	b_2	30^1	1304.6	1379.4	1385.0
25	*3*	b_2	29^1	*19b*	b_2	29^1	*19b*	b_2	29^1	1428.4	1483.2	1484.9
26	*19b*	b_2	28^1	*19a*	a_1	7^1	*9b*	b_2	28^1	1560.6	1530.9	1512.0
27	*19a*	a_1	7^1	*9b*	b_2	28^1	*19a*	a_1	7^1	1619.6	1625.5	1574.5
28	*8b*	b_2	27^1	*8a*	a_1	6^1	*8b*	b_2	27^1	1709.0	1677.5	1636.2
29	*8a*	a_1	6^1	*8b*	b_2	27^1	*8a*	a_1	6^1	1741.7	1845.4	1773.8
30	$\nu_{C\equiv C}$	a_1	5^1	$\nu_{C\equiv C}$	a_1	5^1	$\nu_{C\equiv C}$	a_1	5^1	2250.5	2174.5	2150.1
31	*20a*	a_1	4^1	*20a*	a_1	4^1	*7a*	a_1	4^1	3333.7	3354.1	3371.6
32	*7b*	b_2	26^1	*7b*	b_2	26^1	*7b*	b_2	26^1	3343.7	3362.2	3381.3
33	*7a*	a_1	3^1	*7a*	a_1	3^1	*20a*	a_1	3^1	3355.4	3372.7	3386.0
34	*20b*	b_2	25^1	*20b*	b_2	25^1	*20b*	b_2	25^1	3364.2	3380.5	3395.4
35	*2*	a_1	2^1	*2*	a_1	2^1	*2*	a_1	2^1	3369.4	3388.0	3398.0
36	ν_{CH}	a_1	1^1	ν_{CH}	a_1	1^1	ν_{CH}	a_1	1^1	3622.6	3621.4	3580.6

Supplementary Table 2: The (10,10)-CASSCF vibrational frequencies and assignments found at SACCI optimized geometries. # = Vibrational mode number, V = Varsanyi notation, S = symmetry, M = Mulliken notation.

#	Assignment									(10,10)-CASSCF Freq @ SACCI geometry		
	S_0			S_1			D_0					
	V	S	M	V	S	M	V	S	M	S_0	S_1	D_0
1	$\beta_{C\equiv C}$	b_1	24^1	$\gamma_{C\equiv C}$	b_1	36^1	$\gamma_{C\equiv C}$	b_1	24^1	87.1	61.9	85.6
2	$\gamma_{C\equiv C}$	b_2	36^1	$\beta_{C\equiv C}$	b_2	24^1	$\beta_{C\equiv C}$	b_2	36^1	93.2	92.2	90.4
3	16b	b_1	23^1	16b	b_1	23^1	16b	b_1	23^1	338.5	263.2	294.4
4	16a	a_2	16^1	16a	a_2	16^1	16a	a_2	16^1	420.3	265.5	371.8
5	6a	a_1	13^1	γ_{CC}	b_1	22^1	γ_{CC}	b_1	22^1	490.7	406.4	483.9
6	β_{CC}	b_2	35^1	γ_{CH}	a_1	21^1	6a	a_1	13^1	499.3	445.8	486.6
7	γ_{CH}	b_1	22^1	6a	b_1	13^1	β_{CC}	b_2	35^1	520.1	452.3	486.6
8	γ_{CC}	b_1	21^1	β_{CC}	b_2	35^1	6b	b_2	34^1	541.3	489.8	577.6
9	β_{CH}	b_2	34^1	4	b_1	20^1	β_{CH}	b_2	33^1	562.7	504.2	605.4
10	6b	b_2	33^1	β_{CH}	b_2	34^1	4	b_1	21^1	664.3	542.6	653.9
11	4	b_1	20^1	11	b_1	19^1	γ_{CH}	b_1	20^1	706.7	554.4	678.2
12	11	b_1	19^1	10a	b_2	15^1	1	a_1	12^1	762.5	587.1	790.4
13	1	a_1	12^1	6b	a_2	33^1	11	b_1	19^1	800.8	602.0	828.6
14	10a	a_2	15^1	17b	b_1	18^1	10a	a_2	15^1	845.0	638.6	837.6
15	17b	b_1	18^1	17a	a_2	14^1	17b	b_1	18^1	920.9	674.6	1003.0
16	17a	a_2	14^1	5	b_1	17^1	17a	a_2	14^1	974.1	714.3	1025.2
17	5	b_1	17^1	1	a_1	12^1	5	b_1	17^1	995.5	763.0	1033.3
18	12	a_1	11^1	18a	a_1	11^1	18a	a_1	11^1	1067.3	997.7	1038.5
19	18a	a_1	10^1	18b	b_2	32^1	12	a_1	10^1	1097.1	1033.6	1063.2
20	18b	b_2	32^1	12	a_1	10^1	18b	b_2	32^1	1149.7	1036.8	1155.2
21	14	b_2	31^1	14	a_1	31^1	14	b_2	31^1	1202.4	1236.5	1221.7
22	9a	a_1	9^1	9a	b_2	9^1	9a	a_1	9^1	1255.6	1238.9	1267.6
23	13	a_1	8^1	13	a_1	8^1	13	a_1	8^1	1269.6	1256.3	1313.2
24	9b	b_1	30^1	3	b_2	30^1	3	b_2	30^1	1302.8	1388.7	1382.6
25	3	b_2	29^1	19b	b_2	29^1	19b	b_2	29^1	1423.7	1490.2	1487.7
26	19b	b_2	28^1	19a	a_1	7^1	9b	b_2	28^1	1562.5	1539.3	1510.8
27	19a	a_1	7^1	8b	b_2	28^1	19a	a_1	7^1	1616.9	1660.6	1567.8
28	8b	b_2	27^1	8a	a_1	6^1	8b	b_2	27^1	1714.2	1710.0	1638.8
29	8a	a_1	6^1	9b	b_2	27^1	8a	a_1	6^1	1748.8	1886.9	1777.1
30	$\nu_{C\equiv C}$	a_1	5^1	$\nu_{C\equiv C}$	a_1	5^1	$\nu_{C\equiv C}$	a_1	5^1	2286.7	2209.8	2173.0
31	20a	a_1	4^1	20a	a_1	4^1	20a	a_1	4^1	3378.0	3391.2	3414.9
32	7b	b_2	26^1	7b	b_2	26^1	7b	b_2	26^1	3384.6	3398.8	3419.0
33	7a	a_1	3^1	7a	a_1	3^1	7a	a_1	3^1	3393.7	3404.0	3421.6
34	20b	b_2	25^1	20b	b_2	25^1	20b	b_2	25^1	3402.9	3413.9	3440.8
35	2	a_1	2^1	2	a_1	2^1	2	a_1	2^1	3412.1	3424.0	3444.4
36	ν_{CH}	a_1	1^1	ν_{CH}	a_1	1^1	ν_{CH}	a_1	1^1	3642.3	3642.8	3597.5

Supplementary Figure 1: The Duschinsky matrices for the (a) SACCI and (b) CASSCF Franck-Condon analyses for S_1-S_0 and S_0-S_1 electronic transitions. Both graphs (a) and (b) show the mixing of the γ_{CC} mode for the S_1-S_0 electronic (top window) and S_0-S_1 fluorescence (side window) transitions. Mode ordering on ordinate and abscissa may be related to the appropriate vibration by comparison to Supplementary Tables 1 and 2.



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Supplementary Figure 2: The Duschinsky matrices for the (a) D_0-S_1 TPES and (b) D_0-S_0 MATI CASSCF Franck-Condon analyses for ionizing transitions. The mixing of various modes is shown in each window (side windows are not shown as these correspond to $S_1 - D_0$ and $S_0 - D_0$ processes). Some minor differences between mixed modes may be noticed compared to the Duschinsky matrices for S_1-S_0 and S_0-S_1 type transitions. Mode ordering on ordinate and abscissa may be related to the appropriate vibration by comparison to Supplementary Table 1.