Supporting information for "Time-dependent density-functional description of the ^1L_a state in polycyclic aromatic hydrocarbons: Charge-transfer character in disguise?"

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Abstract

This document tabulates TD-DFT excitation energies for the various PAHs and density functionals that are considered in this work. For easy comparison, both experimental as well as CC2 excitation energies, taken from the work of Grimme and Parac, are reproduced here. Values of the Λ metric for the nonlinear PAHs are also tabulated here. Cartesian coordinates for each of the PAHs are available in a separate document.

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L_a															
Number of Rings	Exp.	B3LYP	LRC-ωPBE	LRC-ωPBEh	B3LYP$^{\dagger\,a}$	LRC-ωPBE†	LRC-ωPBEh†	BP86	CC2	LRC-μBLYP	LRC-μBLYP†	LRC-μBLYP$^{*\,b}$	LRC-μBLYP*†	LRC-μBOP	LRC-μBOP†
2	4.66(266)	4.35(285)	4.76(261)	4.66(266)	4.54(273)	5.01(248)	4.89(254)	4.11(302)	4.88(254)	4.38(283)	4.60(270)	4.73(262)	4.97(249)	4.86(255)	5.11(243)
3	3.60(344)	3.18(390)	3.64(341)	3.53(351)	3.40(365)	3.92(316)	3.80(3.26)	2.95(420)	3.69(336)	3.28(378)	3.54(350)	3.61(343)	3.89(319)	3.75(331)	4.04(307)
4	2.88(431)	2.41(515)	2.88(431)	2.78(446)	2.64(470)	3.19(389)	3.07(404)	2.17(571)	2.90(428)	2.56(484)	2.86(434)	2.86(434)	3.17(391)	2.99(415)	3.30(376)
5	2.37(523)	1.86(667)	2.35(528)	2.26(549)	2.11(588)	2.69(461)	2.57(482)	1.63(761)	2.35(528)	2.07(599)	2.39(519)	2.33(532)	2.66(466)	2.43(510)	2.76(449)
6	2.02(614)	1.47(844)	1.97(629)	1.88(660)	1.72(721)	2.31(537)	2.21(561)	1.23(1008)	1.95(636)	1.72(721)	2.06(602)	1.95(636)	2.29(541)	2.03(611)	2.37(523)
MAE	0.00(0)	N/A^{c}	0.04(5.9)	0.08(18.7)	N/A	0.27(33.3)	0.19(28.7)	N/A	0.08(10.0)	0.30(57.5)	0.04(5.7)	0.04(8.0)	0.29(42.2)	0.16(11)	0.41(55.8)

L_b															
Number of Rings	Exp.	B3LYP	LRC-ωPBE	LRC-ωPBEh	B3LYP†	LRC-ωPBE†	LRC-ωPBEh†	BP86	CC2	LRC-μBLYP	LRC-μBLYP†	LRC-μBLYP*	LRC-μBLYP*†	LRC-μBOP	LRC-μBOP†
2	4.13(300)	4.44(279)	4.57(271)	4.59(270)	4.46(278)	4.65(267)	4.65(267)	4.26(291)	4.46(278)	4.38(283)	4.40(282)	4.55(273)	4.62(268)	4.65(267)	4.78(259)
3	3.64(341)	3.83(324)	4.00(310)	4.02(308)	3.85(322)	4.09(303)	4.08(304)	3.64(341)	3.89(319)	3.83(324)	3.85(322)	3.98(312)	4.07(305)	4.06(305)	4.21(295)
4	3.39(366)	3.45(359)	3.63(342)	3.65(340)	3.46 (358)	3.49(355)	3.48(356)	3.24(383)	3.52(352)	3.49(355)	3.51(353)	3.62(343)	3.71(334)	3.67(338)	3.83(324)
5	3.12(397)	3.18(390)	3.38(367)	3.41(364)	3.20(388)	3.49(355)	3.48(356)	2.96(419)	3.27(379)	3.26(381)	3.29(377)	3.37(368)	3.47(357)	3.40(365)	3.58(346)
6	2.87(432)	3.00(413)	3.20(388)	3.23(384)	3.01(412)	3.32(373)	3.31(375)	2.76(449)	3.09(401)	3.11(399)	3.14(395)	3.19(389)	3.30(376)	3.20(388)	3.39(366)
MAE	0.00(0)	0.15(14.0)	0.33(31.8)	0.35(34.1)	0.17(15.6)	0.43(41.0)	0.42(40.3)	0.11(13.0)	0.22(21.3)	0.18(18.8)	0.21(21.4)	0.31(30.6)	0.40(39.0)	0.37(34.8)	0.53(49.3)

[a] "†" indicates the use of the Tamm-Dancoff approximation

[b] " * " indicates the use of a Coloumb attenuation parameter of 0.30 a.u.$^{-1}$

[c] An MAE of "N/A" means the MAE was omitted because the data fails to properly predict the experimental trend

TABLE S1: Vertical excitation energies for both the ^1L_a and ^1L_b states, in eV. (Values in nm are given in parenthesis.) CC2 and TD-BP86 values are from Grimme and Parac. (Grimme, S.; Parac, M. *ChemPhysChem* **2003**, *4*, 292.) Experimental values are from Bierman and Schidt.(Biermann, D.; Schmidt, J. *J. Am. Chem. Soc.* **1980**,*102*, 3163.)

Molecule[a]	Expt.	TD-DFT		
		B3LYP	LRC-ωPBE	LRC-ωPBEh
1	4.24	4.18	4.63	4.53
2	3.71	3.65	4.06	3.96
3	4.54	4.15	4.61	4.52
4	3.89	3.79	4.28	4.18
5	3.63	3.31	3.83	3.72
6	2.85	2.79	3.25	3.13
7	3.73	3.69	4.18	4.07
8	3.22	3.12	3.56	3.46
9	3.80	3.69	4.22	4.12
10	3.84	3.42	4.00	3.88
11	3.84	3.45	4.02	3.90
12	3.86	3.48	4.03	3.92
13	3.40	3.07	3.63	3.51
14	2.86	2.80	3.18	3.09
15	3.72	3.41	3.87	3.77
MAE	—	0.21	0.28	0.18

[a]See the labels in the main paper.

TABLE S2: Vertical excitation energies (in eV) and mean absolute errors (MAEs) for the ^1L_a state in various PAHs. Experimental band maxima in non-polar solvents (from Birks, J. B. *Photophysics of Aromatic Molecules;* Wiley: New York, 1970.)

Molecule[a]	Expt.	TD-DFT		
		B3LYP	LRC-ωPBE	LRC-ωPBEh
1	3.76	3.94	4.25	4.23
2	3.53	3.72	3.93	3.93
3	3.89	3.95	4.33	4.29
4	3.43	3.72	4.06	4.03
5	3.22	3.54	3.91	3.87
6	—	3.58	4.00	3.95
7	3.37	3.60	3.95	3.92
8	3.06	3.39	3.69	3.67
9	3.30	3.53	3.92	3.89
10	3.32	3.37	3.80	3.75
11	3.31	3.61	4.04	4.00
12	3.14	3.38	3.83	3.77
13	3.23	3.45	3.82	3.79
14	—	3.26	3.49	3.48
15	—	3.19	3.48	3.46
MAE	—	0.22	0.58	0.55

[a]See the labels in the main paper.

TABLE S3: Vertical excitation energies (in eV) and mean absolute errors (MAEs) for the ^1L_b state in various PAHs. Experimental band maxima in non-polar solvents (from Birks, J. B. *Photophysics of Aromatic Molecules;* Wiley: New York, 1970.)

PAH	$\Lambda(^1L_a)$			$\Lambda(^1L_b)$		
	B3LYP	LRC-ωPBE	LRC-ωPBEh	B3LYP	LRC-ωPBE	LRC-ωPBEh
1	0.85	0.85	0.85	0.68	0.70	0.69
2	0.90	0.89	0.89	0.70	0.70	0.70
3	0.86	0.85	0.85	0.72	0.71	0.71
4	0.74	0.79	0.78	0.72	0.66	0.67
5	0.80	0.78	0.80	0.64	0.67	0.65
6	0.80	0.80	0.80	0.61	0.61	0.62
7	0.80	0.80	0.80	0.58	0.61	0.61
8	0.84	0.83	0.84	0.66	0.68	0.67
9	0.78	0.78	0.79	0.68	0.71	0.71
10	0.87	0.87	0.87	0.67	0.67	0.67
11	0.83	0.83	0.83	0.67	0.67	0.67
12	0.73	0.77	0.76	0.73	0.69	0.70
13	0.78	0.78	0.78	0.63	0.63	0.63
14	0.95	0.94	0.94	0.70	0.71	0.71
15	0.81	0.81	0.81	0.66	0.66	0.66

TABLE S4: Values of the CT metric, Λ, for the nonlinear PAHs.