Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Theoretical assessment of vibrationally-resolved C1s X-ray photoelectron spectra of simple cyclic molecules

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This PDF file contains

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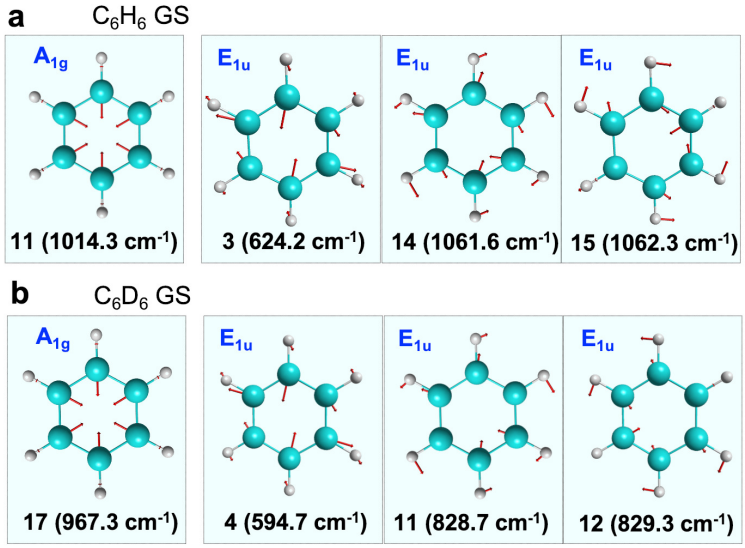

Figure S1 Active ground-state vibrational modes for (a) C_6H_6 and (b) C_6D_6 selected with $S_i \geq 0.1$ (see Table S1–S2). Modes are grouped by symmetries (horizontally) and according to similar vibrational features in different molecules (vertically).

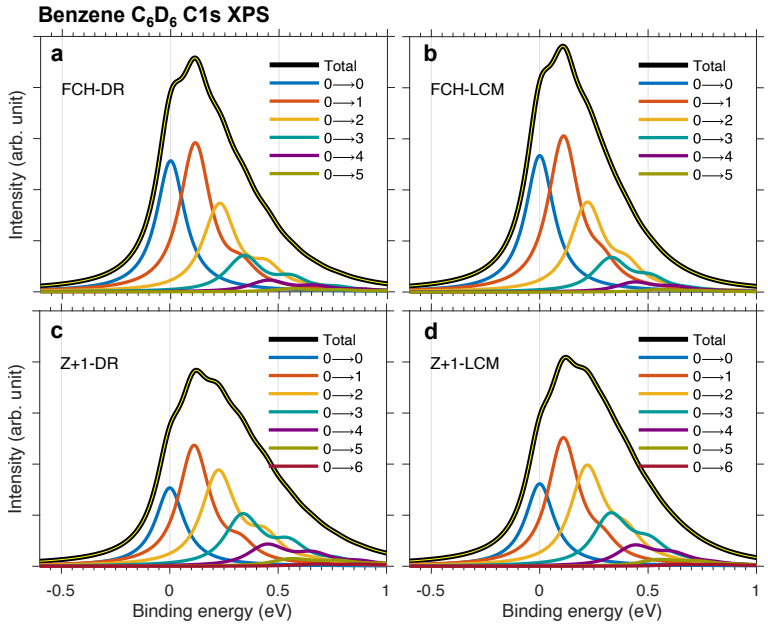

Figure S2 Decomposition of 0-n transitions (until convergence) for simulated vibrationally-resolved C1s XPS spectra of benzene C_6D_6 by four methods. The E_{00} energy was taken as energy zero.

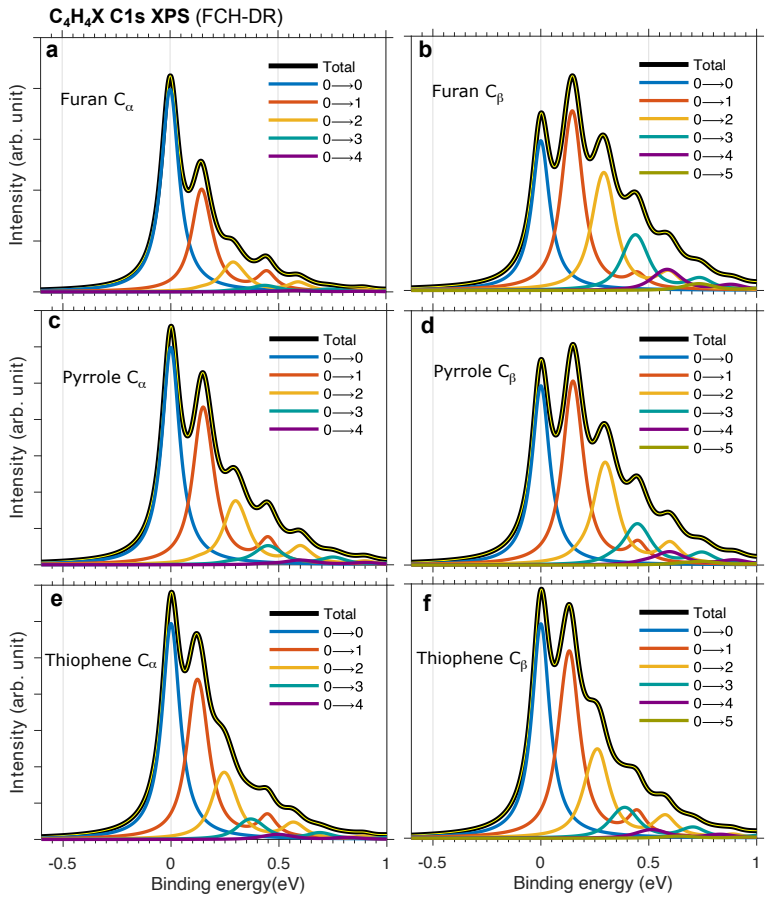

Figure S3 Decomposition of 0-n transitions (until convergence) for simulated vibrationally resolved C_α/C_β 1s XPS of (a-b) furan, (c-d) pyrrole, and (e-f) thiophene by the FCH-DR method. The 0-0 transition energy E_{00}^{DR} is taken as zero.

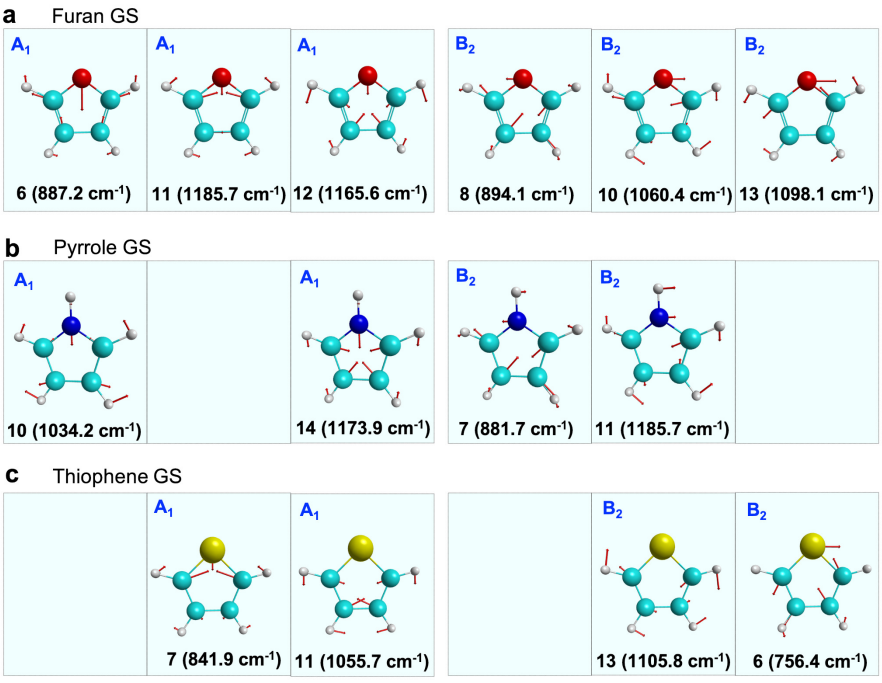

Figure S4 Active ground-state vibrational modes for (a) furan, (b) pyrrole, and (c) thiophene selected with $S_i \geq 0.1$. Modes are grouped by symmetries (horizontally) and according to similar vibrational features in different molecules (vertically).

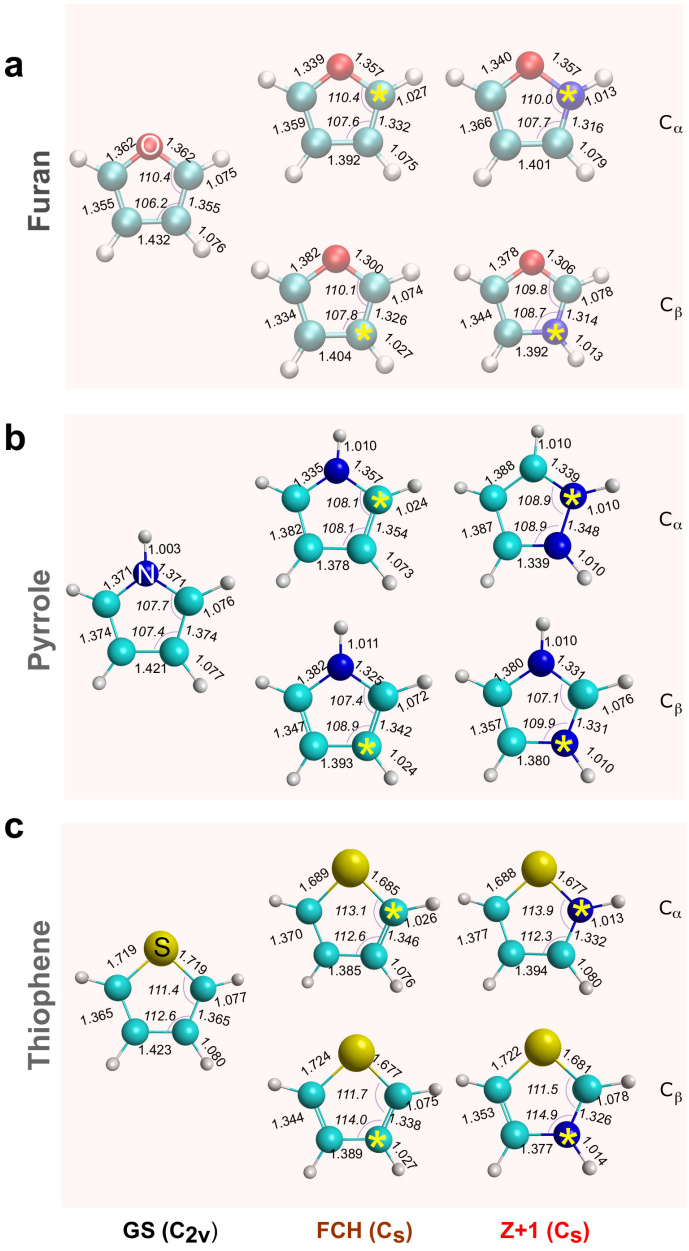

Figure S5 Comparison of optimized geometries at the GS, FCH and Z+1 states: (a) furan, (b) pyrrole, and (c) thiophene. Optimized geometries with bond lengths (in Å), bond angles (°), and symmetry (in parentheses) labeled. Stars indicate the core holes.

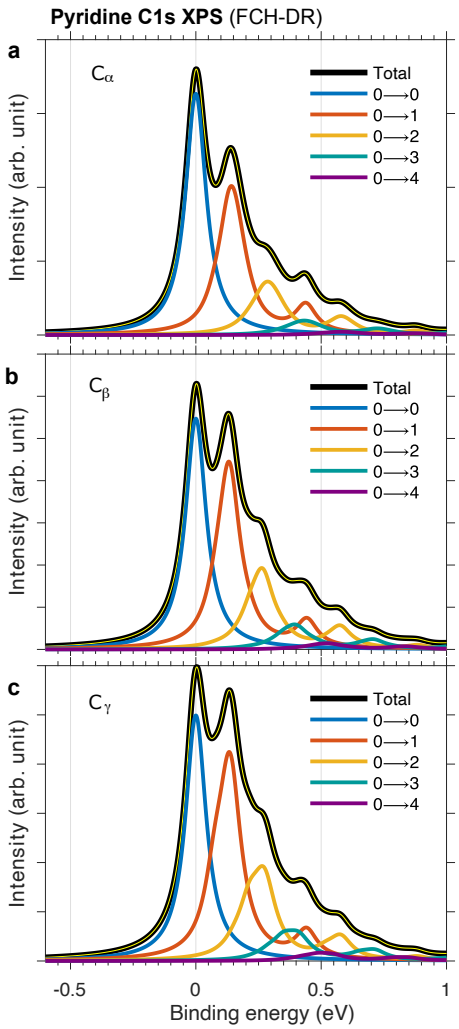

Figure S6 Decomposition of 0-n transitions (until convergence) for simulated vibrationally-resolved (a) C_α, (b) C_β, and (c) C_γ 1s XPS of pyridine by the FCH-DR method. The 0-0 transition energy E_{00}^{DR} is taken as zero.

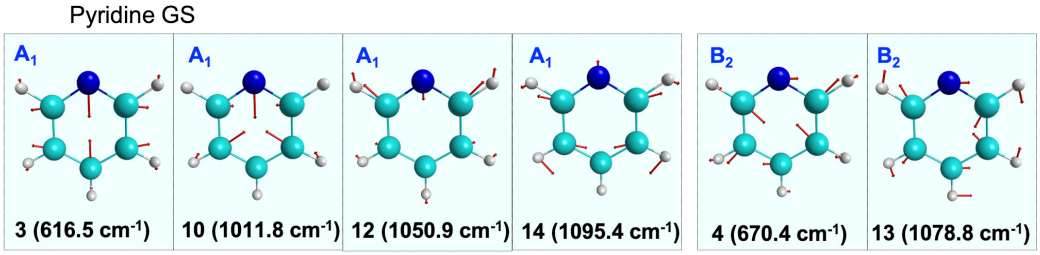

Figure S7 Active ground-state vibrational modes for pyridine selected with $S_i \geq 0.1$ (see Table S6). Modes are grouped by symmetries.

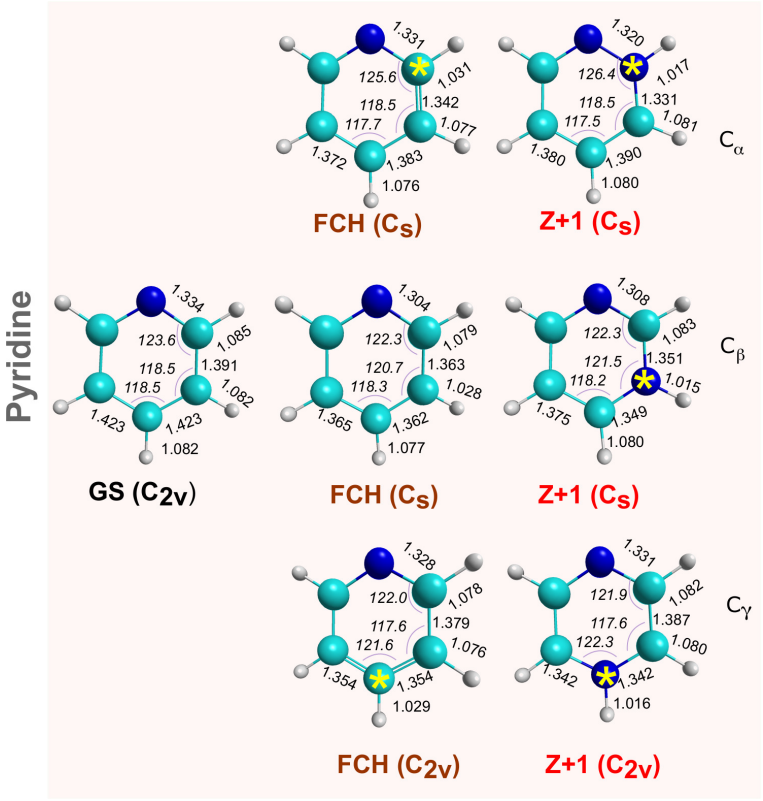

Figure S8 The same as Figure S5 for pyridine.

Table S1 Computed FCFs of benzene (C_6H_6 and C_6D_6), furan (C_α/C_β), pyrrole (C_α/C_β), thiophene (C_α/C_β), and pyridine (C_α/C_β/C_γ) at each individual 0-n excitations by four methods and sum of FCFs until n, $\sum_{j=0}^{n}\langle 0|j\rangle^2$. The convergence threshold for sum of FCFs was set to 0.99.

Method	FCH-DR		FCH-LCM		Z+1-DR		Z+1-LCM	
	FCFs	sum	FCFs	sum	FCFs	sum	FCFs	sum
C_6H_6								
$\langle 0\|0\rangle^2$	0.326	0.326	0.337	0.337	0.219	0.219	0.228	0.228
$\langle 0\|1\rangle^2$	0.353	0.679	0.367	0.704	0.322	0.541	0.338	0.566
$\langle 0\|2\rangle^2$	0.203	0.882	0.199	0.903	0.248	0.789	0.249	0.815
$\langle 0\|3\rangle^2$	0.083	0.965	0.072	0.975	0.131	0.920	0.122	0.937
$\langle 0\|4\rangle^2$	0.026	0.991	0.020	0.995	0.054	0.974	0.046	0.983
$\langle 0\|5\rangle^2$	–	–	–	–	0.019	0.993	0.013	0.996
C_6D_6								
$\langle 0\|0\rangle^2$	0.260	0.260	0.271	0.271	0.156	0.156	0.164	0.164
$\langle 0\|1\rangle^2$	0.339	0.599	0.354	0.625	0.281	0.437	0.296	0.460
$\langle 0\|2\rangle^2$	0.232	0.831	0.231	0.856	0.262	0.699	0.268	0.728
$\langle 0\|3\rangle^2$	0.110	0.942	0.101	0.956	0.168	0.867	0.162	0.890
$\langle 0\|4\rangle^2$	0.041	0.983	0.033	0.989	0.083	0.950	0.073	0.963
$\langle 0\|5\rangle^2$	0.013	0.996	0.009	0.998	0.034	0.983	0.026	0.989
$\langle 0\|6\rangle^2$	–	–	–	–	0.012	0.995	0.008	0.997
Furan C_α								
$\langle 0\|0\rangle^2$	0.505	0.505	0.525	0.525	0.396	0.396	0.419	0.419
$\langle 0\|1\rangle^2$	0.325	0.829	0.338	0.863	0.344	0.740	0.365	0.783
$\langle 0\|2\rangle^2$	0.124	0.954	0.109	0.972	0.172	0.912	0.159	0.942
$\langle 0\|3\rangle^2$	0.036	0.989	0.023	0.996	0.063	0.975	0.046	0.988
$\langle 0\|4\rangle^2$	0.008	0.998	–	–	0.019	0.994	0.010	0.998
Furan C_β								
$\langle 0\|0\rangle^2$	0.224	0.224	0.241	0.241	0.148	0.148	0.161	0.161
$\langle 0\|1\rangle^2$	0.317	0.541	0.343	0.584	0.270	0.418	0.294	0.456
$\langle 0\|2\rangle^2$	0.242	0.783	0.244	0.828	0.258	0.676	0.268	0.724
$\langle 0\|3\rangle^2$	0.131	0.914	0.116	0.944	0.172	0.849	0.163	0.887
$\langle 0\|4\rangle^2$	0.056	0.970	0.041	0.985	0.090	0.939	0.074	0.962
$\langle 0\|5\rangle^2$	0.021	0.991	0.012	0.997	0.039	0.978	0.027	0.989
$\langle 0\|6\rangle^2$	–	–	–	–	0.015	0.993	0.008	0.997
Pyrrole C_α								
$\langle 0\|0\rangle^2$	0.379	0.379	0.403	0.403	0.278	0.278	0.301	0.301
$\langle 0\|1\rangle^2$	0.344	0.723	0.366	0.769	0.334	0.612	0.361	0.662
$\langle 0\|2\rangle^2$	0.179	0.903	0.167	0.936	0.222	0.834	0.217	0.879
$\langle 0\|3\rangle^2$	0.069	0.971	0.051	0.986	0.106	0.940	0.087	0.966
$\langle 0\|4\rangle^2$	0.021	0.993	0.011	0.998	0.041	0.981	0.026	0.992
$\langle 0\|5\rangle^2$	–	–	–	–	0.014	0.995	–	–
Pyrrole C_β								
$\langle 0\|0\rangle^2$	0.268	0.268	0.290	0.290	0.178	0.178	0.193	0.193
$\langle 0\|1\rangle^2$	0.331	0.599	0.359	0.648	0.292	0.470	0.318	0.511
$\langle 0\|2\rangle^2$	0.226	0.825	0.222	0.871	0.254	0.724	0.261	0.772
$\langle 0\|3\rangle^2$	0.111	0.936	0.092	0.963	0.156	0.879	0.143	0.915
$\langle 0\|4\rangle^2$	0.044	0.979	0.028	0.991	0.075	0.954	0.059	0.974
$\langle 0\|5\rangle^2$	0.015	0.994	–	–	0.030	0.985	0.019	0.993

$\langle 0\|6\rangle^2$	–	–	–	–	0.011	0.995	–	–
Thiophene C_α								
$\langle 0\|0\rangle^2$	0.377	0.377	0.392	0.392	0.279	0.279	0.292	0.292
$\langle 0\|1\rangle^2$	0.353	0.729	0.367	0.759	0.343	0.622	0.359	0.651
$\langle 0\|2\rangle^2$	0.180	0.909	0.172	0.931	0.224	0.846	0.221	0.873
$\langle 0\|3\rangle^2$	0.066	0.975	0.054	0.985	0.102	0.948	0.091	0.963
$\langle 0\|4\rangle^2$	0.019	0.994	0.013	0.997	0.037	0.985	0.028	0.991
$\langle 0\|5\rangle^2$	–	–	–	–	0.011	0.996	–	–
Thiophene C_β								
$\langle 0\|1\rangle^2$	0.321	0.321	0.337	0.337	0.205	0.205	0.218	0.218
$\langle 0\|2\rangle^2$	0.348	0.669	0.367	0.703	0.312	0.518	0.332	0.550
$\langle 0\|3\rangle^2$	0.205	0.874	0.199	0.903	0.250	0.767	0.253	0.803
$\langle 0\|4\rangle^2$	0.086	0.960	0.072	0.975	0.139	0.907	0.128	0.931
$\langle 0\|5\rangle^2$	0.029	0.989	0.020	0.995	0.061	0.968	0.049	0.980
$\langle 0\|6\rangle^2$	0.008	0.997	–	–	0.022	0.990	0.015	0.995
Pyridine C_α								
$\langle 0\|0\rangle^2$	0.414	0.414	0.431	0.431	0.294	0.294	0.308	0.308
$\langle 0\|1\rangle^2$	0.347	0.761	0.363	0.794	0.345	0.639	0.363	0.671
$\langle 0\|2\rangle^2$	0.163	0.924	0.152	0.947	0.217	0.856	0.213	0.884
$\langle 0\|3\rangle^2$	0.056	0.980	0.043	0.989	0.096	0.953	0.084	0.968
$\langle 0\|4\rangle^2$	0.015	0.995	0.009	0.998	0.034	0.987	0.025	0.993
$\langle 0\|5\rangle^2$	–	–	–	–	0.010	0.997	–	–
Pyridine C_β								
$\langle 0\|0\rangle^2$	0.347	0.347	0.360	0.360	0.229	0.229	0.240	0.240
$\langle 0\|1\rangle^2$	0.353	0.700	0.368	0.728	0.327	0.557	0.342	0.582
$\langle 0\|2\rangle^2$	0.194	0.894	0.188	0.916	0.244	0.800	0.244	0.827
$\langle 0\|3\rangle^2$	0.075	0.969	0.064	0.980	0.126	0.926	0.116	0.943
$\langle 0\|4\rangle^2$	0.023	0.992	0.016	0.996	0.051	0.977	0.042	0.985
$\langle 0\|5\rangle^2$	–	–	–	–	0.017	0.994	0.012	0.996
Pyridine C_γ								
$\langle 0\|0\rangle^2$	0.316	0.316	0.326	0.326	0.202	0.202	0.210	0.210
$\langle 0\|1\rangle^2$	0.354	0.670	0.365	0.691	0.315	0.517	0.328	0.538
$\langle 0\|2\rangle^2$	0.208	0.878	0.205	0.896	0.253	0.770	0.256	0.794
$\langle 0\|3\rangle^2$	0.085	0.963	0.077	0.973	0.140	0.910	0.133	0.927
$\langle 0\|4\rangle^2$	0.027	0.991	0.021	0.994	0.060	0.970	0.052	0.978
$\langle 0\|5\rangle^2$	–	–	–	–	0.021	0.991	0.016	0.995

Table S2 Ground-state vibrational frequency ω_i' (in cm^{-1}) for each mode i of C_6H_6. Also displacement k_i (in au$\cdot\sqrt{\text{amu}}$) and Huang-Rhys factor S_i between the C 1s core-ionized and ground state potential energy surfaces is given (computed with either the FCH or the Z+1 method). Indexes and frequencies of active modes are in bolded fonts, where a threshold of $S_i \geq 0.1$ (by any method) was used.

i	ω_i'	C (FCH)		C (Z+1)	
		k_i	S_i	k_i	S_i
1	414.7	0.0	0.00	0.0	0.00
2	414.7	0.0	0.00	0.0	0.00
3	**624.2**	8.3	0.10	7.9	0.09
4	624.2	-4.4	0.03	-4.2	0.02
5	691.0	0.0	0.00	0.0	0.00
6	726.6	0.0	0.00	0.0	0.00
7	867.1	0.0	0.00	0.0	0.00
8	867.2	0.0	0.00	0.0	0.00
9	988.0	0.0	0.00	0.0	0.00
10	988.1	0.0	0.00	0.0	0.00
11	**1014.3**	-15.0	0.52	-14.1	0.46
12	1021.2	0.0	0.00	0.0	0.00
13	1030.2	-1.7	0.01	-2.6	0.02
14	**1061.6**	-9.5	0.22	-14.1	0.48
15	**1062.3**	5.5	0.07	8.1	0.16
16	1176.1	-0.0	0.00	-0.0	0.00
17	1199.8	1.6	0.01	3.6	0.04
18	1200.0	-0.9	0.00	-2.1	0.01
19	1334.7	-0.0	0.00	-0.0	0.00
20	1389.3	-0.0	0.00	-0.0	0.00
21	1518.0	-0.8	0.00	0.5	0.00
22	1518.5	-0.4	0.00	0.3	0.00
23	1636.4	-0.5	0.00	1.1	0.00
24	1636.9	0.3	0.00	-0.6	0.00
25	3154.5	-1.5	0.02	-1.9	0.03
26	3164.4	-1.9	0.03	-2.5	0.05
27	3164.4	-0.7	0.00	-0.9	0.01
28	3179.8	-2.1	0.03	-2.7	0.05
29	3179.8	-1.0	0.01	-1.3	0.01
30	3190.0	-2.5	0.05	-2.5	0.04

Table S3 The same as Table S2 for C_6D_6.

i	ω_i'	C (FCH)		C (Z+1)	
		k_i	S_i	k_i	S_i
1	359.9	0.0	0.00	0.0	0.00
2	360.0	0.0	0.00	0.0	0.00
3	507.4	0.0	0.00	0.0	0.00
4	**594.7**	9.4	0.12	9.6	0.12
5	594.8	-5.3	0.04	-5.3	0.04
6	615.9	0.0	0.00	0.0	0.00
7	674.6	0.0	0.00	0.0	0.00
8	674.7	0.0	0.00	0.0	0.00
9	805.2	0.0	0.00	0.0	0.00
10	805.3	0.0	0.00	0.0	0.00
11	**828.7**	-12.3	0.28	-17.3	0.56
12	**829.3**	-7.1	0.09	-9.9	0.19
13	839.6	-0.2	0.00	-0.3	0.00
14	852.3	0.0	0.00	0.0	0.00
15	877.0	1.4	0.00	3.6	0.03
16	877.2	-0.8	0.00	-2.1	0.01
17	**967.3**	-16.5	0.60	-15.6	0.53
18	989.0	-2.2	0.01	-3.3	0.02
19	1080.9	0.0	0.00	0.0	0.00
20	1322.5	-0.0	0.00	-0.0	0.00
21	1364.2	1.9	0.01	4.5	0.06
22	1364.6	-1.1	0.00	-2.6	0.02
23	1593.1	0.0	0.00	2.0	0.01
24	1593.5	-0.0	0.00	-1.1	0.00
25	2324.5	-1.9	0.02	-2.5	0.03
26	2335.4	2.4	0.03	3.1	0.05
27	2335.5	1.1	0.01	1.4	0.01
28	2354.3	-2.5	0.03	-3.1	0.05
29	2354.3	-1.3	0.01	-1.6	0.01
30	2366.2	-2.7	0.04	-2.7	0.04

Table S4 The same as Table S2 for furan C_α/C_β.

i	ω_i'	C_α (FCH)		C_α (Z+1)		C_β (FCH)		C_β (Z+1)	
		k_i	S_i	k_i	S_i	k_i	S_i	k_i	S_i
1	617.8	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
2	624.4	-0.0	0.00	-0.0	0.00	-0.0	0.00	-0.0	0.00
3	736.6	-0.0	0.00	-0.0	0.00	-0.0	0.00	-0.0	0.00
4	760.0	-0.0	0.00	0.0	0.00	-0.0	0.00	-0.0	0.00
5	856.4	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
6	**887.2**	-3.9	0.03	-3.9	0.03	7.5	0.11	7.6	0.12
7	890.9	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
8	**894.1**	-2.8	0.02	-2.6	0.01	-9.3	0.18	-10.4	0.22
9	1013.6	-0.3	0.00	-2.7	0.02	4.2	0.04	6.7	0.10
10	**1060.4**	4.4	0.05	7.1	0.12	11.8	0.34	13.5	0.44
11	**1085.7**	8.5	0.18	7.8	0.15	7.3	0.13	8.3	0.17
12	**1165.6**	7.1	0.13	6.5	0.11	12.3	0.40	14.3	0.54
13	**1198.1**	-5.8	0.09	-5.9	0.10	4.7	0.06	2.2	0.01
14	1293.7	-1.0	0.00	-3.0	0.03	0.8	0.00	0.5	0.00
15	1414.7	-2.0	0.01	-1.6	0.01	3.8	0.05	3.3	0.03
16	1511.1	2.8	0.03	4.4	0.07	2.3	0.02	2.3	0.02
17	1594.0	-2.0	0.01	-4.6	0.08	0.7	0.00	-1.8	0.01
18	3240.2	-0.9	0.01	-1.2	0.01	2.0	0.03	2.8	0.06
19	3250.9	0.9	0.01	1.5	0.02	-2.5	0.04	-3.2	0.07
20	3272.7	2.4	0.04	3.2	0.07	0.7	0.00	1.0	0.01
21	3279.1	-2.2	0.04	-2.5	0.05	-1.4	0.01	-1.3	0.01

Table S5 The same as Table S2 for pyrrole C_α/C_β.

i	ω_i'	C_α (FCH)		C_α (Z+1)		C_β (FCH)		C_β (Z+1)	
		k_i	S_i	k_i	S_i	k_i	S_i	k_i	S_i
1	480.0	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
2	631.3	0.0	0.00	-0.0	0.00	0.0	0.00	0.0	0.00
3	642.9	0.0	0.00	-0.0	0.00	-0.0	0.00	-0.0	0.00
4	694.1	-0.0	0.00	0.0	0.00	0.0	0.00	-0.0	0.00
5	732.5	-0.0	0.00	0.0	0.00	0.0	0.00	-0.0	0.00
6	837.7	0.0	0.00	-0.0	0.00	0.0	0.00	0.0	0.00
7	**881.7**	-0.3	0.00	0.5	0.00	-6.9	0.10	-8.1	0.13
8	883.4	0.0	0.00	-0.0	0.00	0.0	0.00	-0.0	0.00
9	902.7	6.4	0.08	6.6	0.09	-3.2	0.02	-3.3	0.02
10	**1034.2**	0.1	0.00	-2.6	0.02	7.2	0.12	10.3	0.25
11	**1068.7**	-7.3	0.13	-11.3	0.31	-9.1	0.20	-11.7	0.33
12	1091.7	-6.6	0.11	-6.3	0.10	-1.5	0.01	-1.7	0.01
13	1158.0	-1.3	0.00	0.4	0.00	3.4	0.03	2.0	0.01
14	**1173.9**	11.7	0.37	12.1	0.39	14.3	0.55	15.8	0.67
15	1317.4	0.8	0.00	1.2	0.00	-1.5	0.01	-1.1	0.00
16	1417.3	-1.8	0.01	-0.4	0.00	4.2	0.06	3.3	0.03
17	1449.8	-5.3	0.09	-5.6	0.10	3.2	0.03	1.5	0.01
18	1501.7	-0.4	0.00	-1.0	0.00	0.0	0.00	-0.4	0.00
19	1577.0	-0.7	0.00	1.3	0.01	-0.8	0.00	1.1	0.00
20	3230.1	-1.0	0.01	-1.3	0.01	2.1	0.03	2.9	0.06
21	3240.9	-1.2	0.01	-1.8	0.02	2.3	0.04	3.0	0.07
22	3256.3	-2.6	0.05	-3.4	0.08	-0.9	0.01	-1.3	0.01
23	3261.9	-2.4	0.04	-2.6	0.05	-2.0	0.03	-2.0	0.03
24	3672.2	0.4	0.00	0.4	0.00	0.7	0.00	0.7	0.00

Table S6 The same as Table S2 for thiophene C_α/C_β.

i	ω_i'	C_α (FCH)		C_α (Z+1)		C_β (FCH)		C_β (Z+1)	
		k_i	S_i	k_i	S_i	k_i	S_i	k_i	S_i
1	464.0	-0.0	0.00	-0.0	0.00	-0.0	0.00	0.0	0.00
2	582.0	-0.0	0.00	0.0	0.00	-0.0	0.00	-0.0	0.00
3	616.5	-2.9	0.01	-1.5	0.00	4.5	0.03	4.2	0.02
4	693.2	-0.0	0.00	-0.0	0.00	-0.0	0.00	-0.0	0.00
5	727.8	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
6	**756.4**	3.0	0.02	4.5	0.04	11.5	0.23	12.2	0.26
7	**841.9**	15.3	0.45	17.2	0.56	4.5	0.04	4.0	0.03
8	881.1	0.0	0.00	2.8	0.02	0.2	0.00	-0.7	0.00
9	887.9	-0.0	0.00	-0.0	0.00	-0.0	0.00	-0.0	0.00
10	928.9	-0.0	0.00	0.0	0.00	-0.0	0.00	-0.0	0.00
11	**1055.7**	8.9	0.19	7.2	0.12	15.0	0.54	18.3	0.80
12	1104.6	-3.2	0.03	-4.2	0.05	-3.8	0.04	-3.9	0.04
13	**1105.8**	6.2	0.10	8.3	0.17	4.3	0.05	6.9	0.12
14	1283.9	-1.9	0.01	-3.3	0.03	-0.5	0.00	-1.7	0.01
15	1395.3	2.4	0.02	2.9	0.03	2.4	0.02	2.9	0.03
16	1440.1	-0.7	0.00	0.5	0.00	3.5	0.04	2.9	0.03
17	1550.5	-1.5	0.01	-3.6	0.05	0.5	0.00	-1.7	0.01
18	3194.6	-0.5	0.00	-0.7	0.00	2.3	0.04	3.1	0.07
19	3208.3	0.3	0.00	0.8	0.00	-2.9	0.06	-3.5	0.09
20	3243.0	2.8	0.06	3.6	0.09	0.6	0.00	0.7	0.00
21	3245.7	2.5	0.05	2.9	0.06	1.0	0.01	0.8	0.00

Table S7 The same as Table S2 for pyridine $C_\alpha/C_\beta/C_\gamma$.

i	ω_i'	C_α (FCH)		C_α (Z+1)		C_β (FCH)		C_β (Z+1)		C_γ (FCH)		C_γ (Z+1)	
		k_i	S_i	k_i	S_i	k_i	S_i	k_i	S_i	k_i	S_i	k_i	S_i
1	385.9	0.0	0.00	0.0	0.00	0.0	0.00	-0.0	0.00	0.0	0.00	0.0	0.00
2	421.3	-0.0	0.00	0.0	0.00	-0.0	0.00	-0.0	0.00	-0.0	0.00	-0.0	0.00
3	**616.5**	-3.8	0.02	-3.8	0.02	-0.1	0.00	0.4	0.00	13.1	0.24	12.4	0.22
4	**670.4**	5.4	0.04	4.6	0.03	-9.5	0.14	-9.2	0.13	0.0	0.00	0.0	0.00
5	720.9	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	-0.0	0.00	-0.0	0.00
6	768.7	-0.0	0.00	0.0	0.00	-0.0	0.00	0.0	0.00	-0.0	0.00	-0.0	0.00
7	899.8	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	-0.0	0.00	-0.0	0.00
8	963.3	0.0	0.00	0.0	0.00	-0.0	0.00	0.0	0.00	-0.0	0.00	-0.0	0.00
9	1010.6	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
10	**1011.8**	-8.4	0.16	-8.1	0.15	-11.8	0.32	-12.5	0.36	-7.2	0.12	-6.0	0.08
11	1022.4	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
12	**1050.9**	-6.9	0.11	-5.9	0.08	-8.3	0.16	-8.4	0.17	-12.5	0.38	-14.8	0.52
13	**1078.8**	8.7	0.19	12.0	0.35	9.2	0.21	14.0	0.48	-0.0	0.00	-0.0	0.00
14	**1095.4**	5.0	0.06	8.2	0.17	-3.8	0.04	-5.2	0.07	-9.9	0.24	-14.0	0.49
15	1172.1	2.5	0.02	3.2	0.03	-1.3	0.00	-3.0	0.02	-0.1	0.00	-0.1	0.00
16	1243.2	1.4	0.01	1.8	0.01	-0.7	0.00	-2.1	0.01	1.6	0.01	2.6	0.02
17	1282.5	4.9	0.07	3.7	0.04	-0.9	0.00	-0.8	0.00	0.0	0.00	0.0	0.00
18	1389.9	-1.2	0.00	-2.2	0.02	0.3	0.00	0.9	0.00	0.0	0.00	0.0	0.00
19	1475.6	1.4	0.01	3.3	0.04	0.2	0.00	0.8	0.00	0.0	0.00	0.0	0.00
20	1516.9	-2.3	0.02	-2.1	0.02	0.7	0.00	0.5	0.00	0.5	0.00	-0.4	0.00
21	1619.8	0.4	0.00	1.3	0.01	2.2	0.02	0.4	0.00	0.0	0.00	0.0	0.00
22	1625.5	1.7	0.01	2.9	0.03	-1.2	0.01	-0.8	0.00	-1.9	0.01	-3.9	0.06
23	3141.3	2.3	0.04	3.2	0.07	-0.3	0.00	-0.4	0.00	-0.0	0.00	-0.0	0.00
24	3144.2	3.1	0.07	3.7	0.10	-0.2	0.00	-0.7	0.00	0.8	0.01	0.6	0.00
25	3168.3	0.7	0.00	0.8	0.01	1.4	0.01	1.7	0.02	-2.6	0.05	-3.7	0.10
26	3184.1	0.5	0.00	0.7	0.00	2.5	0.05	3.3	0.08	-0.0	0.00	-0.0	0.00
27	3191.6	-1.0	0.01	-0.8	0.00	-2.9	0.06	-3.1	0.07	-2.9	0.06	-3.2	0.07

Cartesian coordinates of optimized geometries

All structures were relaxed by using Gamess-US with the B3LYP functional. Geometries in the GS, FCH, and Z+1 states were respectively optimized with basis sets χ_{GS}, χ_{FCH}, and χ_{Z+1} (defined in Table 1 in the text).

```
benzene/benzene.gs.xyz
   12
C          -0.6955396203       -1.2047099611       -0.0000000000
C           0.6955396203       -1.2047099611       -0.0000000000
C           1.3910792406       -0.0000000000       -0.0000000000
C           0.6955396203        1.2047099611       -0.0000000000
C          -0.6955396203        1.2047099611       -0.0000000000
C          -1.3910792406        0.0000000000       -0.0000000000
H          -1.2367265477       -2.1420732157       -0.0000000000
H           1.2367265477       -2.1420732157       -0.0000000000
H           2.4734530954       -0.0000000000       -0.0000000000
H           1.2367265477        2.1420732157       -0.0000000000
H          -1.2367265477        2.1420732157       -0.0000000000
H          -2.4734530954        0.0000000000       -0.0000000000

benzene/benzene.fch.xyz
  12
C          -0.6682348010       -1.1574132054        0.0000000000
C           0.6911206175       -1.1851291756        0.0000000000
C           1.3860498542       -0.0062141047        0.0000000000
C           0.6876733190        1.1910941462        0.0000000000
C          -0.6984010803        1.1972890981        0.0000000000
C          -1.3719073702        0.0059859116        0.0000000000
H          -1.1816094409       -2.0466156746        0.0000000000
H           1.1645137064       -2.1513831097        0.0000000000
H           2.4619633602       -0.0249934864        0.0000000000
H           1.2268414724        2.1249551551        0.0000000000
H          -1.2526116695        2.1196748842        0.0000000000
H          -2.4453979678       -0.0672504387        0.0000000000

benzene/benzene.z+1.xyz
  12
N          -0.6639291289       -1.1499887609        0.0000000000
C           0.6829712292       -1.1874512629        0.0000000000
C           1.3904853203       -0.0053193172        0.0000000000
C           0.6930856903        1.2005008829        0.0000000000
C          -0.6998554365        1.2015451603        0.0000000000
C          -1.3698161664       -0.0022562499        0.0000000000
H          -1.1708073061       -2.0278613169        0.0000000000
H           1.1425469538       -2.1644375697        0.0000000000
H           2.4699378993       -0.0321386170        0.0000000000
H           1.2338809824        2.1371709162        0.0000000000
H          -1.2627962546        2.1229772881        0.0000000000
H          -2.4457037828       -0.0927411530        0.0000000000

furan/furan.Calpha.fch.xyz
   9
C          -0.3745220055        0.0794852555        0.0001664285
C           0.9574188996        0.0862241428        0.0001512365
C           1.3714006121        1.4156989021       -0.0001561281
C           0.2241206252        2.1441211671       -0.0003034044
O          -0.8534667705        1.3496847937       -0.0001119528
H          -1.0644714429       -0.6815986246        0.0003041013
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H          1.5363444277       -0.8200154349        0.0003749555
H          2.3790334524        1.7813727905       -0.0002664644
H          0.0073429221        3.1964443678       -0.0005187717

furan/furan.gs.xyz
   9
C         -0.3924465359        0.0653634525        0.0000417987
C          0.9623738812        0.0541686483        0.0001721802
C          1.3722002665        1.4265758976       -0.0000504615
C          0.2330860363        2.1601252374       -0.0002842616
O         -0.8576145973        1.3450497913       -0.0002251052
H         -1.1397566334       -0.7073749941        0.0001566632
H          1.5948005479       -0.8168005201        0.0003992621
H          2.3786415633        1.8081914809       -0.0000150934
H          0.0319161916        3.2161183662       -0.0005549822

furan/furan.Calpha.z+1.xyz
   9
N         -0.3596075120        0.0751979680        0.0004529749
C          0.9567584660        0.0832981751        0.0001205810
C          1.3753301091        1.4199161954       -0.0004225288
C          0.2179649911        2.1445565679       -0.0003694125
O         -0.8530002713        1.3388223954        0.0001656027
H         -1.0559468008       -0.6606498313        0.0008696917
H          1.5208945258       -0.8369867708        0.0002795962
H          2.3859044082        1.7878493592       -0.0008007723
H         -0.0050971959        3.1994133011       -0.0006557326

furan/furan.Cbeta.fch.xyz
   9
C         -0.3928374310        0.0911504784       -0.0005029479
C          0.9332453918        0.0949944224       -0.0002039688
C          1.3580931337        1.4328642351        0.0003127164
C          0.2437067876        2.1661449006        0.0002937196
O         -0.8421020906        1.3111546738       -0.0002202090
H         -1.0680948836       -0.7442712718       -0.0009176900
H          1.5335686103       -0.7381639905       -0.0003334822
H          2.3895204950        1.7226896173        0.0006322424
H          0.0281007069        3.2148542948        0.0005796199

furan/furan.Cbeta.z+1.xyz
   9
C         -0.3874225312        0.0899635098       -0.0008290114
N          0.9260650127        0.1044953345        0.0000391521
C          1.3589461882        1.4278108313        0.0006666721
C          0.2372910340        2.1682408775        0.0001469616
O         -0.8430702690        1.3135612720       -0.0008109666
H         -1.0521967305       -0.7584913306       -0.0015320188
H          1.5181149423       -0.7173923389        0.0002462846
H          2.3987083076        1.7012466724        0.0014078558
H          0.0267647661        3.2219825320        0.0003050709

pyrrole/pyrrole.gs.xyz
  10
C          0.1982567323       -0.4602467887        0.0000570063
C          1.5719091834       -0.4546971186        0.0000267955
C          1.9918864890        0.9031885891       -0.0000965633
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C          0.8612272914        1.6833628578       -0.0001368115
N         -0.2231748490        0.8444013032       -0.0000424569
H         -1.1818561005        1.1408467816       -0.0000520271
H         -0.5049536060       -1.2745182385        0.0001400972
H          2.2045358751       -1.3260701691        0.0000794062
H          3.0059571256        1.2653461176       -0.0001470456
H          0.7404013586        2.7524470653       -0.0002304008

pyrrole/pyrrole.Calpha.fch.xyz
  10
C          0.2149493352       -0.4289643379        0.0001153721
C          1.5693557428       -0.4228001885        0.0001098049
C          1.9919241854        0.8890194960       -0.0001074319
C          0.8504169434        1.6681197068       -0.0002311538
N         -0.2116049808        0.8590588855       -0.0000952417
H         -1.1928028220        1.0981208299       -0.0001252704
H         -0.4275039408       -1.2269601979        0.0002497999
H          2.1375011282       -1.3334102128        0.0002579330
H          3.0051531548        1.2373121283       -0.0001685333
H          0.7268007538        2.7345642905       -0.0004072788

pyrrole/pyrrole.Calpha.z+1.xyz
  10
N          0.2261084804       -0.4232436747       -0.0001856111
C          1.5655847227       -0.4250087538        0.0003096051
C          1.9970997867        0.8933879244        0.0003368725
C          0.8489807520        1.6727729409       -0.0001627241
N         -0.2091921942        0.8523552024       -0.0004729775
H         -1.1952853912        1.0725604602       -0.0008460263
H         -0.4189388920       -1.2008534701       -0.0003586597
H          2.1162994769       -1.3506388951        0.0006062887
H          3.0144215809        1.2406998156        0.0006770122
H          0.7191111776        2.7420288505       -0.0003057799

pyrrole/pyrrole.Cbeta.fch.xyz
  10
C          0.1980911314       -0.4310902743       -0.0003312668
C          1.5407852741       -0.4135128630       -0.0006342820
C          1.9748385250        0.9101636810       -0.0001092242
C          0.8717534103        1.6826786280        0.0005183741
N         -0.2138832415        0.8278271986        0.0003663777
H         -1.1843067239        1.1096294820        0.0007282354
H         -0.4331616204       -1.2979400557       -0.0005966665
H          2.1404068081       -1.2441466950       -0.0011658770
H          3.0104452365        1.1827933513       -0.0002253763
H          0.7592207002        2.7476579468        0.0010477057

pyrrole/pyrrole.Cbeta.z+1.xyz
  10
C          0.2039172849       -0.4327836836       -0.0000274475
N          1.5344528568       -0.4034363929        0.0000274577
C          1.9759276154        0.9045321952       -0.0000155490
C          0.8668010923        1.6860381990       -0.0000960215
N         -0.2160398111        0.8298505055       -0.0001015595
H         -1.1868792578        1.1098844535       -0.0001511583
H         -0.4155759602       -1.3125030416       -0.0000080930
H          2.1250146264       -1.2232291372        0.0000954067
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H          3.0195937680        1.1606360569        0.0000214841
H          0.7569772853        2.7550712450       -0.0001465197

thiophene/thiophene.gs.xyz
   9
C         -1.6060065839        0.2764509174        0.0006329533
C         -0.2416237952        0.3021826095       -0.0002006541
C          0.2803692671        1.6255608594       -0.0002918021
C         -0.6990233492        2.5758051348        0.0004743070
S         -2.2645186012        1.8647697260        0.0013152235
H         -2.2572759753       -0.5813070849        0.0008836648
H          0.3700470201       -0.5880681915       -0.0007475756
H          1.3350601546        1.8586359278       -0.0009108505
H         -0.5893796270        3.6471947115        0.0005767336

thiophene/thiophene.Calpha.fch.xyz
   9
C         -1.5872290074        0.3144835321        0.0009684313
C         -0.2408811068        0.3252991763       -0.0002582000
C          0.2799316463        1.6084789649       -0.0005808492
C         -0.7180786221        2.5473130634        0.0004321694
S         -2.2606002682        1.8595819544        0.0017456976
H         -2.1686294041       -0.5312568687        0.0013808307
H          0.3115599276       -0.5984616963       -0.0008837835
H          1.3299693281        1.8363935183       -0.0015226812
H         -0.6183939835        3.6193929656        0.0004503848

thiophene/thiophene.Calpha.z+1.xyz
   9
N         -1.5762191975        0.3167828162        0.0005182719
C         -0.2438592729        0.3197730907       -0.0002336568
C          0.2825251147        1.6101574324       -0.0002345044
C         -0.7231603663        2.5508033373        0.0005545273
S         -2.2584435734        1.8482419282        0.0012597637
H         -2.1563458892       -0.5137565878        0.0006507668
H          0.2947310013       -0.6166127964       -0.0007589672
H          1.3359544727        1.8392889026       -0.0007757697
H         -0.6275337794        3.6265464868        0.0007515683

thiophene/thiophene.Cbeta.fch.xyz
   9
C         -1.6018880603        0.3040963638        0.0005902446
C         -0.2644435176        0.3418193937       -0.0004088025
C          0.2651029575        1.6258779990       -0.0003413179
C         -0.6976697076        2.5639315604        0.0007386426
S         -2.2643236319        1.8447056265        0.0016573855
H         -2.1764410510       -0.6044987022        0.0007021004
H          0.3168662570       -0.5051069709       -0.0011507689
H          1.3281708375        1.7794822869       -0.0011022126
H         -0.5777255736        3.6309170530        0.0010467288

thiophene/thiophene.Cbeta.z+1.xyz
   9
C         -1.5958866208        0.3051205564        0.0007388084
N         -0.2705596915        0.3512235840       -0.0003442404
C          0.2647444216        1.6199055211       -0.0004375949
C         -0.7022153411        2.5663857336        0.0006240366
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S         -2.2661883778        1.8465695113        0.0017192377
H         -2.1579235153       -0.6151879009        0.0009531222
H          0.3015242171       -0.4858043781       -0.0010505982
H          1.3337483410        1.7564770565       -0.0012868172
H         -0.5795949231        3.6365349261        0.0008160456

pyridine/pyridine.Calpha.fch.xyz
  11
C         -2.9640085387       -0.7650253907        0.0002980029
C         -1.6221899180       -0.7784176764       -0.0000266660
C         -0.9501139253        0.4297691422       -0.0005023026
C         -1.7010343728        1.5774720559       -0.0006114242
C         -3.0972877249        1.4754482471       -0.0002414879
N         -3.7288076429        0.3243385756        0.0002067150
H          0.1261798089        0.4469353581       -0.0007737597
H         -3.4893270271       -1.6518299791        0.0006499845
H         -1.1317018699       -1.7375021402        0.0000989091
H         -1.2353192321        2.5498749492       -0.0009780889
H         -3.7298747873        2.3479734783       -0.0003088822

pyridine/pyridine.Calpha.z+1.xyz
  11
N         -2.9568804852       -0.7617241653        0.0003875197
C         -1.6255306081       -0.7808361799       -0.0000061655
C         -0.9440574454        0.4301223475       -0.0005655960
C         -1.6988761029        1.5848848602       -0.0006913972
C         -3.0982714887        1.4734437725       -0.0002409415
N         -3.7253734156        0.3119635726        0.0002985230
H          0.1360146526        0.4430114476       -0.0008881781
H         -3.4814275565       -1.6326525854        0.0008020850
H         -1.1498194090       -1.7514256064        0.0001379090
H         -1.2348805909        2.5616756288       -0.0011143566
H         -3.7443827802        2.3405735279       -0.0003084020

pyridine/pyridine.Cbeta.fch.xyz
  11
C         -3.0032215698       -0.7777944072       -0.0000756089
C         -1.6405762921       -0.7502715740       -0.0000331518
C         -0.9695102282        0.4345263076       -0.0001709507
C         -1.6963005519        1.5897583450       -0.0003351553
C         -3.0817253262        1.4807681931       -0.0003713174
N         -3.7233063029        0.3099412704       -0.0002503532
H          0.1066336398        0.4000443087       -0.0001190200
H         -3.4853179561       -1.7428539053        0.0000300408
H         -1.1189646116       -1.6362001956        0.0000934412
H         -1.2069646855        2.5479504102       -0.0004488338
H         -3.7042313454        2.3631678671       -0.0005080909

pyridine/pyridine.Cbeta.z+1.xyz
  11
C         -2.9959980224       -0.7783097985       -0.0004503090
N         -1.6452190576       -0.7428520693       -0.0001449653
C         -0.9716249393        0.4257147279        0.0000704435
C         -1.6965168435        1.5938614277       -0.0000292623
C         -3.0881394292        1.4866269019       -0.0003678347
N         -3.7230736166        0.3088677858       -0.0005688060
H          0.1076584067        0.3754345027        0.0003074136
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H         -3.4651262099       -1.7541366418       -0.0005949313
H         -1.1303884882       -1.6179468895       -0.0000683254
H         -1.1991368036        2.5521996683        0.0001426776
H         -3.7159202262        2.3695770050       -0.0004851006

pyridine/pyridine.Cgamma.fch.xyz
  11
C         -3.0020880647       -0.7931627730        0.0002133877
C         -1.6229261341       -0.7804854367       -0.0002130352
C         -1.0058902390        0.4248809945       -0.0005604884
C         -1.7091125148        1.5820912254       -0.0004745579
C         -3.0855155498        1.4941568402       -0.0000483738
N         -3.7162375817        0.3259655137        0.0002845920
H          0.0224968871        0.4624337548       -0.0008920139
H         -3.5374217482       -1.7290751481        0.0005045615
H         -1.0133283795       -1.6673234512       -0.0002828071
H         -1.1657913173        2.5110133000       -0.0007387286
H         -3.6876705879        2.3885418005        0.0000184636

pyridine/pyridine.Cgamma.z+1.xyz
  11
C         -3.0056067395       -0.7943404209        0.0002485064
C         -1.6186320563       -0.7742555365       -0.0001622741
N         -1.0144741500        0.4245404335       -0.0005357345
C         -1.7043371775        1.5761516380       -0.0005178752
C         -3.0890915050        1.4951447239       -0.0001005777
N         -3.7248833664        0.3256956922        0.0002685715
H          0.0008309658        0.4615543065       -0.0008496419
H         -3.5381907836       -1.7364066254        0.0005653104
H         -0.9943295181       -1.6552965472       -0.0002056031
H         -1.1458806608        2.5003375768       -0.0008210473
H         -3.6888902384        2.3959113791       -0.0000786344

pyridine/pyridine.gs.xyz
  11
C         -3.0049268951       -0.7881208894        0.0001546192
C         -1.6143394374       -0.7917526824       -0.0001060657
C         -0.9488087669        0.4269422848       -0.0004210586
C         -1.7013270446        1.5939366628       -0.0004785416
C         -3.0879941249        1.4889809147       -0.0002178356
N         -3.7396433872        0.3251447491        0.0001026620
H          0.1327868328        0.4663692424       -0.0006184584
H         -3.5545011923       -1.7233485671        0.0004298142
H         -1.0719248427       -1.7276187661       -0.0000516260
H         -1.2285221854        2.5668372545       -0.0007178688
H         -3.7042841862        2.3816664168       -0.0002646407
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