Electronic Supplementary Information

Interpreting the Charge Transfer to Solvent State in Photoionization of Potassium ferrocyanide in Aqueous Solution

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Content:

Figures:

Tables:

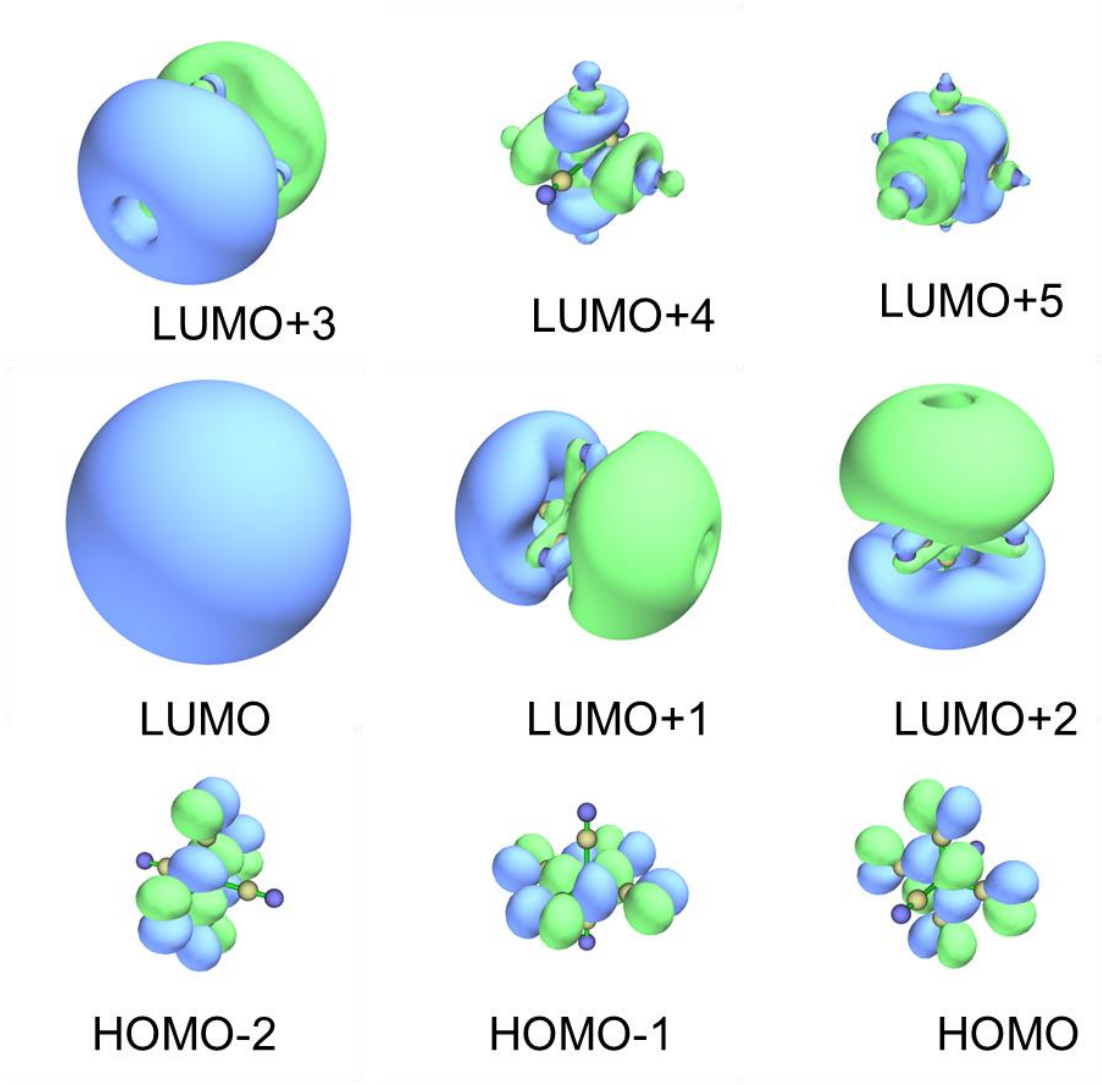


Figure S1. The relevant molecular orbitals of ferrocyanide (the geometry was optimized in the gas phase) are shown. The PBE0 functional is used, with the Fe atom using the SDD pseudopotential basis set while C and N use the 6-31G(d) basis set. The isosurface level is 0.010.

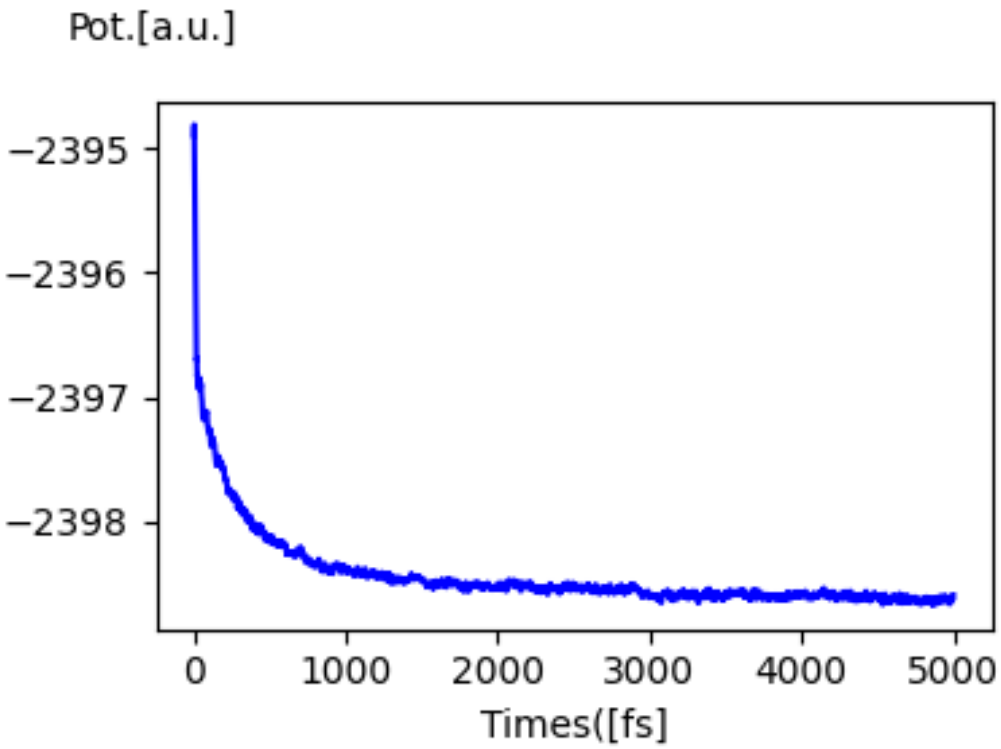


Figure S2. The first 5ps potential energy curve is from a Molecular Dynamics simulation of the 15.65-angstrom box with 120 water molecules and one potassium ferrocyanide molecule at NVT and 298.15 K.

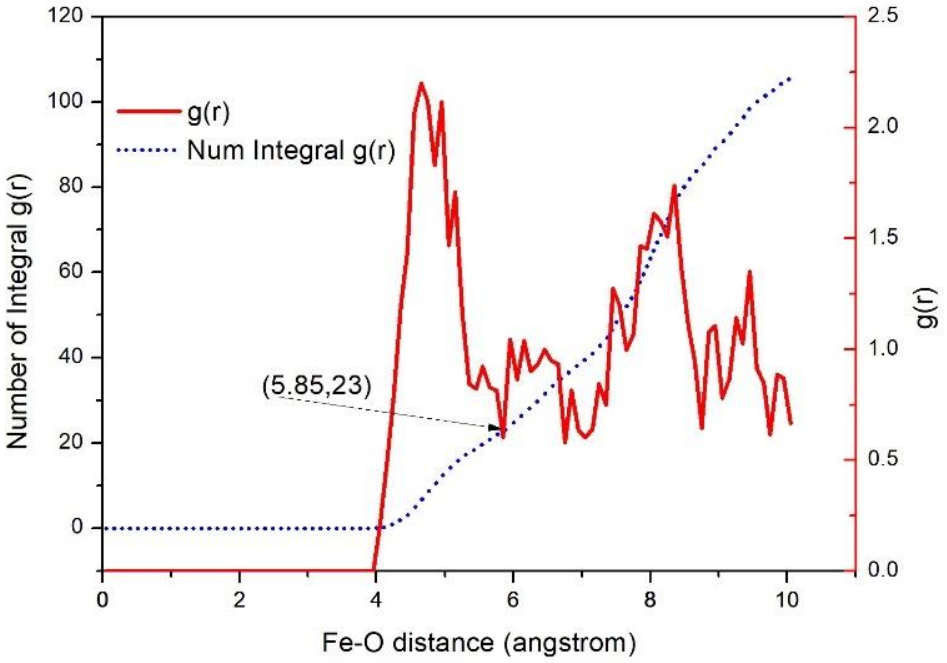


Figure S3. The radial distribution function of Fe-O is shown.

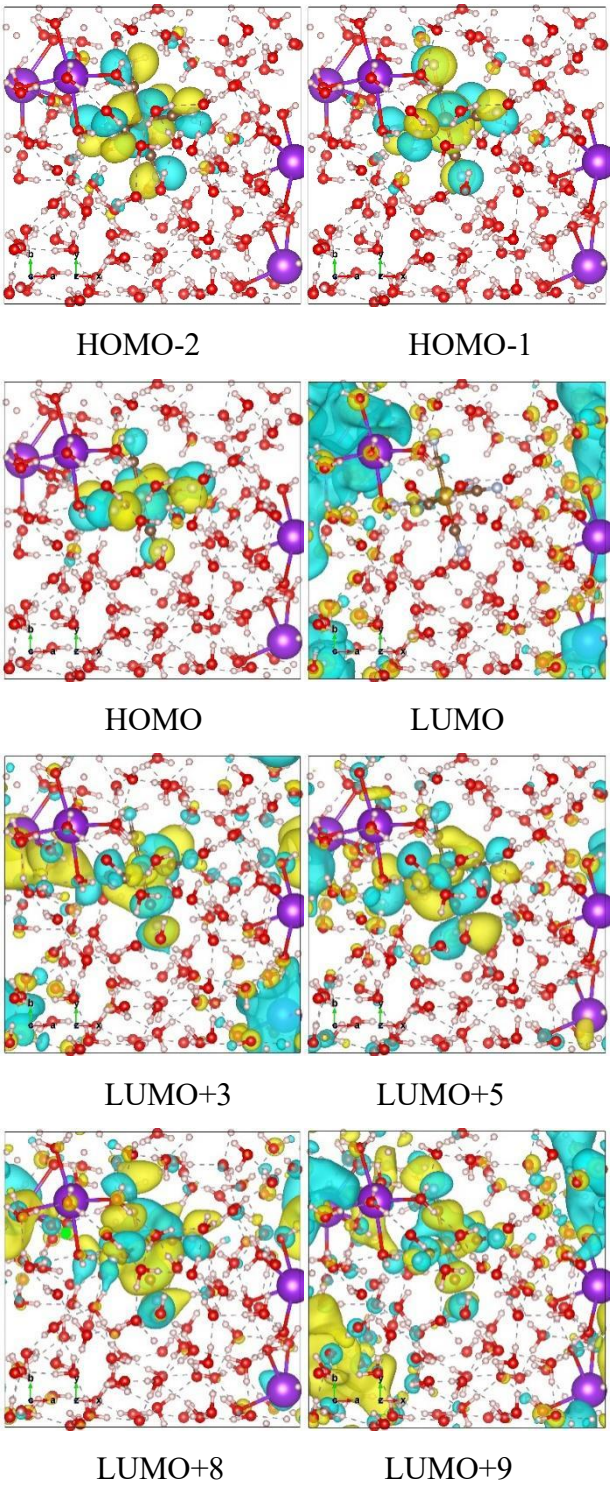


Figure S4. Some important orbitals of potassium ferrocyanide in a periodic box under an explicit water model, in which the $[Fe(CN)_6]^{4-}$ ion is highlighted with a cyan color.

Table S1. The vertical excited energies of the optimized geometry of ferrocyanide were calculated using an implicit model. The PBE0 functional is used, with the Fe atom using the SDD pseudopotential basis set while C and N use the 6-311+G(d) basis set. Where H represents the highest occupied molecular orbital (HOMO), L represents the lowest unoccupied molecular orbital (LUMO), and f represents the oscillator strength.

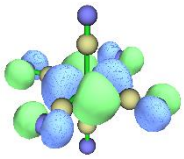
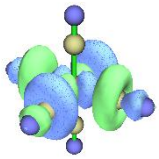
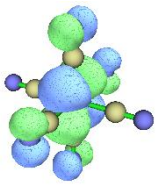
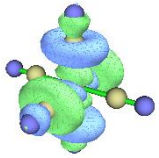
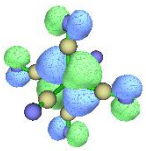
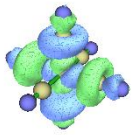
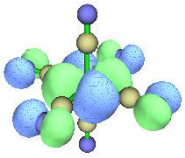
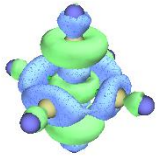
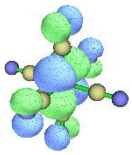
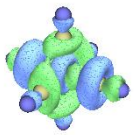
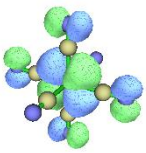
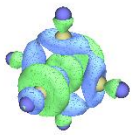
State	excited energy (eV)	wavelength (nm)	f	MOs
1	3.6578	338.96	0	H-2 -> L+16 49.7%, H-2 -> L+4 20.5%, H-2 -> L+17 20.4%
2	3.6578	338.96	0	H-1 -> L+17 70.0%, H-1 -> L+5 25.0%
3	3.6578	338.96	0	H -> L+16 55.3%, H -> L+4 17.0%, H -> L+17 14.8%, H -> L+5 8.1%
4	4.3465	285.25	0	H-2 -> L+17 42.7%, H-2 -> L+5 23.3%, H-2 -> L+16 17.6%, H-2 -> L+4 5.3%
5	4.3465	285.25	0	H-1 -> L+16 60.1%, H-1 -> L+4 28.4%
6	4.3465	285.25	0	H -> L+17 47.6%, H -> L+5 19.4%, H -> L+16 12.7%, H -> L+4 9.2%
7	4.4034	281.56	0	H-1 -> L 97.5%
8	4.4034	281.56	0	H-2 -> L 97.5%
9	4.4034	281.56	0	H -> L 97.5%
10	5.0661	244.73	0	H -> L+1 49.7%, H-1 -> L+3 49.7%
11	5.0661	244.73	0	H -> L+2 49.7%, H-2 -> L+3 49.7%
12	5.0661	244.73	0	H-1 -> L+2 49.7%, H-2 -> L+1 49.7%
13	5.0714	244.48	0.0673	H -> L+2 49.7%, H-2 -> L+3 49.7%
14	5.0714	244.48	0.0673	H-1 -> L+2 49.7%, H-2 -> L+1 49.7%
15	5.0714	244.48	0.0673	H -> L+1 49.7%, H-1 -> L+3 49.7%

16	5.0765	244.23	0	H -> L+3 33.1%, H-1 -> L+1 33.1%, H-2 -> L+2 33.1%
17	5.091	243.54	0	H-2 -> L+2 63.2%, H-1 -> L+1 30.2%, H -> L+3 6.0%
18	5.091	243.54	0	H -> L+3 60.3%, H-1 -> L+1 36.1%
19	5.4337	228.18	0	H-2 -> L+9 45.4%, H-1 -> L+8 45.4%
20	5.4337	228.18	0	H-2 -> L+7 45.4%, H -> L+8 45.4%
21	5.4337	228.18	0	H-1 -> L+7 45.4%, H -> L+9 45.4%
22	5.6356	220	0	H-2 -> L+8 59.4%, H -> L+7 23.4%, H-1 -> L+9 8.2%
23	5.6356	220	0	H-1 -> L+9 52.5%, H -> L+7 37.3%
24	5.7588	215.3	0	H-1 -> L+7 40.1%, H -> L+9 40.1%, H-2 -> L+5 9.6%
25	5.7588	215.3	0	H-2 -> L+9 40.1%, H-1 -> L+8 40.1%, H -> L+5 8.0%
26	5.7588	215.3	0	H-2 -> L+7 40.1%, H -> L+8 40.1%, H-1 -> L+4 11.8%
27	5.9291	209.11	0	H-1 -> L+6 96.7%
28	5.9291	209.11	0	H-2 -> L+6 96.7%
29	5.9291	209.11	0	H -> L+6 96.7%
30	6.1075	203	0	H-2 -> L+4 59.8%, H-2 -> L+16 17.0%, H-2 -> L+5 13.6%, H-2 -> L+17 7.0%

Table S2. The vertical excited energies of the lowest 15 excited states of ferrocyanide (in the gas phase) are shown. The PBE0 functional is used, with the Fe atom using the SDD pseudopotential basis set while C and N use the 6-31G(d) basis set. Where H represents the highest occupied molecular orbital (HOMO), L represents the lowest unoccupied molecular orbital (LUMO), and f represents the oscillator strength.

State	excited energy (eV)	wavelength (nm)	f	MOs
1	0.1203	10309	0	H -> L 100%
2	0.1203	10309	0	H-1 -> L 100%
3	0.1203	10309	0	H-2 -> L 100%
4	2.1475	577.34	0	H-3 -> L 99.8%
5	2.1475	577.34	0	H-4 -> L 99.8%
6	2.1475	577.34	0	H-5 -> L 99.8%
7	2.6605	466.02	0	H-7 -> L 99.8%
8	2.6605	466.02	0	H-6 -> L 99.8%
9	2.6605	466.02	0	H-8 -> L 99.8%
10	2.9297	423.2	0	H-9 -> L 99.7%
11	2.9297	423.2	0	H-10 -> L 99.7%
12	2.9297	423.2	0	H-11 -> L 99.7%
13	3.0615	404.98	0.0673	H -> L+4 97.1%
14	3.0615	404.98	0.0673	H-1 -> L+5 72.8%, H-1 -> L+4 24.3%
15	3.0615	404.98	0.0673	H-2 -> L+5 72.8%, H-2 -> L+4 24.3%

Table S3. Natural Transient Orbital (NTO) pairs of the lowest 10 excited states of ferrocyanide in the implicit model. The isosurface level for the unoccupied NTOs of S7-S10 was 0.010, while the isosurface level for the other orbitals was 0.020.

State	Contributions %	Major NTOs	
		Occupied	Unoccupied
S1	**100**		
S2	**100**		
S3	**100**		
S4	**92.4**		
S5	**92.4**		
S6	**92.4**		

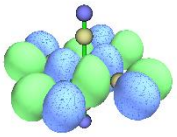
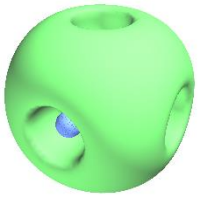
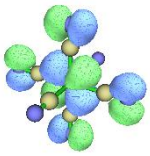
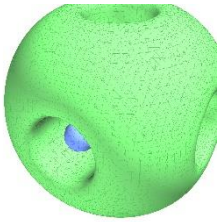
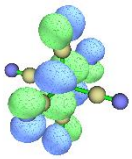
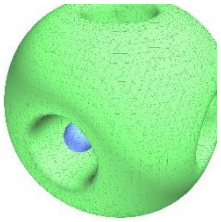
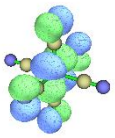
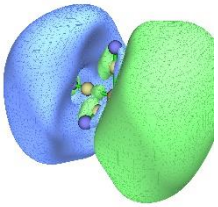
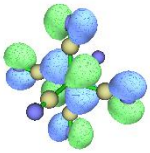
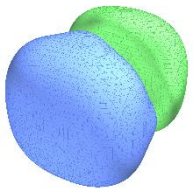
S7	**99.8**		
S8	**99.8**		
S9	**99.8**		
S10	**49.9**		
	49.9		

Table S4. The bond lengths and angles of the optimized geometry of ferrocyanide in a periodic water box.

bond：length(angstrom)

Fe-C2:1.90380
Fe-C4:1.88966
Fe-C6:1.88293
Fe-C8:1.88192
Fe-C10:1.85864
Fe-C12:1.88852
C2-N3:1.17316
C4-N5:1.17717
C6-N7:1.17538
C8-N9:1.18210
C10-N11:1.18009
C12-N13:1.17862

Angle：(degree)

C2-Fe-C10:177.35669
C4-Fe-C8:176.93019
C6-Fe-C12:179.03693
C2-Fe-C8:91.23743
C2-Fe-C4:89.75422

Table S5. The vertical excited energies were calculated for the optimized geometry of a periodic box containing 120 water molecules and one $K_4Fe(CN)_6$ molecule. Where H represents the highest occupied molecular orbital (HOMO), L represents the lowest unoccupied molecular orbital (LUMO), and f represents the oscillator strength.

State	excited energy (eV)	wavelength (nm)	f	MOs
1	3.8195	324.61	0.00209	H-1 -> L+8 9.7%, H-1 -> L+6 9.1%, H-2 -> L+8 7.2%, H-1 -> L+3 5.2%
2	4.0538	305.85	4.80E-04	H -> L+3 16.8%, H -> L+20 14.6%, H -> L+1 6.8%, H -> L+12 5.1%
3	4.068	304.78	5.40E-04	H-2 -> L+6 14.8%, H-1 -> L+6 8.9%, H-1 -> L+17 5.5%, H-2 -> L+8 5.3%
4	4.5193	274.35	0.00123	H -> L+6 20.5%, H-1 -> L+3 9.3%, H-1 -> L+6 8.1%, H -> L+17 6.3%
5	4.5335	273.49	2.80E-04	H-1 -> L+3 12.9%, H -> L+5 10.4%, H -> L+6 8.4%, H -> L+8 5.7%

6	4.7296	262.14	0.00127	H-2 -> L+3 20.1%, H-2 -> L+6 14.6%, H-2 -> L+17 6.7%, H-2 -> L+1 5.6%
7	5.229	237.11	2.70E-04	H -> L+5 32.3%, H-1 -> L+3 8.6%, H -> L+7 8.4%, H -> L+6 7.9%
8	5.3285	232.68	9.80E-04	H-1 -> L+5 44.5%, H-1 -> L+8 9.8%, H-1 -> L+7 9.3%, H-1 -> L+9 6.7%
9	5.4223	228.65	0.00158	H-2 -> L+9 13.7%, H -> L+9 8.8%, ,
10	5.5012	225.38	0.00609	H -> L+3 16.0%, H-2 -> L+5 11.2%, H -> L+9 11.1%, H -> L+8 8.2%
11	5.6117	220.94	0.00724	H-1 -> L+9 11.8%, H -> L+5 9.0%, H-2 -> L+3 8.0%, H -> L 7.6%
12	5.7088	217.18	0.00313	H -> L 32.2%, H-2 -> L+6 6.5%, H-2 -> L+5 6.0%

				, H-1 -> L+9 5.4%
13	5.7351	216.18	0.00415	H -> L 15.6%, H-2 -> L+9 14.0%, H -> L+8 8.0%, H -> L+9 5.5%
14	5.7782	214.57	0.00107	H -> L 21.4%, H-1 -> L 13.2%, H-2 -> L+5 8.4%, H-1 -> L+9 7.7%
15	5.8014	213.71	0.00783	H-1 -> L 48.9%, H -> L+9 7.5%,
16	5.8716	211.16	0.00233	H-2 -> L 10.1%, H-1 -> L 9.9%, H -> L+6 8.6%, H-2 -> L+8 7.2%
17	5.9113	209.74	0.00176	H-2 -> L 48.1%
18	5.9475	208.46	0.00198	H -> L+8 22.3%, H -> L+10 9.1%, H -> L 6.4%, H -> L+11 5.2%
19	5.9986	206.69	0.00693	H -> L+12 15.0%, H-1 -> L+12 12.7%, H-2 -> L 11.7%, H-1 -> L 5.7%

20	6.0210	205.92	0.00505	H-1 -> L+12 29.6%, H -> L+12 10.9%, H-2 -> L+12 8.3%, H-1 -> L+10 7.0%
21	6.0585	204.65	0.01299	H-1 -> L+8 18.7%, H-1 -> L 7.6%, H-1 -> L+10 7.3%, H-2 -> L 6.5%
22	6.1559	201.41	0.00602	H-2 -> L+12 42.0%, H-2 -> L+10 11.7%, H-2 -> L+13 7.5%, H-2 -> L+3 6.7%
23	6.3132	196.39	0.12751	H-2 -> L+8 12.6%, H-2 -> L+2 7.5%, H -> L+12 7.2%, H-2 -> L+17 5.2%
24	6.3370	195.65	0.00759	H -> L+14 29.6%, H -> L+16 20.6%, H -> L+13 6.5%, H -> L+20 5.6%
25	6.3712	194.6	0.012	H-1 -> L+14 28.6%, H-1 -> L+16 16.1%, H-1

				-> L+13 9.5%, H-1 -> L+10 5.1%
26	6.3910	194	0.01192	H -> L+17 18.8%, H -> L+15 17.7%, H -> L+20 11.0%, H -> L+1 6.9%
27	6.4307	192.8	0.03991	H-1 -> L+20 16.4%, H-1 -> L+17 12.7%, H-1 -> L+15 12.7%, H-1 -> L+4 6.2%
28	6.4384	192.57	0.00848	H-2 -> L+14 23.5%, H-2 -> L+16 16.0%, H-2 -> L+20 13.7%,
29	6.4651	191.77	7.90E-04	H -> L+2 38.5%, H -> L+1 12.9%, H -> L+4 11.5%, H -> L+5 10.2%
30	6.5080	190.51	0.00217	H -> L+1 44.1%, H -> L+2 11.5%, H -> L+3 10.9%, H-1 -> L+2 6.5%
31	6.5281	189.9200	0.0025	H-1 -> L+2 48.8%, H-1 -> L+5 7.2%,

				H -> L+1 7.2%,
32	6.5899	188.1400	0.0003	H-1 -> L+1 65.2%, H-1 -> L+3 15.1%,
33	6.6172	187.3700	0.0180	H -> L+21 17.5%, H -> L+19 9.2%, H -> L+4 8.7%, H -> L+2 7.6%
34	6.6307	186.9900	0.0141	H-2 -> L+2 48.3%, H-2 -> L+15 6.6%,
35	6.6498	186.4500	0.0269	H-2 -> L+1 27.9%, H -> L+4 14.1%, H-2 -> L+4 6.0%, H-2 -> L+5 5.8%
36	6.6671	185.9600	0.0046	H -> L+4 40.2%, H -> L+21 6.9%, H -> L+3 5.6%, H-2 -> L+1 5.5%
37	6.7060	184.8800	0.0320	H-2 -> L+1 30.5%, H-2 -> L+3 9.8%, H-2 -> L+17 5.8%, H-2 -> L+15 5.7%
38	6.7317	184.1800	0.0015	H-1 -> L+4 52.3%, H-1 -> L+3 9.1%, H-1 -> L+2 8.2%,

39	6.7615	183.3700	0.0217	H-1 -> L+21 16.7%, H-1 -> L+18 12.6%, H-1 -> L+19 9.1%, H-1 -> L+13 6.5%
40	6.8207	181.7800	0.0004	H-2 -> L+4 46.7%, H-2 -> L+2 9.1%, H-2 -> L+3 8.5%, H-2 -> L+21 7.8%
41	6.8546	180.8800	0.0055	H -> L+7 44.9%, H -> L+6 10.1%, H-2 -> L+4 5.2%,
42	6.8638	180.6300	0.0070	H -> L+7 16.5%, H-2 -> L+21 12.4%, H-2 -> L+4 8.3%, H-2 -> L+19 7.5%
43	6.9322	178.8500	0.0241	H-1 -> L+7 29.5%, H-1 -> L+6 10.5%, H-1 -> L+25 7.9%, H-1 -> L+5 5.7%
44	6.9472	178.4700	0.0088	H-1 -> L+7 29.5%, H-1 -> L+21 8.1%, H-1 -> L+19 5.6%, H-1 -> L+25 5.4%

45	7.0144	176.7600	0.0101	H-2 -> L+7 36.8%, H-2 -> L+6 10.3%, H-2 -> L+25 8.6%, H-2 -> L+5 7.2%
46	7.0498	175.8700	0.0639	H-2 -> L+7 20.4%, H-1 -> L+25 19.7%, H-1 -> L+18 6.2%, H -> L+25 5.6%
47	7.1039	174.5300	0.0210	H-2 -> L+25 20.0%, H-2 -> L+21 5.9%, H -> L+9 5.1%,
48	7.1153	174.2500	0.0041	H -> L+10 17.5%, H -> L+9 14.0%, H-2 -> L+25 12.1%, H -> L+8 9.7%
49	7.1599	173.1700	0.0363	H -> L+10 10.7%, H-2 -> L+25 9.6%, H -> L+25 8.1%, H -> L+11 6.2%
50	7.1882	172.4800	0.0006	H -> L+11 18.6%, H-1 -> L+10 14.1%, H-1 -> L+9 9.7%,

				H -> L+10 9.6%
51	7.2294	171.5000	0.0283	H -> L+11 20.3%, H -> L+25 12.3%, H-1 -> L+10 12.3%,
52	7.2398	171.2500	0.0106	H-3 -> L 72.7%, H-3 -> L+1 9.3%, ,
53	7.2696	170.5500	0.0111	H-1 -> L+11 46.0%, H-1 -> L+10 14.4%, H-1 -> L+17 5.4%,
54	7.2849	170.1900	0.0178	H-2 -> L+10 13.6%, H-2 -> L+9 12.8%, H-2 -> L+8 10.2%,
55	7.3030	169.7700	0.0337	H-5 -> L+3 14.7%, H-2 -> L+10 10.8%, H-4 -> L+3 9.4%, H-5 -> L+1 5.5%
56	7.3058	169.7100	0.0079	H-9 -> L 33.8%, H-11 -> L 26.4%, H-7 -> L 8.2%,
57	7.3617	168.4200	0.0042	H-2 -> L+11 36.7%, H-2 ->

				L+10 16.8%, H-2 -> L+17 6.1%,
58	7.3743	168.1300	0.0096	H -> L+13 13.3%, H -> L+29 13.1%, H -> L+15 10.4%, H -> L+21 7.3%
59	7.3848	167.8900	0.0372	H-7 -> L+3 18.4%, H -> L+13 9.3%, H-7 -> L+1 9.2%, H-2 -> L+11 6.0%
60	7.4074	167.3800	0.0248	H -> L+16 9.0%, H -> L+29 7.7%, ,