

Table S1: Vertical Electron detachment Energies of 2-ethynylthiophene and the corresponding Dyson Orbitals

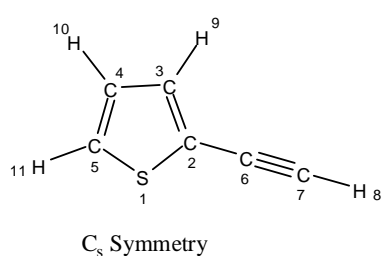

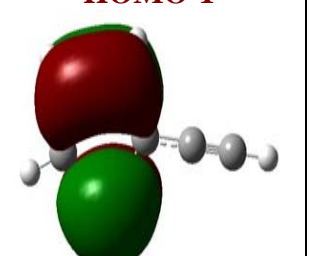
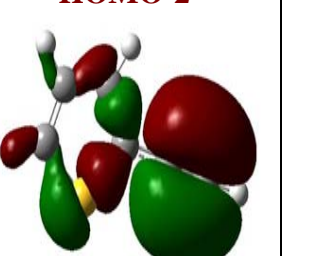
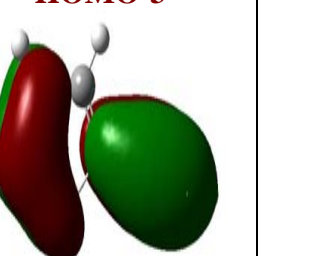
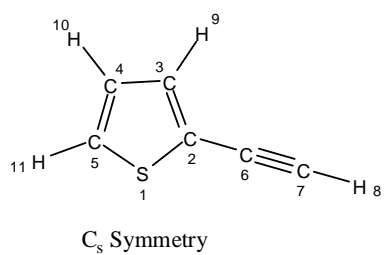
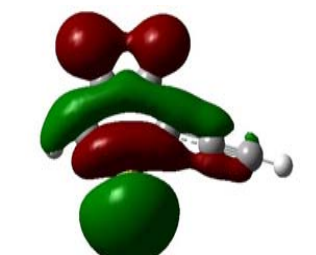
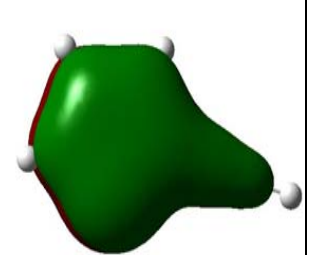
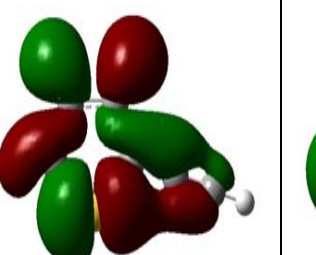
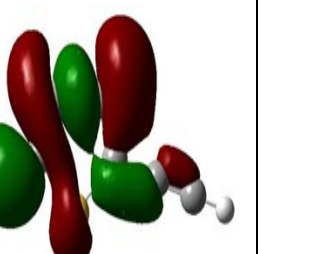
 <p>C_s Symmetry</p>	HOMO		HOMO-1		HOMO-2		HOMO-3	
								
	A''		A''		A'		A''	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	8.40	8.46	9.65	9.73	10.75	10.83	11.75	11.82
Second Order	8.22	8.26	9.11	9.17	10.23	10.24	10.94	10.96
Third Order	8.52	8.59	9.50	9.59	10.50	10.60	11.31	11.40
OVGF	8.43	8.49	9.40	9.37	10.43	10.33	11.04	11.11
P3	8.71	8.78	9.47	9.54	10.63	10.70	11.34	11.41
Experiment (ref. 20)	8.47		9.46		10.41		11.01	
 <p>C_s Symmetry</p>	HOMO-4		HOMO-5		HOMO-6		HOMO-7	
								
	A'		A''		A'		A'	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	13.22	13.29	14.83	14.89	15.03	15.11	15.53	15.62
Second Order	11.66	11.72	12.70	12.74	13.13	13.18	13.12	13.16
Third Order	12.57	12.64	13.76	13.84	14.23	14.32	14.46	14.56
OVGF	12.21	12.28	13.30	13.36	13.70	13.79	13.82	13.89
P3	12.25	12.31	13.33	13.40	13.95	14.03	14.11	14.19
Experiment (ref. 20)	12.20		13.05		13.45		14.09	

Table S2: Vertical Electron detachment Energies of 3-ethynylthiophene and the corresponding Dyson Orbitals

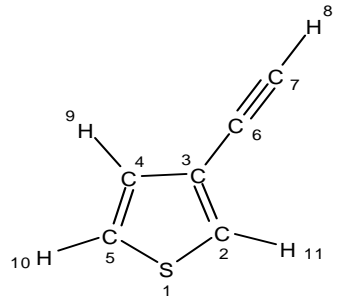
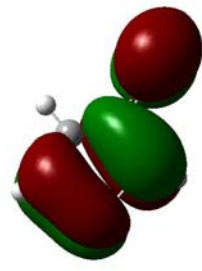
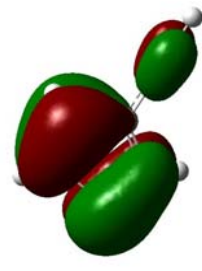
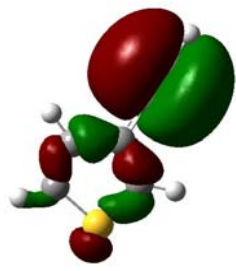
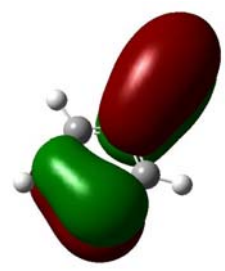
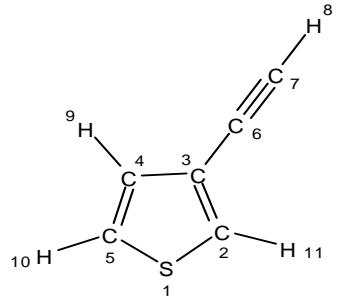
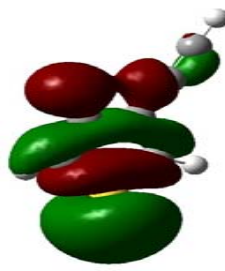
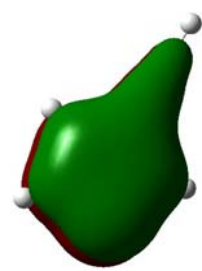
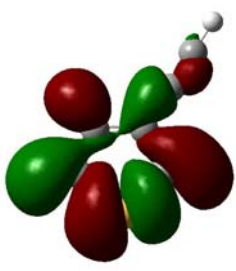
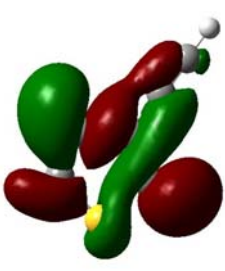
 <p>C_s Symmetry</p>	HOMO		HOMO-1		HOMO-2		HOMO-3	
								
	A''		A''		A'		A''	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	8.62	8.69	9.39	9.45	10.71	10.79	11.80	11.88
Second Order	8.39	8.44	8.95	9.00	10.23	10.25	11.05	11.08
Third Order	8.68	8.76	9.32	9.39	10.39	10.49	11.33	11.41
OVGf	8.60	8.67	9.22	9.28	10.35	10.42	11.11	11.18
P3	8.85	8.92	9.35	9.42	10.58	10.66	11.38	11.45
Experiment (ref. 20)	8.62		9.31		10.34		11.14	
 <p>C_s Symmetry</p>	HOMO-4		HOMO-5		HOMO-6		HOMO-7	
								
	A'		A''		A'		A'	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	13.33	13.40	14.82	14.88	14.94	15.02	15.61	15.70
Second Order	11.79	11.84	12.73	12.77	13.12	13.17	13.20	13.24
Third Order	12.62	12.70	13.73	13.81	14.15	14.23	14.66	14.76
OVGf	12.30	12.37	13.29	13.35	13.68	13.75	13.95	14.03
P3	12.32	12.38	13.32	13.39	13.87	13.94	14.29	14.37
Experiment (ref. 20)	12.14		12.76		13.50		13.80	

Table S3: Vertical Electron detachment Energies of 2, 5-diethynylthiophene and the corresponding Dyson Orbitals

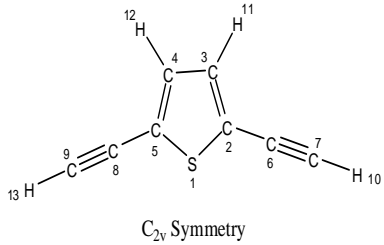
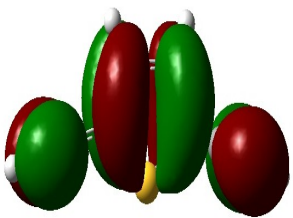
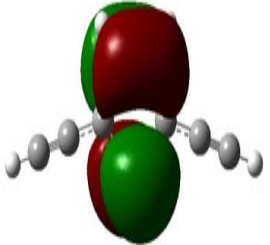
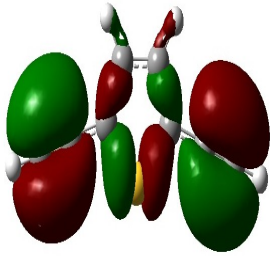
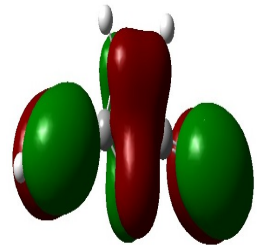
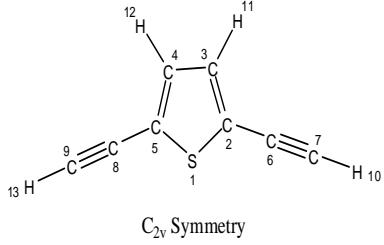
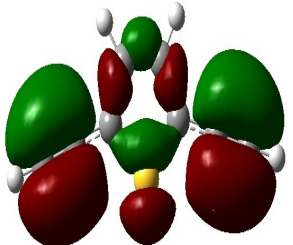
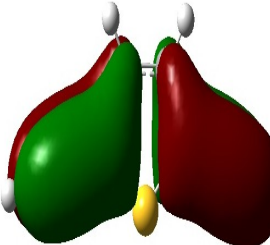
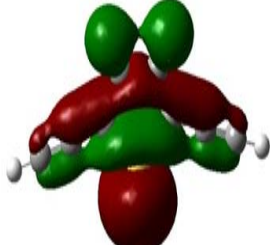
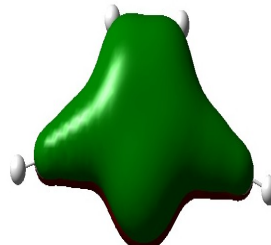
 <p>C_{2v} Symmetry</p>	HOMO		HOMO-1		HOMO-2		HOMO-3	
								
	A2		B1		B2		B1	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	8.16	8.34	9.89	9.96	10.79	10.95	11.03	11.12
Second Order	7.98	8.10	9.16	9.27	10.21	10.33	10.43	10.50
Third Order	8.26	8.42	9.66	9.76	10.47	10.64	10.60	10.73
OVGf	8.17	8.32	9.40	9.50	10.24	10.40	10.41	10.52
P3	8.52	8.65	9.60	9.71	10.61	10.76	10.72	10.84
Experiment (ref. 20)	8.28		9.45		10.39		10.73	
 <p>C_{2v} Symmetry</p>	HOMO-4		HOMO-5		HOMO-6		HOMO-7	
								
	A1		A2		A1		B1	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	11.10	11.19	12.70	12.69	13.53	13.78	15.27	15.42
Second Order	10.47	10.53	11.56	11.56	11.80	12.01	12.91	13.05
Third Order	10.74	10.86	12.15	12.19	12.84	13.06	14.13	14.27
OVGf	10.50	10.61	11.77	11.80	12.41	12.64	13.58	13.73
P3	10.86	10.97	12.12	12.15	12.49	12.70	13.66	13.79
Experiment (ref. 20)	10.94		11.66		12.25		13.11	

Table S4: Vertical Electron detachment Energies of 3, 4-diethynylthiophene and the corresponding Dyson Orbitals

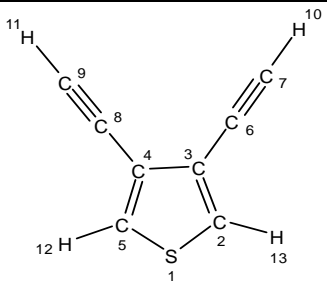
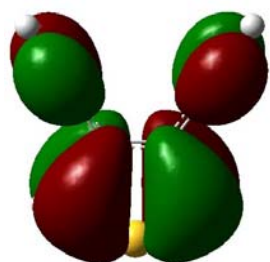
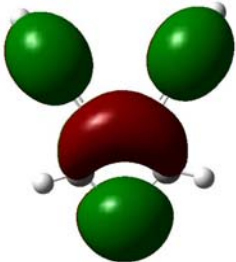
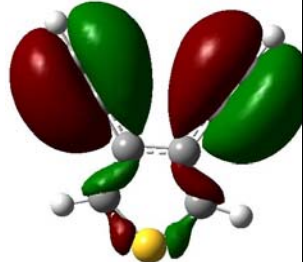
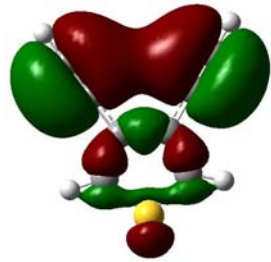
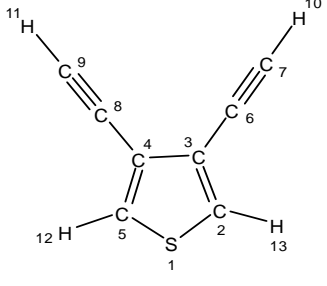
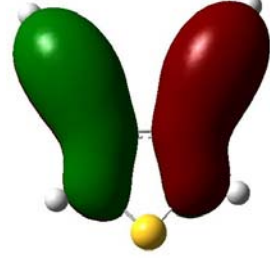
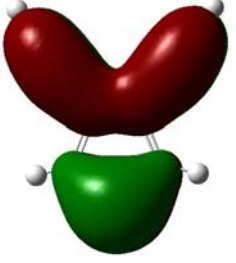
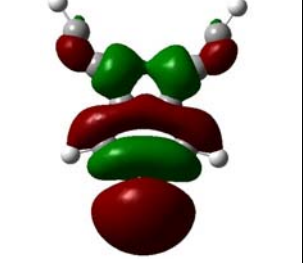
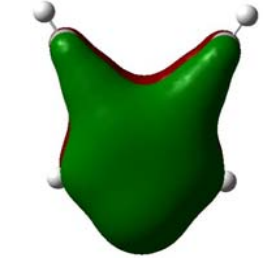
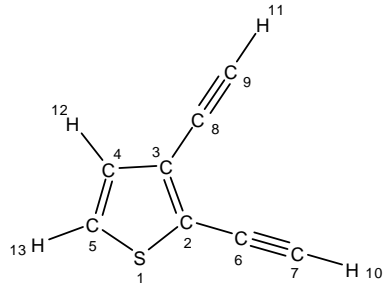
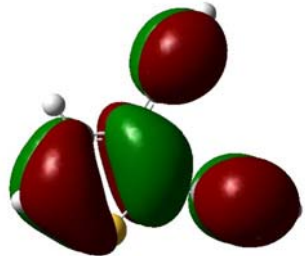
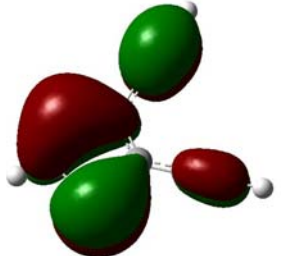
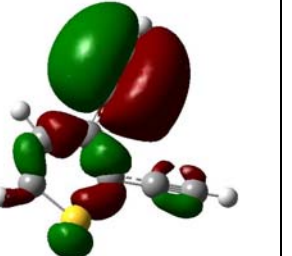
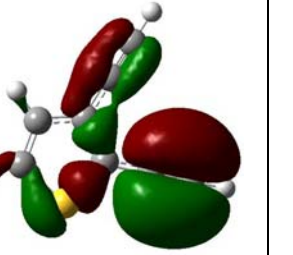
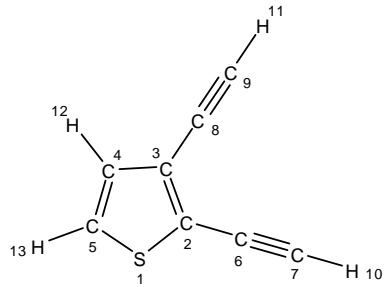
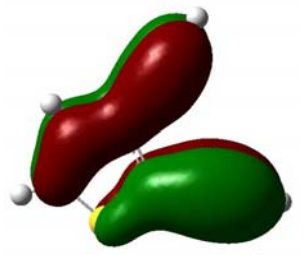
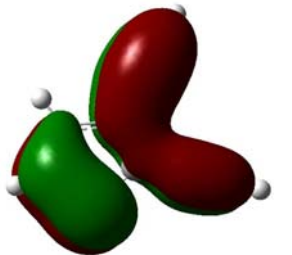
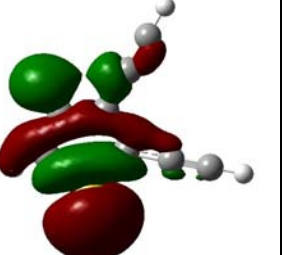
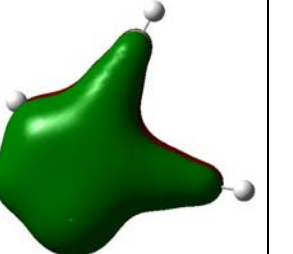
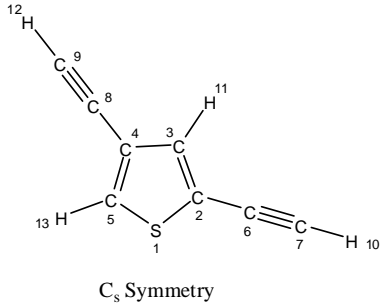
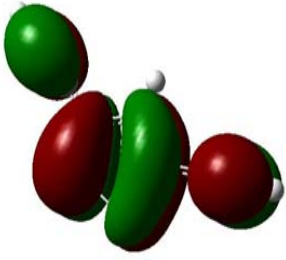
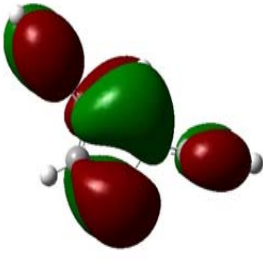
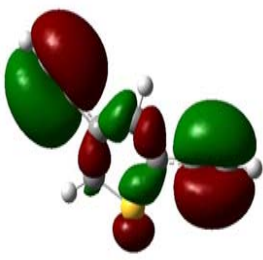
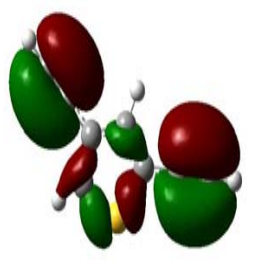
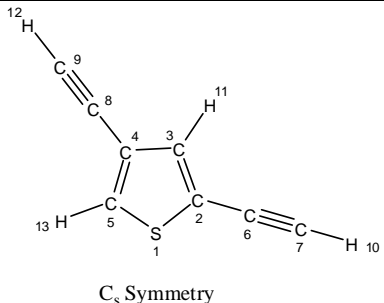
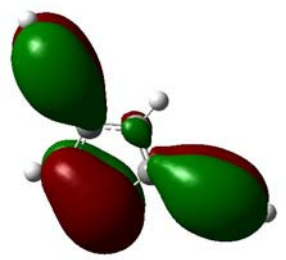
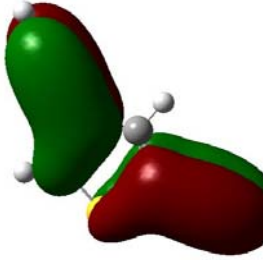
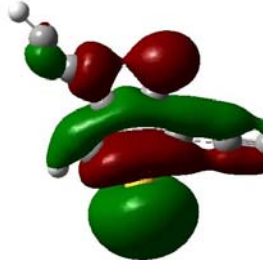
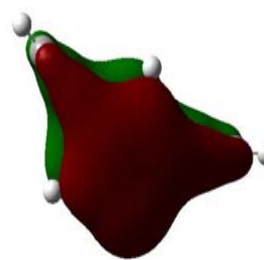
 <p>C_{2v} Symmetry</p>	HOMO		HOMO-1		HOMO-2		HOMO-3	
								
	A2		B1		B2		A1	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	8.78	8.83	8.84	8.92	10.72	10.80	10.80	10.88
Second Order	8.45	8.48	8.50	8.55	10.26	10.27	10.18	10.20
Third Order	8.83	8.90	8.75	8.83	10.42	10.51	10.44	10.54
OVGf	8.71	8.77	8.68	8.75	10.38	10.44	10.19	10.26
P3	8.99	9.05	8.91	8.98	10.61	10.68	10.61	10.69
Experiment (ref. 20)	8.84		10.44		10.81		11.10	
 <p>C_{2v} Symmetry</p>	HOMO-4		HOMO-5		HOMO-6		HOMO-7	
								
	A2		B1		A1		B1	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	11.86	11.93	11.96	12.04	13.75	13.82	15.29	15.35
Second Order	11.03	11.05	11.09	11.12	12.02*	12.07	12.95	12.99
Third Order	11.41	11.50	11.41	11.50	12.93	12.99	14.16	14.24
OVGf	11.11	11.17	11.19	11.26	12.56	12.62	13.60	13.67
P3	11.51	11.58	11.41	11.48	12.61	12.67	13.70	13.78
Experiment (ref. 20)	11.35		12.37		13.55			

Table S5: Vertical Electron detachment Energies of 2, 3-diethynylthiophene and the corresponding Dyson Orbitals

 <p>C_s Symmetry</p>	HOMO		HOMO-1		HOMO-2		HOMO-3	
								
	A''		A''		A'		A'	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	8.32	8.39	9.36	9.44	10.79	10.88	10.85	10.93
Second Order	8.09	8.13	8.85	8.90	10.19	10.21	10.25	10.26
Third Order	8.42	8.50	9.20	9.29	10.42	10.51	10.54	10.63
OVGF	8.31	8.38	9.11	9.18	10.17	10.25	10.28	10.35
P3	8.65	8.72	9.25	9.33	10.60	10.68	10.67	10.75
Experiment (ref. 20)	8.41		9.15		10.30		10.64	
 <p>C_s Symmetry</p>	HOMO-4		HOMO-5		HOMO-6		HOMO-7	
								
	A''		A''		A'		A''	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	11.83	11.90	11.94	12.02	13.54	13.61	15.30	15.37
Second Order	11.04	11.06	10.97	11.00	11.83	11.89	12.91	12.95
Third Order	11.38	11.47	11.39	11.48	12.79	12.87	14.20	14.29
OVGF	11.10	11.16	11.12	11.19	12.41	12.48	13.61	13.68
P3	11.48	11.55	11.38	11.45	12.45	12.52	13.73	13.80
Experiment (ref. 20)	10.96		11.19		12.24		13.10	

TableS6: Vertical Electron detachment Energies of 2, 4-diethynylthiophene and the corresponding Dyson Orbitals

 <p>C_s Symmetry</p>	HOMO		HOMO-1		HOMO-2		HOMO-3	
								
	A''		A''		A'		A'	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	8.43	8.49	9.40	9.47	10.78	10.86	11.02	11.10
Second Order	8.18	8.23	8.92	8.97	10.24	10.25	10.51	10.52
Third Order	8.48	8.56	9.25	9.33	10.44	10.53	10.70	10.79
OVGF	8.39	8.46	9.16	9.23	10.39	10.29	10.65	10.56
P3	8.70	8.77	9.34	9.42	10.61	10.68	10.85	10.93
Experiment (ref. 20)	8.44		9.23		10.36		10.72	
 <p>C_s Symmetry</p>	HOMO-4		HOMO-5		HOMO-6		HOMO-7	
								
	A''		A''		A'		A''	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	11.40	11.47	12.54	12.61	13.65	13.72	15.29	15.36
Second Order	10.67	10.69	11.54	11.56	11.92	11.98	12.96	12.99
Third Order	10.92	11.00	12.03	12.12	12.88	12.96	14.13	14.21
OVGF	10.72	10.79	11.69	11.75	12.49	12.56	13.60	13.67
P3	10.96	11.03	12.05	12.12	12.56	12.62	13.68	13.75
Experiment (ref. 20)	10.98		11.72		12.35		13.82	