Supporting Information for:

A Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge Transfer States, and Better Performance on Average than B3LYP for Ground States

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Geometries and basis sets

The TDDFT calculation of the CO, N_2, and HCHO molecules employed the augmented Sadlej pVTZ basis set [1,2] and experimental geometries. The 6-31+G(d,p) basis set was employed for the calculations on $NH_3 \cdots F_2$. The geometry for the charge-transfer complex, $NH_3 \cdots F_2$, was optimized at the MC-QCISD/3 level, then the intermolecular distance of two monomer was changed to 6 Å, without reoptimization. The 6-31G* basis set was employed for the $C_2H_4 \cdots C_2F_4$ complex, and we used experimental geometries for each monomer with the intermolecular distance being 8 Å. The geometry of tetracene was optimized at the B3LYP/6-31+G(d,p) level, and all TDDFT calculation for tetracene employed the 6-311G(2d,p) basis set.

All calculations for the AE6, MGAE109/05, IP13/3, EA13/3, HTBH38/04, and NHTBH38/05 databases are single-point calculations at QCISD/MG3 geometries, where QCISD is quadratic configuration interaction with single and double excitations,[3] and MG3 is the modified[4,5] G3Large[6] basis set. The MG3 basis set,[4] also called G3LargeMP2,[5] is the same as 6-311++G(3d2f, 2df, 2p)[7,8] for H-Si, but improved[6] for P-Ar. Geometries for the PA8/06 database are at the MP2(full)/6-31G(2df,p) level of theory.

Geometries for all molecules in the HB6/04, CT7/04, DI6/04, and WI7/05 noncovalent databases and the $(C_2H_4)_2$ and $(C_2H_2)_2$ dimers in the PPS5/05 database are optimized at the MC-QCISD/3 level, where MC-QCISD is the multi-coefficient QCISD method.[9,10] The geometries for the benzene dimers in the PPS5/05 database are taken from Sinnokrot and Sherrill.[11]

Geometries for all molecules in the ABDE4/05 database are optimized at the B3LYP/6-31G(d) level, and they are given in the supporting information of a previous paper.[12] The 6-

311+G(3df,2p) basis set is used for the calculations of ABDEs; and this choice is made for the purpose of comparison with the previous results.

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Table S1: MGAE109/05 database of zero-point-exclusive atomization energies (kcal/mol)

Molecule	D_e	Molecule	D_e	Molecule	D_e
CH ($^2\Pi$)	84.00	S_2	101.67	H_2CCH	445.79
CH_2 ($^3B_1$)	190.72	Cl_2	57.98	$HCOOCH_3$	785.26
CH_2 ($^1A_1$)	181.37	SiO	192.08	HCOOH	500.98
CH_3 ($^2A''_2$)	307.44	SC	171.11	NF_3	204.53
CH_4	420.11	SO	125.22	PF_3	363.87
NH	83.67	ClO	64.49	SH	86.98
NH_2	181.90	ClF	61.48	$SiCl_4$	384.94
NH_3	297.90	Si_2H_6	534.66	SiF_4	574.35
OH	107.09	CH_3Cl	395.51	C_2H_5	603.75
OH_2	232.60	CH_3SH	473.84	C_4H_6 [d]	987.20
FH	141.18	HOCl	164.81	C_4H_6 [e]	1001.61
SiH_2 ($^1A_1$)	151.79	SO_2	258.62	HCOCOH	633.35
SiH_2 ($^3B_1$)	131.05	$AlCl_3$	306.26	CH_3CHO	677.03
SiH_3	227.58	AlF_3	426.50	C_2H_4O	650.70
SiH_4	322.40	BCl_3	322.90	C_2H_5O	698.64
PH_2	153.20	BF_3	470.04	H_3COCH_3	798.05
PH_3	241.56	C_2Cl_4	466.28	H_3CCH_2OH	810.36
SH_2	182.60	C_2F_4	589.36	C_3H_4 [f]	703.20
ClH	106.48	C_3H_4 [a]	704.79	C_3H_4 [g]	682.74
HCCH	405.36	C_4H_4O	993.74	H_3CCOOH	803.04
H_2CCH_2	563.51	C_4H_4S	962.73	H_3CCOCH_3	977.96
H_3CCH_3	712.80	C_4H_5N	1071.57	C_3H_6	853.41
CN	180.58	C_4H_6 [b]	1012.37	H_3CCHCH_2	860.61
HCN	313.05	C_4H_6 [c]	1004.13	C_3H_8	1006.87
CO	259.27	C_5H_5N	1237.69	$C_2H_5OCH_3$	1095.12
HCO	278.39	CCH	265.13	C_4H_{10} [h]	1303.04
H_2CO	373.82	CCl_4	312.74	C_4H_{10} [i]	1301.32
H_3COH	513.22	CF_3CN	639.85	C_4H_8 [j]	1149.01

N_2	228.42	CF_4	476.32	C_4H_8 [k]	1158.61
H_2NNH_2	438.60	CH_2OH	409.76	C_5H_8 [l]	1284.28
NO	152.05	CH_3CN	615.84	C_6H_6	1367.56
O_2	120.22	CH_3NH_2	582.56	CH_3CO	581.58
HOOH	268.57	CH_3NO_2	601.27	$(CH_3)_2CH$	900.75
F_2	38.20	$CHCl_3$	343.18	$(CH_3)_3C$	1199.34
CO_2	389.14	CHF_3	457.50	H_2CCO	532.32
Si_2	75.72	ClF_3	125.33		
P_2	117.09	H_2	109.48		

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[a] propyne

[b] *trans*-1,3-butadiene

[c] 2-butyne

[d] bicylobutane

[e] cyclobutene

[f] allene

[g] cyclopropene

[h] isobutane

[i] antiperiplanar butane

[j] cyclobutane

[k] isobutene

[l] spiropentane

Table S2: Zero-point-exclusive ionization potentials (IP13/3) and electron affinities (EA13/3) databases (kcal/mol)

	IP	EA
C	259.7	29.1
S	238.9	47.9
SH	238.9	53.3
Cl	299.1	83.4
Cl_2	265.3	55.6
OH	299.1	42.1
O	313.9	33.7
O_2	278.9	10.8
P	241.9	17.2
PH	234.1	23.2
PH_2	226.3	29.4
S_2	216.0	38.5
Si	187.9	31.9

Table S3. Zero-point-exclusive proton affinities (PA8) database (kcal/mol)

Molecule	proton affinities
NH_3	211.9
H_2O	171.8
C_2H_2	156.6
SiH_4	156.5
PH_3	193.1
H_2S	173.7
HCl	137.1
H_2	105.9

Table S4: HTBH38/04 database (kcal/mol)

Reaction	best estimate	
A + BC → AB + C	$V_f^{\neq}$	$V_r^{\neq}$
1. H + HCl → H_2 + Cl	5.7	8.7
2. OH + H_2 → H + H_2O	5.7	21.2
3. CH_3 + H_2 → H + CH_4	12.1	15.3
4. OH + CH_4 → CH_3 + H_2O	6.7	19.6
5. H + H_2 → H_2 + H	9.6	9.6
6. OH + NH_3 → H_2O + NH_2	3.2	12.7
7. HCl + CH_3 → Cl + CH_4	1.7	7.9
8. OH + C_2H_6 →H_2O + C_2H_5	3.4	19.9
9. F + H_2 → HF + H	1.8	33.4
10. O + CH_4 →OH + CH_3	13.7	8.1
11. H + PH_3→ PH_2 + H_2	3.1	23.2
12. H + HO → H_2 +O	10.7	13.1
13. H + H_2S → H_2 + HS	3.5	17.3
14. O + HCl → OH + Cl	9.8	10.4
15. NH_2 + CH_3→ CH_4 + NH	8.0	22.4
16. NH_2 + C_2H_5 → C_2H_6 + NH	7.5	18.3
17. C_2H_6 + NH_2 → NH_3 + C_2H_5	10.4	17.4
18. NH_2 + CH_4 → CH_3 + NH_3	14.5	17.8
19. *s-trans cis*-C_5H_8 → *s-trans cis*-C_5H_8	38.4	38.4

Table S5: NHTBH38/04 databases

Reactions	Best Estimate (kcal/mol)	
Heavy-atom transfer reactions	$V_f^{\neq}$	$V_r^{\neq}$
H + N_2O → OH + N_2	18.14	83.22
H + FH → HF + H	42.18	42.18
H + ClH → HCl + H	18.00	18.00
H + FCH_3 → HF + CH_3	30.38	57.02
H + F_2 → HF + F	2.27	106.18
CH3 + FCl → CH_3 F + Cl	7.43	61.01
Nucleophilic substitution reactions		
F- + CH_3F → FCH_3 + F-	-0.34	-0.34
F-···CH_3F → FCH_3 ··· F-	13.38	13.38
Cl- + CH_3Cl → $ClCH_3$ + Cl-	3.10	3.10
Cl-···CH_3Cl → $ClCH_3$···Cl-	13.61	13.61
F- + CH_3Cl → FCH_3 + Cl-	-12.54	20.11
F-···CH_3Cl → FCH_3···Cl-	2.89	29.62
OH- + CH_3F → $HOCH_3$ + F-	-2.78	17.33
OH-···CH_3F → $HOCH_3$···F-	10.96	47.20
Unimolecular and association reactions		
H + N_2 → HN_2	14.69	10.72
H + CO → HCO	3.17	22.68
H + C_2H_4 → CH_3CH_2	1.72	41.75
CH_3 + C_2H_4 → $CH_3CH_2CH_2$	6.85	32.97
HCN → HNC	48.16	33.11

Table S6: Noncovalent interaction databases (kcal/mol)

HB6/04		CT7/04		DI6/04		WI7/05		PPS5/05	
Complex	D_e	Complex	D_e	Complex	D_e	Complex	D_e	Complex	D_e
$(NH_3)_2$	3.15	$C_2H_4\cdots F_2$	1.06	$(H_2S)_2$	1.66	HeNe	0.04	$(C_2H_2)_2$	1.34
$(HF)_2$	4.57	$NH_3\cdots F_2$	1.81	$(HCl)_2$	2.01	HeAr	0.06	$(C_2H_4)_2$	1.42
$(H_2O)_2$	4.97	$C_2H_2\cdots ClF$	3.81	$HCl\cdots H_2S$	3.35	Ne_2	0.08	Sandwich $(C_6H_6)_2$	1.81
$NH_3\cdots H_2O$	6.41	$HCN\cdots ClF$	4.86	$CH_3Cl\cdots HCl$	3.55	NeAr	0.13	T-Shaped $(C_6H_6)_2$	2.74
$(HCONH_2)_2$	14.94	$NH_3\cdots Cl_2$	4.88	$HCN\cdots CH_3SH$	3.59	$CH_4\cdots Ne$	0.22	Parallel-Displaced $(C_6H_6)_2$	2.78
$(HCOOH)_2$	16.15	$H_2O\cdots ClF$	5.36	$CH_3SH\cdots HCl$	4.16	$C_6H_6\cdots Ne$	0.47		
		$NH_3\cdots ClF$	10.62			$(CH_4)_2$	0.51		
Average	8.37		4.63		3.07		0.22		2.01

Table S7: π system databases (kcal/mol)[a]

π		PA-P5		PA-SB5	
E2-E1	-1.40	P-2	167.81	SB-2	214.46
E4-E3	-8.80	P-4	193.45	SB-4	226.15
E6-E5	-14.30	P-6	209.68	SB-6	233.44
		P-8	219.67	SB-8	238.16
		P-10	225.95	SB-10	240.97

[a] See Figure S1, S2, and S3 for the structures of the molecules in these databases.

Table S8: Charge-transfer excitation energies (in eV) of the $C_2H_4 \cdots C_2F_4$ dimer along the intermolecular distances *R* (in Å)

R	TPSSh	B3LYP	B98	PBEh	BMK	M05-2X	M06-HF	HF	SAC-CI
5.00	6.17	6.73	6.87	7.06	8.19	8.92	11.45	12.69	11.49
6.00	6.27	6.87	7.03	7.23	8.44	9.23	11.98	13.23	12.00
7.00	6.32	6.96	7.12	7.34	8.61	9.45	12.35	13.60	12.36
8.00	6.36	7.03	7.19	7.41	8.73	9.60	12.62	13.88	12.63
9.00	6.39	7.08	7.25	7.47	8.82	9.73	12.83	14.09	12.83
10.00	6.41	7.11	7.29	7.52	8.89	9.82	12.99	14.25	12.99

Table 9: Cartesian coordinates for TDDFT calculations

CO

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.128000

N_2

N	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.098000

HCHO

O	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.203000
H	0.935567	0.000000	1.785339
H	-0.935567	0.000000	1.785339

$NH_3\cdots F_2$ 6 Å

N	0.000000	-0.234913	-3.520527
H	0.000000	0.704739	-3.904943
H	0.813763	-0.704739	-3.904943
H	-0.813763	-0.704739	-3.904943
F	0.000000	-0.234913	2.479473
F	0.000000	-0.234913	3.904943

$C_2H_4\cdots C_2F_4$ 8 Å

C	0	-4.000000	0.000000	0.655500
C	0	-4.000000	0.000000	-0.655500
F	0	-4.000000	1.096100	1.389300
F	0	-4.000000	-1.096100	1.389300
F	0	-4.000000	-1.096100	-1.389300
F	0	-4.000000	1.096100	-1.389300
C	0	4.000000	0.000000	0.669500
C	0	4.000000	0.000000	-0.669500
H	0	4.000000	0.928900	1.232100
H	0	4.000000	-0.928900	1.232100
H	0	4.000000	0.928900	-1.232100
H	0	4.000000	-0.928900	-1.232100

Tetracene

C	4.893500	0.715900	0.000000
C	4.893500	-0.715900	0.000000
C	3.714000	-1.410400	0.000000
C	2.452300	-0.726200	0.000000
C	2.452300	0.726200	0.000000
C	3.714000	1.410400	0.000000
C	1.236200	-1.407700	0.000000
C	0.000000	-0.726500	0.000000
C	0.000000	0.726500	0.000000
C	1.236200	1.407700	0.000000
C	-1.236200	-1.407700	0.000000
C	-2.452300	-0.726200	0.000000
C	-2.452300	0.726200	0.000000
C	-1.236200	1.407700	0.000000
C	-3.714000	-1.410400	0.000000
C	-4.893500	-0.715900	0.000000
C	-4.893500	0.715900	0.000000
C	-3.714000	1.410400	0.000000
H	5.840100	1.248500	0.000000
H	5.840100	-1.248500	0.000000
H	3.713200	-2.497500	0.000000
H	3.713200	2.497500	0.000000
H	1.236300	-2.495400	0.000000
H	1.236300	2.495400	0.000000
H	-1.236300	-2.495400	0.000000
H	-1.236300	2.495400	0.000000
H	-3.713200	-2.497500	0.000000
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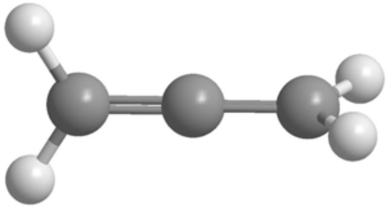
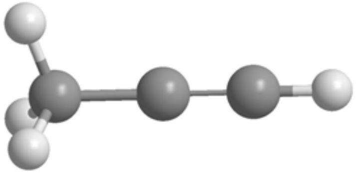
H	-5.840100	1.248500	0.000000
H	-3.713200	2.497500	0.000000



1: allene (C_3H_4)



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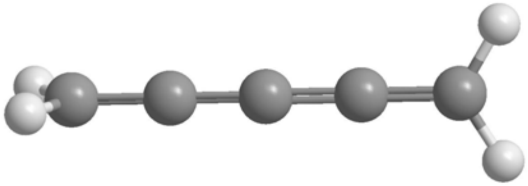
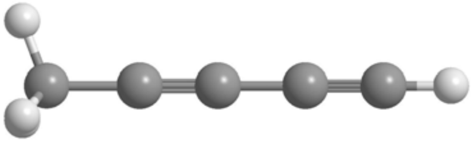
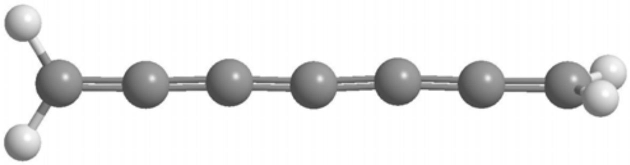


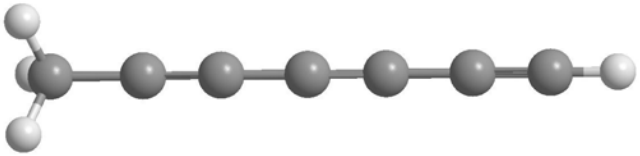
3: penta-1,2,3,4-tetraene (C_5H_4)



4: penta-1,3-diyne (C_5H_4)

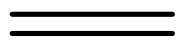


5: hepta-1,2,3,4,5,6-hexaaene (C_7H_4)



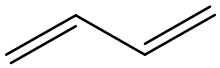
6: hepta-1,3,5-triyne (C_7H_4)

Figure S1. Structures of cumulenes and poly-ynes



P-2

P-2P



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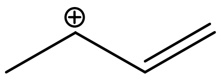

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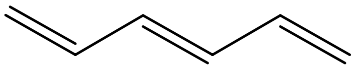

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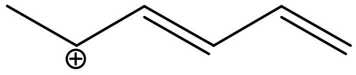

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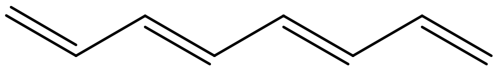

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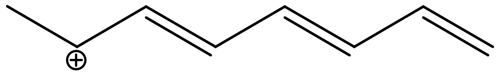

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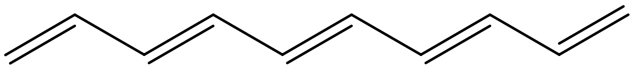
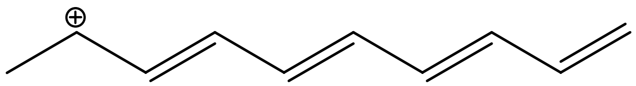
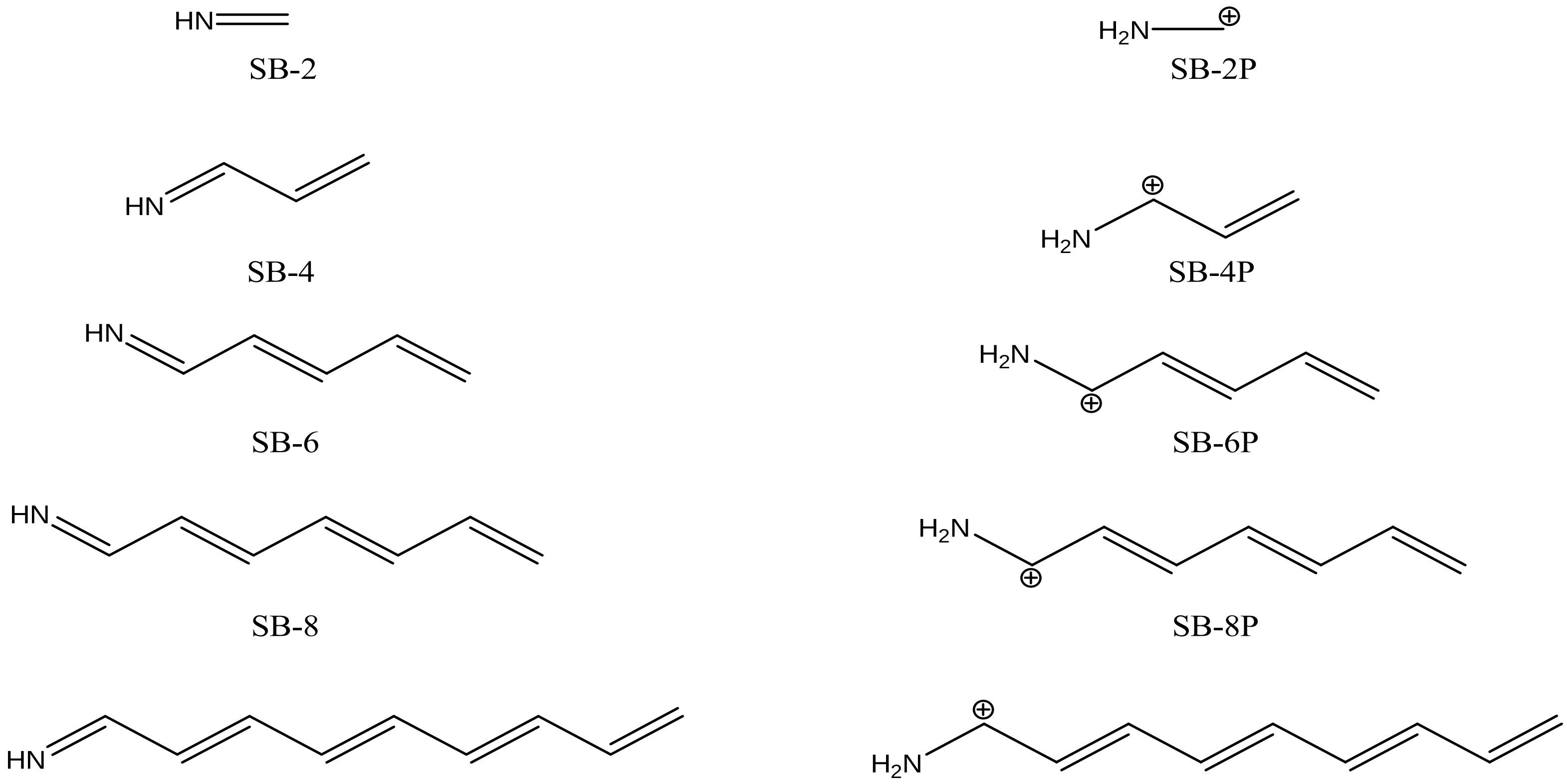


P-10



P-10P

Figure S2. Structures of conjugated polyenes and protonated polyenes



SB-2 SB-2P

SB-4 SB-4P

SB-6 SB-6P

SB-8 SB-8P

SB-10 SB-10P

Figure S3. Structures of conjugated Schiff bases and protonated conjugated Schiff bases

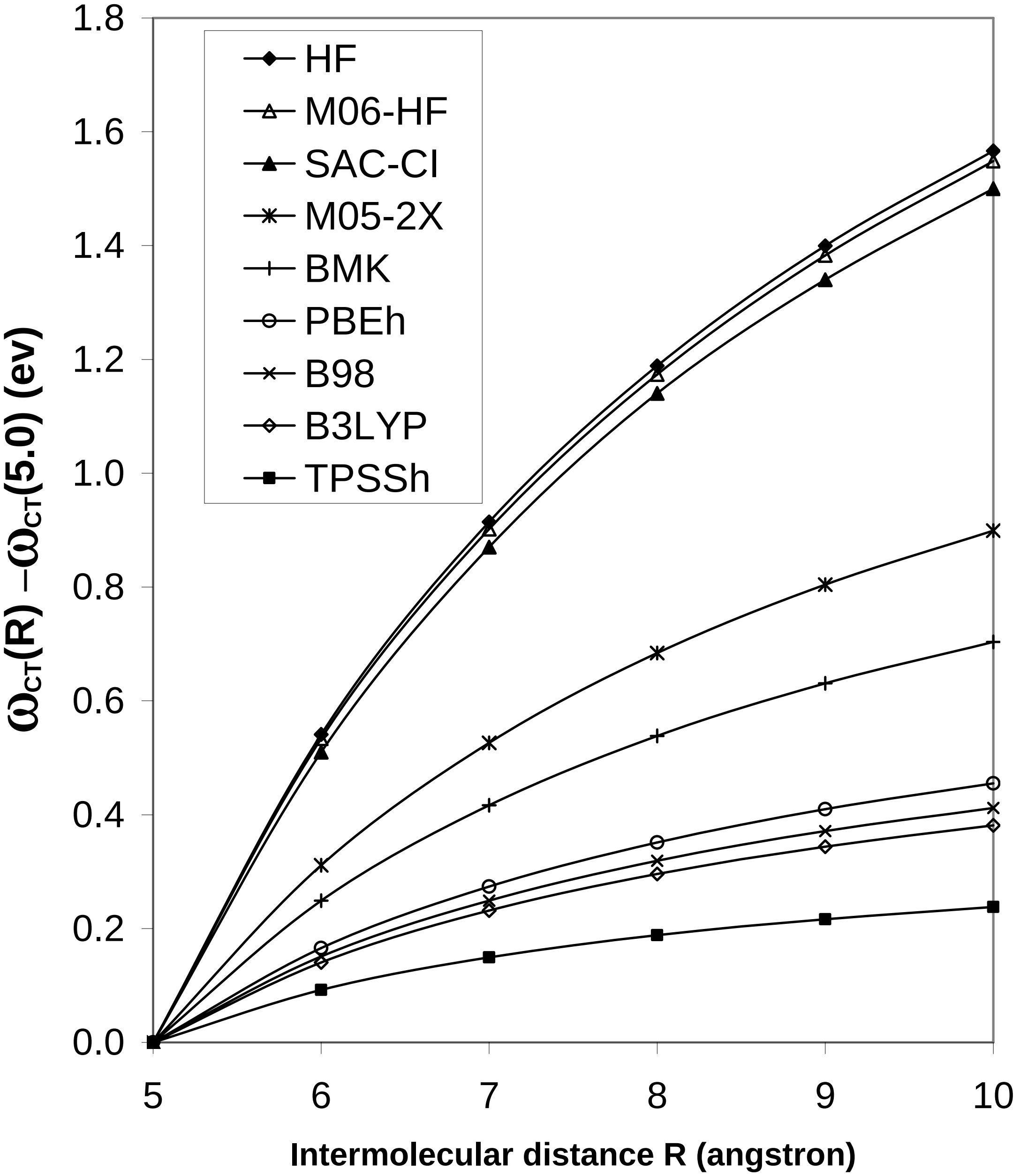


Figure S4. The charge transfer excitation energy of ethylene-tetrafluoroethylene dimer. For all functionals, the excitation energy at 5.0 Å is set to zero. The SAC-CI results are taken from Tawada et al.[13] The figure shows that only HF and M06-HF calculations show the correct long-range behavior. The curves arrange themselves roughly in the order of their percentage of Hartree-Fock exchange because a functional with a percentage *X* of Hartree-Fock exchange has a long-range behavior (in atomic units) of –X/100*R*, as compared to the correct long-range behavior of -1/*R*.