Appendix A

GAUSSIAN 98 Results

A.1 Geometries

Table A.1: Symmetry Groups, Dipole Moments, Rotational Constants.

Molecule	Symmetry Group	Dipole Moment (Debye)	Rotational Constants (GHz) A	B	C
Benzene					
C_6H_6	D_{6h}	0.0000	5.70390	5.70358	2.85187
$C_6H_7^+$	C_{2v}	0.8729	5.44292	5.31711	2.73189
Naphthalene					
$C_{10}H_8$	D_{2h}	0.0000	3.12608	1.23304	0.88426
1–$C_{10}H_9^+$	C_s	2.0089	3.02746	1.19994	0.86371
2–$C_{10}H_9^+$	C_s	1.9098	3.00985	1.20301	0.86381
Anthracene					
$C_{14}H_{10}$	D_{2h}	0.0004	2.15007	0.45211	0.37356
1–$C_{14}H_{11}^+$	C_s	3.6691	2.09822	0.44507	0.36799
2–$C_{14}H_{11}^+$	C_s	2.9302	2.09404	0.44523	0.36795
9–$C_{14}H_{11}^+$	C_{2v}	18.0182	2.09785	0.44552	0.36829
Phenanthrene					
$C_{14}H_{10}$	C_{2v}	0.0148	1.61849	0.55146	0.41132
1–$C_{14}H_{11}^+$	C_s	3.6954	1.60553	0.53656	0.40312
2–$C_{14}H_{11}^+$	C_s	3.5894	1.56116	0.54831	0.40675
3–$C_{14}H_{11}^+$	C_s	2.9631	1.60847	0.53527	0.40256
4–$C_{14}H_{11}^+$	C_s	3.5209	1.56388	0.54928	0.40749
9–$C_{14}H_{11}^+$	C_s	2.6637	1.56907	0.54629	0.40618
Pyrene					
$C_{16}H_{10}$	D_{2h}	0.0006	1.01227	0.55629	0.35900
1–$C_{16}H_{11}^+$	C_s	0.9957	1.01056	0.54208	0.35356
2–$C_{16}H_{11}^+$	C_{2v}	3.5447	0.98544	0.55087	0.35408
4–$C_{16}H_{11}^+$	C_s	3.3564	0.98697	0.55073	0.35422

A.1.1 Z-Matrices

Table A.2: Benzene (C_6H_6) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.394654				
C	2	1.394666	1	120.001991		
C	3	1.394666	2	119.996074	1	0.000000
C	4	1.394654	3	120.001976	2	0.000000
C	1	1.394667	2	120.001971	3	0.000000
H	1	1.084426	2	119.998426	3	180.000000
H	2	1.084425	1	119.999042	6	180.000000
H	3	1.084418	2	120.001991	1	180.000000
H	4	1.084426	3	119.998977	2	180.000000
H	5	1.084426	4	119.998467	3	180.000000
H	6	1.084418	1	120.002023	2	180.000000

Table A.3: Protonated benzene ($C_6H_7^+$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.368727				
C	2	1.410091	1	119.091029		
C	3	1.410091	2	122.978924	1	0.000000
C	4	1.368727	3	119.091029	2	0.000000
C	1	1.468723	2	120.870021	3	0.000000
H	1	1.085006	2	120.934222	3	180.000000
H	2	1.082815	1	121.103374	6	180.000000
H	3	1.086011	2	118.510538	1	180.000000
H	4	1.082815	3	119.805596	2	180.000000
H	5	1.085006	4	120.934222	3	180.000000
H	6	1.107768	1	109.582298	2	-125.565642
H	6	1.107768	1	109.582298	2	125.565642

Table A.4: Naphthalene ($C_{10}H_8$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.374287				
C	2	1.419949	1	120.859505		
C	3	1.431358	2	118.849618	1	0.000000
C	4	1.419949	3	118.849618	2	0.000000
C	5	1.374287	4	120.859505	3	0.000000
H	3	2.162862	2	96.213583	1	180.000000
H	1	1.084246	2	120.105825	3	180.000000
H	2	1.085201	1	120.354128	6	180.000000
C	3	1.419949	2	122.300764	1	180.000000
C	4	1.419949	3	118.849618	2	180.000000
H	5	1.085201	4	118.786367	3	180.000000
H	6	1.084246	5	120.105825	4	180.000000
C	11	1.374287	4	120.859505	3	0.000000
C	10	1.374287	3	120.859505	2	180.000000
H	11	1.085201	4	118.786367	3	180.000000
H	14	1.084246	11	120.105825	4	180.000000
H	15	1.084246	10	120.105825	3	180.000000

Table A.5: Protonated naphthalene (1–$C_{10}H_9^+$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.474279				
C	2	1.494690	1	116.787133		
C	3	1.431159	2	119.092662	1	0.000000
C	4	1.404226	3	119.070231	2	0.000000
C	1	1.364716	2	122.183322	3	0.000000
H	3	2.150313	2	96.202424	1	180.000000
H	1	1.085343	2	117.497804	3	180.000000
H	2	1.103342	1	108.112234	6	-124.958072
C	3	1.389728	2	122.030912	1	180.000000
C	4	1.422179	3	120.071957	2	180.000000
H	5	1.086579	4	118.059944	3	180.000000
H	6	1.082676	1	121.003188	2	180.000000
C	11	1.375768	4	119.879439	3	0.000000
C	10	1.393535	3	120.053953	2	180.000000
H	11	1.083991	4	119.251121	3	180.000000
H	14	1.082707	11	120.532382	4	180.000000
H	15	1.084106	10	119.200021	3	180.000000
H	2	1.103342	1	108.112269	6	124.958072

Table A.6: Protonated naphthalene (2–$C_{10}H_9^+$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.467137				
C	2	1.375120	1	122.320057		
C	3	1.453306	2	118.929699	1	0.000000
C	4	1.437357	3	119.984361	2	0.000000
C	5	1.351281	4	121.171920	3	0.000000
H	3	2.176465	2	95.396030	1	180.000000
H	1	1.105786	2	108.533743	3	125.434348
H	2	1.086393	1	117.910108	6	180.000000
C	3	1.435418	2	121.261956	1	180.000000
C	4	1.400581	3	118.151009	2	180.000000
H	5	1.083869	4	118.198098	3	180.000000
H	6	1.083716	5	120.954631	4	180.000000
C	11	1.386258	4	120.326676	3	0.000000
C	10	1.367430	3	120.103584	2	180.000000
H	11	1.083408	4	119.625693	3	180.000000
H	14	1.084505	11	119.119868	4	180.000000
H	15	1.082661	10	120.737318	3	180.000000
H	1	1.105787	2	108.533724	3	-125.434348

Table A.7: Anthracene ($C_{14}H_{10}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.367410				
C	2	1.429250	1	120.967249		
C	3	1.443006	2	118.582161	1	0.000000
C	4	1.429172	3	118.590960	2	0.000000
C	5	1.367437	4	120.968419	3	0.000000
C	3	1.398763	2	122.305297	1	180.000000
C	4	1.398832	3	119.107531	2	180.000000
C	8	1.398760	4	121.779438	3	0.000000
C	7	1.398812	3	121.778585	2	180.000000
C	10	1.429139	7	122.297882	3	180.000000
H	11	1.085123	10	118.562270	7	0.000000
C	11	1.367419	10	120.972114	7	180.000000
C	13	1.424931	11	120.437315	10	0.000000
C	14	1.367412	13	120.450640	11	0.000000
H	7	1.085938	3	119.114219	2	0.000000
H	1	1.084221	2	120.150061	3	180.000000
H	2	1.085119	1	120.470108	6	180.000000
H	5	1.085112	4	118.566980	3	180.000000
H	6	1.084213	5	120.156221	4	180.000000
H	8	1.085940	4	119.106858	3	180.000000
H	13	1.084214	11	120.159346	10	180.000000
H	14	1.084218	13	119.397937	11	180.000000
H	15	1.085113	14	120.470891	13	180.000000

Table A.8: Protonated anthracene (1–$C_{14}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.479937				
C	2	1.504130	1	116.134837		
C	3	1.446275	2	118.713966	1	0.000000
C	4	1.397695	3	119.648300	2	0.000000
C	1	1.361794	2	122.814749	3	0.000000
C	3	1.367795	2	122.450139	1	180.000000
C	4	1.411540	3	120.113776	2	180.000000
C	8	1.392425	4	121.097815	3	0.000000
C	7	1.423370	3	121.704778	2	180.000000
C	10	1.410808	7	121.877995	3	180.000000
H	11	1.083777	10	119.373319	7	0.000000
C	11	1.378894	10	120.411623	7	180.000000
C	13	1.418182	11	121.286124	10	0.000000
C	14	1.368859	13	120.060713	11	0.000000
H	7	1.085400	3	120.148250	2	0.000000
H	1	1.085497	2	117.205039	3	180.000000
H	2	1.101786	1	107.799292	6	-124.661354
H	5	1.086207	4	118.348002	3	180.000000
H	6	1.082671	1	120.880352	2	180.000000
H	8	1.085112	4	119.110324	3	180.000000
H	13	1.083867	11	119.567690	10	180.000000
H	14	1.082946	13	119.532146	11	180.000000
H	15	1.084048	14	120.796350	13	180.000000
H	2	1.101786	1	107.799292	6	124.661354

Table A.9: Protonated anthracene (2–$C_{14}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.470852				
C	2	1.373405	1	122.499303		
C	3	1.461045	2	119.639274	1	0.000000
C	4	1.446288	3	118.819264	2	0.000000
C	5	1.345776	4	121.680143	3	0.000000
C	3	1.425471	2	120.538285	1	180.000000
C	4	1.376667	3	118.384766	2	180.000000
C	8	1.417533	4	121.864294	3	0.000000
C	7	1.383412	3	121.227119	2	180.000000
C	10	1.432854	7	121.737433	3	180.000000
H	11	1.084028	10	118.843158	7	0.000000
C	11	1.366052	10	120.256134	7	180.000000
C	13	1.421761	11	119.983428	10	0.000000
C	14	1.377650	13	121.548968	11	0.000000
H	7	1.085283	3	118.800838	2	0.000000
H	1	1.104819	2	108.298282	3	125.207578
H	2	1.086639	1	117.878499	6	180.000000
H	5	1.084132	4	117.885071	3	180.000000
H	6	1.083467	5	120.850716	4	180.000000
H	8	1.084449	4	119.633165	3	180.000000
H	13	1.082870	11	120.529047	10	180.000000
H	14	1.084041	13	118.987048	11	180.000000
H	15	1.083601	14	120.244026	13	180.000000
H	1	1.104819	2	108.298282	3	-125.207578

Table A.10: Protonated anthracene (9–$C_{14}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.394050				
C	2	1.390144	1	120.384604		
C	3	1.426659	2	118.563098	1	0.000000
C	4	1.421758	3	120.213063	2	0.000000
C	5	1.376545	4	120.061211	3	0.000000
C	3	1.500143	2	121.279835	1	180.000000
C	4	1.405851	3	119.297043	2	180.000000
C	8	1.405754	4	124.242978	3	0.000000
C	9	1.426652	8	119.299897	4	0.000000
C	10	1.390096	9	118.567217	8	180.000000
H	11	1.084358	10	120.019811	9	180.000000
C	11	1.394074	10	120.385302	9	0.000000
C	13	1.405176	11	121.406514	10	0.000000
C	14	1.376488	13	119.373490	11	0.000000
H	7	1.098956	3	108.760842	2	56.468647
H	1	1.084108	2	119.220050	3	180.000000
H	2	1.084337	1	119.602837	6	180.000000
H	5	1.084148	4	119.192679	3	180.000000
H	6	1.082638	5	120.608464	4	180.000000
H	8	1.087236	4	117.880126	3	180.000000
H	13	1.084112	11	119.225093	10	180.000000
H	14	1.082633	13	120.022690	11	180.000000
H	15	1.084158	14	120.752494	13	180.000000
H	7	1.098957	3	108.760828	2	-56.468647

Table A.11: Phenanthrene ($C_{14}H_{10}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.378471				
C	2	1.413354	1	121.099608		
C	3	1.424475	2	119.606717	1	0.000000
C	4	1.413263	3	117.893357	2	0.000000
C	5	1.380988	4	121.472309	3	0.000000
C	3	1.434162	2	120.693861	1	180.000000
C	4	1.456723	3	119.103793	2	180.000000
C	8	1.424418	4	119.119975	3	0.000000
C	7	1.357291	3	121.194763	2	180.000000
C	9	1.413327	8	119.617736	4	180.000000
H	11	1.085131	9	118.616545	8	180.000000
C	11	1.378483	9	121.099180	8	0.000000
C	13	1.405687	11	119.543123	9	0.000000
C	14	1.380987	13	120.384090	11	0.000000
H	7	1.085024	3	118.339687	2	0.000000
H	1	1.084076	2	120.342319	3	180.000000
H	2	1.085155	1	120.282458	6	180.000000
H	5	1.082285	4	119.966771	3	180.000000
H	6	1.084211	5	119.725356	4	180.000000
H	10	1.085012	7	120.474034	3	180.000000
H	13	1.084075	11	120.345031	9	180.000000
H	14	1.084214	13	119.895385	11	180.000000
H	15	1.082261	14	118.565856	13	180.000000

Table A.12: Protonated phenanthrene (1–$C_{14}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.475058				
C	2	1.495222	1	117.156059		
C	3	1.429831	2	119.928125	1	0.000000
C	4	1.397021	3	117.632924	2	0.000000
C	1	1.357960	2	121.068904	3	0.000000
C	3	1.396177	2	119.977555	1	180.000000
C	4	1.458290	3	119.954821	2	180.000000
C	8	1.429284	4	117.985263	3	0.000000
C	7	1.381595	3	120.200220	2	180.000000
C	9	1.416074	8	120.091030	4	180.000000
H	11	1.083990	9	118.970714	8	180.000000
C	11	1.376454	9	120.402602	8	0.000000
C	13	1.405888	11	119.610147	9	0.000000
C	14	1.384319	13	121.074294	11	0.000000
H	7	1.083982	3	119.908381	2	0.000000
H	1	1.084605	2	117.932331	3	180.000000
H	2	1.102707	1	108.543914	6	-124.640168
H	5	1.083506	4	118.850365	3	180.000000
H	6	1.082766	1	121.086017	2	180.000000
H	10	1.085082	7	119.266283	3	180.000000
H	13	1.082956	11	120.436629	9	180.000000
H	14	1.083552	13	119.585358	11	180.000000
H	15	1.082101	14	118.206244	13	180.000000
H	2	1.102707	1	108.543914	6	124.640168

Table A.13: Protonated phenanthrene (2–$C_{14}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.468189				
C	2	1.371631	1	123.007747		
C	3	1.453814	2	119.369366	1	0.000000
C	4	1.438253	3	118.739306	2	0.000000
C	5	1.352055	4	121.934392	3	0.000000
C	3	1.443040	2	120.413984	1	180.000000
C	4	1.425593	3	118.728614	2	180.000000
C	8	1.438723	4	119.093138	3	0.000000
C	7	1.351442	3	120.404293	2	180.000000
C	9	1.404716	8	119.290368	4	180.000000
H	11	1.083654	9	119.084496	8	180.000000
C	11	1.382611	9	120.739391	8	0.000000
C	13	1.408608	11	120.515032	9	0.000000
C	14	1.374795	13	120.140008	11	0.000000
H	7	1.083471	3	118.420100	2	0.000000
H	1	1.104947	2	109.117261	3	-124.872435
H	2	1.085882	1	117.712241	6	180.000000
H	5	1.080344	4	119.305093	3	180.000000
H	6	1.083960	5	120.448393	4	180.000000
H	10	1.083716	7	120.591244	3	180.000000
H	13	1.083774	11	119.841247	9	180.000000
H	14	1.082905	13	119.841770	11	180.000000
H	15	1.080833	14	118.558351	13	180.000000
H	1	1.104947	2	109.117261	3	124.872435

Table A.14: Protonated phenanthrene (3–$C_{14}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.349837				
C	2	1.437289	1	121.504799		
C	3	1.455246	2	120.547628	1	0.000000
C	4	1.368844	3	117.608897	2	0.000000
C	5	1.472927	4	123.494302	3	0.000000
C	3	1.402309	2	119.988905	1	180.000000
C	4	1.469299	3	119.529611	2	180.000000
C	8	1.426660	4	118.228638	3	0.000000
C	7	1.378836	3	120.535509	2	180.000000
C	9	1.413852	8	120.233021	4	180.000000
H	11	1.083994	9	119.042150	8	180.000000
C	11	1.378811	9	120.359355	8	0.000000
C	13	1.403063	11	119.474904	9	0.000000
C	14	1.388080	13	121.075577	11	0.000000
H	7	1.083173	3	119.380933	2	0.000000
H	1	1.083877	2	121.020169	3	180.000000
H	2	1.083861	1	120.641768	6	180.000000
H	5	1.083615	4	120.416548	3	180.000000
H	6	1.104827	5	108.822075	4	124.978246
H	10	1.085435	7	119.108259	3	180.000000
H	13	1.082886	11	120.465931	9	180.000000
H	14	1.083608	13	119.631552	11	180.000000
H	15	1.082239	14	118.231429	13	180.000000
H	6	1.104827	5	108.822075	4	-124.978246

Table A.15: Protonated phenanthrene (4–$C_{14}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.414522				
C	2	1.400366	1	124.034567		
C	3	1.425577	2	119.275536	1	0.000000
C	4	1.496064	3	118.412385	2	0.000000
C	1	1.359082	2	118.975596	3	0.000000
C	3	1.434704	2	120.212430	1	180.000000
C	4	1.415902	3	119.543093	2	180.000000
C	8	1.438788	4	118.792358	3	0.000000
C	7	1.357530	3	120.045392	2	180.000000
C	9	1.409865	8	119.139024	4	180.000000
H	11	1.083749	9	119.007502	8	180.000000
C	11	1.378720	9	120.716313	8	0.000000
C	13	1.413083	11	120.540746	9	0.000000
C	14	1.372471	13	120.247478	11	0.000000
H	7	1.083473	3	118.883919	2	0.000000
H	1	1.082629	2	119.722248	3	180.000000
H	2	1.086326	1	118.232708	6	180.000000
H	5	1.101896	4	110.145502	3	123.648080
H	6	1.084860	1	120.841278	2	180.000000
H	10	1.083752	7	120.510711	3	180.000000
H	13	1.083638	11	119.922542	9	180.000000
H	14	1.083081	13	119.677417	11	180.000000
H	15	1.082535	14	118.943540	13	180.000000
H	5	1.101896	4	110.145502	3	-123.648080

Table A.16: Protonated phenanthrene (9–$C_{14}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.387024				
C	2	1.395878	1	120.545143		
C	3	1.418994	2	120.003489	1	0.000000
C	4	1.414289	3	118.352881	2	0.000000
C	5	1.380516	4	120.916427	3	0.000000
C	3	1.495940	2	119.564894	1	180.000000
C	4	1.453414	3	119.668931	2	180.000000
C	8	1.454793	4	120.291054	3	0.000000
C	9	1.372561	8	119.859447	4	0.000000
C	9	1.438144	8	120.542370	4	180.000000
H	11	1.084022	9	118.423935	8	180.000000
C	11	1.364187	9	120.472239	8	0.000000
C	13	1.416186	11	118.825375	9	0.000000
C	14	1.384560	13	122.337737	11	0.000000
H	7	1.103694	3	110.793487	2	56.406843
H	1	1.083425	2	119.929275	3	180.000000
H	2	1.084633	1	119.854537	6	180.000000
H	5	1.081033	4	120.497171	3	180.000000
H	6	1.083025	5	119.875098	4	180.000000
H	10	1.086570	9	119.285883	8	180.000000
H	13	1.082451	11	121.136248	9	180.000000
H	14	1.084548	13	118.908638	11	180.000000
H	15	1.080279	14	118.314757	13	180.000000
H	7	1.103694	3	110.793487	2	-56.406843

Table A.17: Pyrene ($C_{16}H_{10}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.391972				
C	2	1.402633	1	120.739411		
C	3	1.426444	2	119.022027	1	0.000000
C	4	1.426438	3	119.872623	2	0.000000
C	1	1.391990	2	120.604218	3	0.000000
C	3	1.436672	2	122.403096	1	180.000000
C	4	1.425474	3	120.063823	2	180.000000
C	8	1.426442	4	120.061143	3	0.000000
C	7	1.359189	3	121.363114	2	180.000000
C	9	1.402616	8	119.026347	4	180.000000
H	11	1.084904	9	119.192936	8	180.000000
C	11	1.391981	9	120.732880	8	0.000000
C	13	1.391970	11	120.604589	9	0.000000
C	14	1.402620	13	120.740171	11	0.000000
C	15	1.436675	14	122.405817	13	180.000000
C	16	1.359181	15	121.363180	14	180.000000
H	17	1.085067	16	120.309077	15	180.000000
H	16	1.085075	15	118.340550	14	0.000000
H	7	1.085085	3	118.339160	2	0.000000
H	1	1.084285	2	119.695651	3	180.000000
H	2	1.084924	1	120.065041	6	180.000000
H	6	1.084910	1	120.073577	2	180.000000
H	10	1.085068	7	120.310576	3	180.000000
H	13	1.084278	11	119.697237	9	180.000000
H	14	1.084911	13	120.063643	11	180.000000

Table A.18: Protonated pyrene (1–$C_{16}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.484870				
C	2	1.495981	1	116.069518		
C	3	1.414417	2	119.884321	1	0.000000
C	4	1.433524	3	120.512709	2	0.000000
C	1	1.348258	2	122.403726	3	0.000000
C	3	1.405577	2	120.558883	1	180.000000
C	4	1.419838	3	119.807855	2	180.000000
C	8	1.419956	4	120.025833	3	0.000000
C	7	1.379499	3	120.814162	2	180.000000
C	9	1.412935	8	119.069663	4	180.000000
H	11	1.084554	9	119.124196	8	180.000000
C	11	1.389014	9	120.955320	8	0.000000
C	13	1.393620	11	120.082406	9	0.000000
C	14	1.407498	13	120.899101	11	0.000000
C	15	1.421901	14	122.171238	13	180.000000
C	16	1.377167	15	121.470626	14	180.000000
H	17	1.083416	16	120.008081	15	180.000000
H	16	1.084811	15	118.824382	14	0.000000
H	7	1.084157	3	119.425269	2	0.000000
H	1	1.084400	2	117.236511	3	180.000000
H	2	1.101319	1	109.050961	6	-123.962510
H	6	1.083807	1	120.603305	2	180.000000
H	10	1.084577	7	119.796588	3	180.000000
H	13	1.082770	11	119.992475	9	180.000000
H	14	1.084523	13	119.870945	11	180.000000
H	2	1.101319	1	109.050961	6	123.962510

Table A.19: Protonated pyrene (2–$C_{16}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.470333				
C	2	1.370219	1	122.014273		
C	3	1.449838	2	119.169522	1	0.000000
C	4	1.449797	3	120.877687	2	0.000000
C	5	1.370208	4	119.187924	3	0.000000
C	3	1.444090	2	121.766917	1	180.000000
C	4	1.404630	3	119.557230	2	180.000000
C	8	1.436828	4	120.047808	3	0.000000
C	7	1.353812	3	120.807526	2	180.000000
C	9	1.396269	8	118.875480	4	180.000000
H	11	1.083632	9	119.501513	8	180.000000
C	11	1.394449	9	120.551358	8	0.000000
C	13	1.394442	11	121.238994	9	0.000000
C	14	1.396281	13	120.563951	11	0.000000
C	15	1.437984	14	121.863348	13	180.000000
C	16	1.353803	15	121.250554	14	180.000000
H	17	1.083581	16	120.875361	15	180.000000
H	16	1.083857	15	118.337050	14	0.000000
H	7	1.083598	3	118.324929	2	0.000000
H	1	1.105615	2	109.416144	3	124.925482
H	2	1.084883	1	117.889640	6	180.000000
H	6	1.084883	5	120.094581	4	180.000000
H	10	1.083847	7	120.424528	3	180.000000
H	13	1.083778	11	119.379209	9	180.000000
H	14	1.083611	13	119.928590	11	180.000000
H	1	1.105614	2	109.416162	3	-124.925482

Table A.20: Protonated pyrene (4–$C_{16}H_{11}^{+}$) Z-Matrix.

Atom 1	Atom 2	Bond, Å	Atom 3	Angle, °	Atom 4	Dihedral Angle, °
C						
C	1	1.403163				
C	2	1.383145	1	120.462718		
C	3	1.424514	2	119.424834	1	0.000000
C	4	1.430585	3	119.996056	2	0.000000
C	1	1.385091	2	120.932708	3	0.000000
C	3	1.500997	2	121.360907	1	180.000000
C	4	1.418265	3	120.735705	2	180.000000
C	8	1.452571	4	121.170269	3	0.000000
C	9	1.372498	8	119.175629	4	0.000000
C	9	1.430775	8	119.986412	4	180.000000
H	11	1.084010	9	118.930752	8	180.000000
C	11	1.373249	9	120.150324	8	0.000000
C	13	1.406652	11	119.749260	9	0.000000
C	14	1.402902	13	122.902081	11	0.000000
C	15	1.435077	14	121.963798	13	180.000000
C	16	1.358524	15	120.464711	14	180.000000
H	17	1.083899	16	120.295556	15	180.000000
H	16	1.083575	15	118.776176	14	0.000000
H	7	1.103321	3	110.887915	2	56.559860
H	1	1.083491	2	119.316120	3	180.000000
H	2	1.084600	1	119.468008	6	180.000000
H	6	1.083747	1	120.135217	2	180.000000
H	10	1.086607	9	119.435423	8	180.000000
H	13	1.082628	11	120.614238	9	180.000000
H	14	1.085420	13	118.748334	11	180.000000
H	7	1.103321	3	110.887948	2	-56.559860

A.2 Vibrational Frequencies

The scaling factors are determined to be 0.9619 for C–H stretching vibrations (frequencies above 2000 cm^{-1}) and 0.9815 for lower frequency vibrations by comparing gas phase experimental and B3LYP 6–311++G(d,p) calculated frequencies for neutral benzene and anthracene (Tables A.21, A.22).

Table A.21: Scaling of the benzene molecule vibrational frequencies.

Mode	Symmetry	Experimental, cm^{-1}	Calculated, cm^{-1}
ν_{16}	e_{2u}	398.131	409.2508
ν_6	e_{2g}	608.13	622.2075
ν_{11}	a_{2u}	673.9747	686.4609
ν_4	b_{2g}	702.24	719.2481
ν_{10}	e_{1g}	847.1062	863.6909
ν_{17}	e_{2u}	967.98	980.5364
ν_5	b_{2g}	992.93	1010.6745
ν_1	a_{1g}	993.071	1011.0642
ν_{12}	b_{1u}	1013.74	1022.4331
ν_{18}	e_{1u}	1038.267	1058.9918
ν_{15}	b_{2u}	1147.6751	1174.6646
ν_9	e_{2g}	1177.776	1197.1716
ν_{14}	b_{2u}	1309.4	1335.6178
ν_3	a_{2g}	1350	1380.8794
ν_{19}	e_{1u}	1483.9854	1510.0520
ν_8	e_{2g}	1609.518	1633.1875
ν_{20}	e_{1u}	3047.908	3154.9144
ν_{13}	b_{1u}	3057	3181.3283
ν_7	e_{2g}	3057.04	3181.6125
ν_2	a_{1g}	3073.942	3191.8678

Experimental data taken from [111].

Table A.22: Scaling of the anthracene molecule vibrational frequencies.

Mode	Symmetry	Experimental, cm^{-1}	Calculated, cm^{-1}
ν_{64}	b_{3u}	465.2	476.961
ν_{49}	b_{2u}	601.4	617.0831
ν_{63}	b_{3u}	725.3	739.3821
ν_{48}	b_{2u}	794.8	820.8065
ν_{62}	b_{3u}	876.7	864.1561
ν_{30}	b_{1u}	907.8	911.1968
ν_{61}	b_{3u}	954.2	972.5292
ν_{47}	b_{2u}	996	1026.1756
ν_{46}	b_{2u}	1128	1159.9346
ν_{29}	b_{1u}	1150.4	1172.6212
ν_{45}	b_{2u}	1165.5	1189.8674
ν_{28}	b_{1u}	1271.3	1290.8509
ν_{27}	b_{1u}	1316.5	1338.2374
ν_{44}	b_{2u}	1341.7	1377.5670
ν_{43}	b_{2u}	1396.8	1416.7486
ν_{26}	b_{1u}	1450	1480.8151
ν_{42}	b_{2u}	1476	1486.1868
ν_{41}	b_{2u}	1539.6	1578.3891
ν_{25}	b_{1u}	1626	1667.6092
ν_{24}	b_{1u}	3028	3157.7870
ν_{23}	b_{1u}	3052	3165.7045
ν_{22}	b_{1u}	3061	3189.7013
ν_{39}	b_{2u}	3067	3190.0427

Experimental data taken from [112].

Table A.23: Benzene and protonated benzene: scaled vibrational frequencies and IR intensities.

C_6H_6		$C_6H_7^+$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
401.6797	0.0000	207.0374	12.1219
402.4736	0.0013	323.8184	0.0000
610.6967	0.0000	406.2831	1.5535
610.7172	0.0000	579.2896	5.4868
673.7614	122.0287	584.4683	0.0265
705.9420	0.0000	647.6300	57.2190
845.1487	0.0000	791.8260	0.0000
847.7126	0.0000	832.6574	16.0955
961.0158	0.0000	882.0701	13.8096
962.3965	0.0041	971.7421	16.5344
991.9770	0.0004	982.5926	0.4828
992.3595	0.0000	992.5469	0.0000
1003.5181	0.0000	995.5653	0.2352
1039.0731	6.3651	1027.9043	0.0152
1039.4005	6.3744	1048.1727	2.5553
1152.9333	0.0000	1129.6961	0.3245
1175.0239	0.0001	1131.1016	0.0000
1175.2203	0.0001	1183.2846	19.5856
1310.9089	0.0002	1190.0769	23.3059
1355.3331	0.0000	1257.4158	113.9668
1482.1160	7.1996	1336.8588	14.3341
1482.3507	7.1487	1393.8416	6.8657
1602.9325	0.0002	1448.8265	175.8423
1602.9735	0.0005	1457.2509	26.4624
3034.7122	0.0463	1541.7174	2.1079
3044.9359	0.0051	1608.1701	74.4622
3045.1460	0.0073	2833.8540	24.0384
3060.1197	36.9916	2839.2640	62.5214
3060.3931	37.1709	3059.5157	0.1546
3070.2576	0.0343	3067.5970	2.5411
		3068.8847	5.5714
		3086.0872	6.7612
		3088.2879	1.7803

Table A.24: Naphthalene and protonated naphthalene: scaled vibrational frequencies and IR intensities.

$C_{10}H_8$		1–$C_{10}H_9^+$		2–$C_{10}H_9^+$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
169.4145	2.8104	115.0238	0.4088	134.2035	5.7151
181.4778	0.0000	169.8269	1.5821	166.2855	0.7202
358.3695	1.8304	242.3699	11.6633	260.9555	1.8114
388.2838	0.0003	350.0190	0.9599	355.7677	2.4700
469.5430	0.0001	399.2639	0.0106	371.0291	1.1248
479.2424	24.1588	427.0042	13.0135	439.1710	3.9478
509.1167	0.0051	486.2705	0.1248	481.1385	21.2405
510.1492	0.0007	492.1717	0.4450	493.5473	4.0892
619.6614	0.0000	495.1976	16.5382	500.4934	0.6442
623.4749	3.2877	599.8496	2.0755	607.4839	1.3968
715.1633	0.0022	662.0221	0.0075	660.0737	2.2940
758.1406	0.0001	730.8713	28.0030	733.5593	4.2081
767.6320	0.0001	735.0980	4.4553	767.5992	34.0881
782.9871	122.5348	776.5801	61.6570	770.8273	4.1169
793.5282	0.3215	783.9355	0.2020	789.7835	12.6599
832.9490	0.0000	849.4712	7.4023	799.7599	20.4370
878.2911	0.0049	909.1840	0.9372	894.4784	9.5482
932.8070	0.0038	912.8521	1.3963	911.6343	25.0571
943.7688	0.0013	953.7979	12.8250	920.3033	0.1440
962.1320	3.5108	979.7361	0.0494	941.7730	20.2299
971.4251	0.0004	1002.8414	5.0216	992.8974	2.6962
979.6829	0.0053	1016.2134	0.3066	1005.8365	1.0672
1015.1555	11.0855	1023.1885	0.0330	1018.1834	2.4280
1025.6051	0.0006	1028.7145	2.5254	1018.9470	0.9761
1129.0893	6.7544	1091.1212	8.4447	1032.6991	14.6466
1147.6323	0.7540	1133.5737	6.1211	1140.4693	5.1158
1149.4143	0.0008	1159.2722	0.8416	1142.4153	0.0952
1163.2484	0.0001	1169.3644	32.8669	1161.8284	20.6217
1208.3148	0.7037	1177.0096	9.5891	1180.2637	18.5647
1245.7875	0.0106	1194.0854	9.3836	1212.1639	5.6154
1262.7006	7.3088	1244.4128	23.9391	1246.2730	6.5326
1364.6736	0.9743	1272.7489	23.7537	1282.3671	68.8119
1371.7347	0.0051	1320.2167	111.1756	1300.1806	109.8671
1390.5500	4.2261	1348.3846	43.0687	1353.4166	34.2552
1461.1824	0.0000	1367.6470	57.7761	1392.1690	98.5422
1461.4239	0.0081	1419.0089	37.1812	1403.9551	8.0366
1517.4368	7.9027	1442.8935	1.8160	1438.3395	1.1747
1581.8685	0.0049	1458.4152	130.5548	1472.0554	126.0498

— continued on the next page —

$C_{10}H_8$		1–$C_{10}H_9^+$		2–$C_{10}H_9^+$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
1606.6887	2.6276	1512.8755	237.3922	1504.3483	30.6534
1636.8155	0.0100	1553.5685	14.5643	1544.3416	4.1690
3036.0010	0.0268	1577.4620	64.4722	1606.5400	29.5076
3037.8480	7.0148	1622.2347	89.2320	1629.3655	241.6182
3040.1955	0.3076	2863.1685	26.2422	2846.5401	10.2962
3042.1915	0.0292	2868.2406	6.8228	2848.6604	53.4301
3053.1975	0.0257	3051.0111	0.3846	3052.8251	0.7085
3054.3243	58.9447	3059.7462	0.1149	3063.5692	0.1470
3065.3029	42.4607	3062.4287	1.4124	3066.1493	1.1471
3066.5056	0.0044	3066.9603	0.0700	3068.5941	0.1373
		3072.3632	0.1745	3077.0909	0.2662
		3086.2220	2.8842	3081.3179	0.5111
		3086.8465	0.1351	3088.0533	0.4251

Table A.25: Anthracene and protonated anthracene: scaled vibrational frequencies and IR intensities.

$C_{14}H_{10}$		1–$C_{14}H_{11}^{+}$		2–$C_{14}H_{11}^{+}$		9–$C_{14}H_{11}^{+}$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
90.6821	1.3556	70.4991	0.2308	81.0081	3.5138	52.4500	0.0381
118.9177	0.0007	102.3111	2.5679	107.3786	0.1345	103.8544	0.0005
231.6094	1.4742	165.4247	3.6131	187.9503	0.2570	176.0060	6.0420
233.5255	0.0002	228.8075	1.2144	230.6508	2.8025	221.8039	0.0036
261.1006	0.0000	251.6879	0.0927	242.4070	0.3530	230.7709	0.2675
382.1054	0.0382	275.5286	2.6684	296.2451	1.6753	314.6469	9.1203
388.3877	0.0003	380.2106	0.2830	382.0541	0.2912	374.6915	0.2133
390.2435	0.0001	388.4608	7.3321	383.8827	1.7159	377.8337	2.9451
468.1372	25.9027	403.2874	5.4686	388.9133	1.4807	407.4422	8.9731
476.2223	0.5999	425.4458	7.6603	436.2109	13.3598	439.2496	0.1560
501.7094	0.0089	474.1534	11.6914	461.6315	14.5126	484.6544	0.0271
525.3630	0.0002	503.7022	0.0121	504.2975	0.1064	512.6018	0.8791
580.9104	0.0002	513.3926	28.7446	516.0975	4.5531	524.3009	32.7964
605.6671	8.4296	576.6563	1.0079	592.2181	4.6479	595.7877	2.9941
629.9297	0.0001	618.1799	2.5412	618.1121	0.3902	607.6497	17.4426
649.0252	0.5412	642.7178	0.2692	639.5392	7.7584	658.2665	19.3567
725.7035	90.3199	644.6349	5.7943	640.5587	18.3765	661.9430	0.1347
745.6664	0.0142	717.5431	25.3305	730.8010	3.4168	723.8486	0.3923
749.4274	0.0005	735.3701	7.6471	748.2718	6.5237	731.5772	0.0516
755.8735	0.0009	750.8957	13.2480	756.6004	44.7187	768.4203	93.4549
770.9059	0.0006	759.2296	29.6253	769.5847	0.0027	778.3522	0.4468
805.6216	0.1077	792.5464	3.5126	793.7256	3.8758	800.0035	5.4294
824.4049	0.0002	846.0901	1.4324	794.6408	3.7219	845.0529	0.6468
848.1692	0.0018	875.3600	3.4960	860.9030	0.1399	881.7706	0.0239
881.2327	63.5914	890.7972	1.6421	884.0419	25.6619	884.7373	0.1553
894.3397	0.0219	902.0789	0.8655	897.7396	9.7448	899.2555	0.1569
901.7842	1.9277	907.9225	40.0565	898.3674	10.7665	922.8449	12.8563
912.1253	0.0001	925.3737	0.3822	908.2952	15.8457	967.2480	0.7584
954.5374	0.0337	947.9224	24.6308	914.5663	22.3771	979.1555	0.0272
959.1014	5.6996	979.9649	1.2422	953.5934	30.7861	997.8273	10.6462
974.8280	0.0001	996.0797	4.1938	982.9509	4.0744	1013.2228	0.1865
976.7700	0.0070	1006.9014	0.1624	995.2328	0.5992	1013.5434	0.6463
1007.1914	8.6096	1013.1386	0.8739	1008.2669	0.3509	1032.8158	1.7735
1011.6642	0.0010	1018.7456	1.1545	1014.8512	4.8722	1033.3012	2.0425
1105.1936	0.0002	1063.8511	14.4432	1022.7683	10.2104	1105.2782	0.0017
1138.4758	1.8229	1133.4439	3.0242	1127.2229	4.0393	1138.4095	8.9628
1150.9277	7.9588	1159.3612	4.5993	1152.4063	0.0641	1164.8411	84.5565
1166.8837	1.7153	1171.8186	2.7104	1160.1667	1.5577	1176.2010	7.9884

— continued on the next page —

$C_{14}H_{10}$		1–$C_{14}H_{11}^{+}$		2–$C_{14}H_{11}^{+}$		9–$C_{14}H_{11}^{+}$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
1167.8549	0.0002	1175.8036	0.6944	1173.9367	39.6052	1184.2331	18.9987
1188.4965	0.0001	1179.1241	22.3166	1186.1471	7.9572	1191.4008	0.1469
1265.5488	0.0279	1194.2698	90.3276	1198.2107	65.5581	1193.5940	0.8249
1266.9702	5.4406	1242.5586	56.7125	1242.0685	19.2167	1207.8722	58.1882
1270.4910	0.0009	1272.3748	11.8002	1277.4508	12.1036	1254.2262	0.6617
1313.4800	4.8217	1295.1931	4.4584	1292.8219	6.1357	1287.8226	0.6233
1352.0820	3.8821	1296.2105	3.5787	1308.6672	69.3597	1294.9944	25.4321
1387.4732	0.0004	1346.1972	129.9891	1329.1923	121.4536	1338.0471	191.5836
1390.5388	1.7148	1356.3985	35.2136	1353.7433	23.5427	1368.0035	22.5466
1402.4687	0.0010	1380.9868	139.6458	1392.6826	192.7469	1372.2968	36.3942
1453.4200	1.0785	1397.3178	15.2257	1401.5619	0.9555	1376.1459	38.1824
1458.6923	1.4026	1423.8461	12.4377	1409.8216	43.3518	1429.4762	43.0552
1488.2130	0.0002	1442.5450	11.4800	1437.0955	19.6411	1460.4157	27.6703
1549.1889	6.8078	1455.4923	315.2885	1467.9159	72.9368	1461.4459	172.5045
1564.2774	0.0021	1492.5786	1.2990	1487.6098	24.0765	1498.1171	17.7025
1592.2151	0.0011	1516.6483	432.8844	1533.6015	25.3365	1526.9723	333.9746
1636.7584	2.2566	1545.5191	99.6921	1552.3349	53.5095	1562.7378	12.4701
1638.1398	1.9693	1579.8629	99.3710	1596.8177	62.0961	1567.1575	37.8833
3035.5251	6.2658	1616.2389	13.6839	1621.4964	468.4955	1606.6280	465.5735
3037.4753	0.0070	1630.0135	239.0029	1641.9146	147.5208	1621.2268	22.8080
3039.0372	0.0228	2869.2120	13.6976	2851.7368	4.2058	2889.8988	5.3718
3040.1899	14.3112	2876.6619	2.2066	2853.1486	45.1824	2909.4276	2.3259
3043.4351	0.0195	3047.7182	1.4657	3049.2952	0.0527	3043.5688	0.2756
3045.0912	0.0036	3052.0445	1.4101	3057.8757	0.0645	3059.6297	0.4408
3056.5217	0.8022	3056.7136	0.2753	3059.8703	0.0859	3060.0267	0.3601
3056.8791	58.1490	3058.7498	0.3353	3062.2724	1.9275	3065.2655	0.5332
3068.1737	51.2160	3059.7848	0.2688	3063.4827	0.7386	3066.3259	0.4517
3068.5021	0.0259	3063.2490	0.2375	3066.8913	0.0191	3074.0746	0.3602
		3073.2910	2.0092	3076.7803	1.1404	3075.0717	0.2486
		3083.8449	1.3084	3079.1873	0.5177	3088.7548	0.2418
		3084.6358	0.2419	3087.1170	0.4328	3089.0265	0.1823

Table A.26: Phenanthrene and protonated phenanthrene: scaled vibrational frequencies and IR intensities.

$C_{14}H_{10}$		1–$C_{14}H_{11}^{+}$		2–$C_{14}H_{11}^{+}$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
94.1967	0.0033	66.8310	0.4078	77.8542	3.0516
99.2912	0.9067	98.6964	2.0581	89.8509	0.7524
223.1468	4.1778	157.7058	0.4744	186.4559	0.2077
238.5203	0.0003	213.0964	4.1247	218.4536	4.4060
242.9889	0.4580	235.8947	1.5378	246.0627	1.1656
394.2872	0.0018	279.8484	10.7683	295.4089	2.3895
403.6186	0.5392	384.2937	0.2044	366.0720	1.1431
428.9911	8.0648	394.0992	3.8387	402.5492	4.2092
437.9531	1.9032	428.4114	3.0333	416.8031	12.4927
496.5687	1.0243	434.9084	3.8347	433.9158	0.6284
497.6790	5.6189	486.5031	1.0467	481.1466	1.6061
533.9579	0.0116	487.3224	1.9428	486.4599	0.5875
546.5301	0.2733	499.0529	4.5097	535.6937	2.7991
587.0511	0.0002	542.7338	17.2577	536.0105	0.3361
631.9821	5.3449	602.1786	0.6744	599.7317	8.3489
709.4696	0.0716	627.1811	9.3719	633.1490	4.1356
710.2180	2.1936	685.6043	1.7118	689.6513	8.2423
713.3346	2.0777	705.8554	0.0620	700.6441	1.2351
733.4026	89.9634	717.6209	22.3442	724.6895	9.5247
753.8650	0.0422	738.6946	3.0845	751.1034	52.1083
784.0600	0.0082	759.9602	47.8919	791.2935	12.8500
812.8769	60.4701	821.7176	4.6482	795.6133	18.9122
827.3557	0.0612	829.0989	39.3086	812.6907	7.2791
860.4947	0.1014	867.3581	2.1852	818.3090	9.8546
865.2298	10.6824	871.1894	4.2033	852.1372	1.9636
871.2405	2.0618	888.7542	3.2588	877.6763	10.0076
942.2343	0.0220	941.6789	15.1545	922.0052	27.8659
950.5919	3.0042	967.1783	0.1676	933.6127	20.6802
966.1769	0.0196	984.7964	2.1972	972.2705	1.6940
976.5710	0.0134	994.5599	5.8541	984.7952	0.4064
977.9282	0.0138	994.6051	0.5520	988.7993	7.9596
997.7435	2.5449	1004.5687	0.4170	999.5386	0.9301
1040.5756	7.2705	1008.5462	0.5162	1008.7296	0.4787
1041.1145	1.6881	1040.8573	1.5861	1026.0300	14.9448
1093.7494	2.2897	1063.0781	1.8768	1041.6504	5.7341
1143.4660	2.2286	1120.9165	4.4267	1110.0456	11.0717
1151.6246	0.0295	1158.1179	24.2629	1143.4355	0.0053

— continued on the next page —

$C_{14}H_{10}$		$1–C_{14}H_{11}^{+}$		$2–C_{14}H_{11}^{+}$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
1163.9952	0.1991	1161.9644	1.1146	1158.8326	6.4067
1167.0895	0.4953	1169.4978	1.1270	1167.1523	23.8018
1201.5408	1.8410	1180.2455	4.3025	1179.6339	12.7273
1218.6117	0.5131	1203.2989	8.9504	1206.5033	1.3420
1242.3857	10.2436	1233.7048	20.7813	1220.6362	20.7024
1279.9567	0.0045	1250.8571	79.8095	1257.3717	26.2570
1299.8082	2.5612	1282.9118	11.3405	1282.2228	11.3503
1342.7728	0.1215	1302.4900	5.8559	1308.3848	127.4549
1349.2786	0.7828	1326.1043	217.1552	1330.7162	90.1603
1417.3657	0.4096	1346.5572	312.6771	1355.1865	14.7231
1423.0397	1.2301	1359.6256	6.8524	1369.6733	112.5547
1442.6138	3.5413	1390.9642	200.7722	1406.3337	41.5622
1461.7055	10.5507	1423.9572	14.8492	1420.4206	4.1091
1505.2961	5.9138	1449.6666	1.1361	1440.4158	10.4778
1531.6928	1.8858	1456.8742	31.9259	1467.0203	108.8570
1576.6635	0.0790	1507.4256	51.1561	1477.4480	107.8114
1610.3195	1.8366	1530.5348	204.1641	1532.6130	10.1197
1622.4005	0.0971	1546.2847	27.3673	1551.0334	23.5177
1627.2943	0.1731	1574.5060	135.7502	1599.7978	224.8536
3036.2905	0.1077	1609.9637	1.0527	1618.4424	94.9944
3039.0293	3.3461	1616.2117	49.5613	1627.6335	108.0935
3040.0193	1.7506	2867.0308	30.7786	2852.5979	7.0315
3048.6770	0.0697	2874.0203	5.3546	2853.1429	49.0977
3049.8867	13.4446	3055.1147	0.0577	3054.3693	0.2865
3055.5026	33.1547	3061.9167	0.7137	3061.8476	0.2341
3061.6454	37.5327	3064.4682	2.2472	3063.9347	0.2851
3064.6472	0.8129	3066.6230	0.4275	3069.8651	0.9510
3071.4832	14.1301	3068.6839	0.3912	3072.5380	0.2769
3083.3012	19.3960	3073.4131	0.9389	3077.5952	0.5478
		3081.1743	1.9590	3080.6354	0.6591
		3085.4837	0.4133	3091.2866	0.4981
		3088.5864	0.6645	3108.2634	0.5539

— continued on the next page —

3–$C_{14}H_{11}^+$		4–$C_{14}H_{11}^+$		9–$C_{14}H_{11}^+$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
67.9947	0.7722	82.5920	0.0418	68.4213	0.3489
98.5772	1.0773	102.3673	0.9208	89.4593	0.1729
185.4722	8.4139	170.6658	6.4054	174.6351	8.9753
226.1071	0.0598	215.7809	2.0827	218.9379	3.2365
237.5229	0.3890	229.2664	1.0655	242.6537	1.8744
282.0925	0.0002	273.5060	7.1988	265.0713	0.8130
394.5469	4.3574	396.4172	3.8341	393.6559	6.6158
396.6824	2.8436	401.1307	10.8642	412.8374	7.7328
407.0016	3.7319	431.5685	0.7363	428.1788	0.0147
433.7555	0.9466	434.8214	0.1069	429.8925	0.7838
490.8570	4.4328	487.4470	1.7129	465.2069	0.8464
491.7979	6.8949	487.8313	1.5712	488.8239	2.4661
511.4307	3.3446	518.8698	3.2033	517.9534	3.3654
538.4446	5.7051	532.6294	5.4806	537.3154	0.2199
601.7457	4.1965	597.4887	0.7408	612.2059	2.6280
640.5680	23.0381	628.3979	0.7553	670.3057	1.5372
695.1468	0.3791	684.2585	17.2016	689.4227	4.3614
706.4309	3.5485	706.1690	3.2121	694.8828	11.7230
726.6655	0.7419	712.6530	47.0578	716.3663	23.0627
759.7846	45.3178	745.0416	21.3160	759.9382	11.6892
778.3826	0.0059	767.9317	8.7694	772.8323	82.6562
803.6541	0.0376	809.7642	29.2338	800.2659	6.2465
815.6690	1.4822	822.1024	0.7905	806.1470	2.5926
858.3347	25.2080	845.0012	0.1111	851.0204	0.3472
861.5825	1.0793	874.0899	19.6783	868.8398	5.9128
880.2520	20.1095	884.7413	12.0839	878.5173	0.0033
913.7954	31.5725	951.8956	13.2277	951.8135	1.9611
937.7633	22.0480	971.6525	0.1309	970.4054	0.0149
969.1507	2.3836	981.7815	1.5604	988.5470	0.7264
988.7445	3.9067	992.2869	5.3997	993.5013	4.1198
997.5475	0.0105	993.6547	1.4459	1005.9900	0.3402
1004.8626	0.1122	1004.2919	0.3685	1014.9348	0.4616
1006.0397	0.0095	1014.7714	0.0003	1025.2669	13.7296
1033.8640	4.3175	1032.3690	1.3793	1035.3078	14.4911
1045.6648	0.2482	1060.9424	6.8796	1047.9238	4.0291
1114.7411	2.0098	1121.6351	11.1129	1106.5516	1.0762
1149.2280	0.0014	1159.6033	7.4670	1149.3712	20.2114
1157.7243	20.0859	1162.1242	0.0922	1159.7551	1.2183
1166.3319	40.8071	1174.0277	5.3250	1176.8140	22.0567

— continued on the next page —

3–$C_{14}H_{11}^+$		4–$C_{14}H_{11}^+$		9–$C_{14}H_{11}^+$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
1178.6581	5.0714	1178.0795	13.8555	1181.3182	43.9946
1221.7659	96.2017	1186.1501	9.4292	1187.1326	0.2769
1238.0347	22.3805	1220.7042	4.8264	1219.4820	5.5773
1259.8949	41.4472	1241.4692	19.3288	1256.6658	69.6261
1286.2212	8.5068	1274.6392	5.5811	1283.6424	1.8351
1296.0576	4.4107	1326.9125	6.5054	1308.1174	69.9866
1319.6674	155.1110	1356.5073	50.8937	1325.4735	111.5601
1344.9203	94.3402	1391.4536	44.1385	1332.7650	89.0793
1362.0603	33.0623	1391.4536	209.8578	1363.6392	13.3516
1404.3831	163.6224	1399.9653	118.6090	1389.2988	73.3719
1428.8197	0.6698	1415.0769	23.6905	1419.9175	16.1036
1441.5497	15.2252	1435.9622	56.1361	1453.8930	197.3566
1465.3018	82.1274	1455.9324	58.6101	1464.9969	23.4654
1513.9608	232.0720	1480.6514	227.3070	1480.3588	90.3283
1524.3456	12.7466	1520.5825	82.3635	1532.0905	39.3648
1552.5484	45.0630	1546.0982	32.9404	1551.1872	5.2345
1579.5118	224.7362	1587.9698	17.2206	1578.6360	24.8403
1606.8414	36.2921	1613.3280	41.8340	1611.4547	54.4120
1638.6240	94.8078	1626.2855	113.2273	1622.8728	222.2757
2851.5043	5.0708	2872.6139	12.8384	2858.2511	30.7022
2852.3017	35.5274	2882.1236	5.1109	2862.3105	5.1553
3056.5632	0.1851	3051.3575	0.8473	3049.2919	0.4121
3063.1680	0.4819	3061.8519	0.3702	3174.8125	1.4671
3064.1178	1.1686	3064.4351	0.2226	3063.9745	0.1645
3066.8565	0.0052	3065.4902	0.9536	3068.0785	0.0523
3073.6479	0.8403	3068.8017	0.0042	3069.9035	0.3538
3077.4879	0.0715	3076.7139	1.0855	3080.2951	0.7615
3079.8730	0.2102	3078.5850	1.2314	3088.2247	0.1210
3082.8876	1.2366	3085.7359	0.9976	3090.4592	0.6643
3087.9075	0.7155	3087.6694	0.5761	3106.8336	0.6655

Table A.27: Pyrene and protonated pyrene: scaled vibrational frequencies and IR intensities.

$C_{16}H_{10}$		1–$C_{16}H_{11}^+$		2–$C_{16}H_{11}^+$		4–$C_{16}H_{11}^+$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
97.1181	0.5821	95.5462	1.5344	83.3823	3.5085	78.6657	0.0415
148.5445	0.0009	110.9925	1.0065	138.6492	0.0001	127.2766	1.6657
208.6291	10.4254	188.6274	2.5206	202.0453	0.8603	183.3704	8.2686
243.5924	0.0001	195.5718	8.9718	213.1682	15.4343	208.5666	8.7083
257.3209	0.0005	249.6784	0.5228	228.6481	0.0007	244.5676	0.0549
351.8438	1.8199	324.7912	2.4638	287.7624	3.2037	271.6604	1.1672
395.9707	0.0005	343.7002	1.8267	350.8490	4.9552	347.2684	1.4075
404.1908	0.0001	400.9396	4.8102	371.2372	0.0001	395.5658	5.0511
453.7523	0.0002	402.3490	1.0714	399.3193	2.2867	419.7240	0.4333
490.5197	2.2572	449.6438	4.3214	443.9150	1.7838	446.2471	0.5545
498.3130	0.0058	463.9985	0.9676	483.6031	0.8495	464.4044	0.0058
498.5643	3.2297	487.7195	0.5154	488.2543	0.0325	488.5639	3.1973
503.7334	0.0570	494.2288	3.7523	493.2542	0.1501	496.6897	0.8321
527.9526	0.0030	497.7693	1.5129	495.2806	0.1378	499.9849	2.2666
544.0087	2.5088	528.3905	1.3358	508.4643	0.0004	518.7121	0.9348
571.7413	0.0002	538.3323	0.5091	537.9310	0.6465	537.6307	2.5327
583.7679	0.0003	584.1907	1.1131	571.2952	2.1281	570.9713	2.0852
674.3892	0.0311	631.8460	15.0741	645.8913	1.3784	599.6938	0.1137
690.5622	0.0155	661.6750	8.0910	662.9864	0.0320	676.8108	2.6968
708.3842	43.8722	674.3356	0.2393	673.6081	1.1642	692.5809	28.5727
735.3980	0.0001	700.6681	12.1358	715.8940	23.6626	715.2946	0.8365
742.5187	17.8701	720.2445	2.0603	728.0312	3.2390	720.0007	1.9308
761.0679	0.3744	765.5098	6.1663	757.1292	10.8156	766.4817	14.5960
799.5707	0.0001	790.1094	0.2612	773.9228	0.1563	785.8267	11.1992
799.8627	0.0442	790.3971	0.0173	782.9817	0.8948	786.3504	1.9686
802.9084	0.6643	816.9432	0.6102	793.1654	0.0045	793.8929	0.2380
818.1137	4.1177	828.3045	16.8187	803.7679	1.5999	804.6890	0.1777
841.0556	111.8551	863.5597	86.5014	841.4280	83.1074	840.2639	89.1334
891.9943	0.0027	901.3692	0.6784	854.2992	0.0000	915.5988	0.2863
904.0837	0.0013	934.3861	15.6847	926.0139	0.0059	933.1823	8.0193
960.5316	0.0040	948.0922	0.0934	946.8781	12.3960	947.0653	4.3745
961.7593	0.0023	966.5755	5.8640	947.3105	3.5174	964.7524	0.0256
967.0518	0.1565	985.0209	0.0753	948.6760	28.7649	981.7520	0.0323
967.3023	1.1345	992.2696	0.0411	984.9485	0.0484	990.4956	1.7576
975.6922	0.0000	993.1250	8.1706	985.8101	0.1118	998.4249	0.4085
995.3900	1.9656	998.5797	1.1418	998.5920	19.7050	1001.1393	0.1302
1069.2168	0.0004	1003.9566	0.0026	1004.0496	0.3997	1040.9955	15.9617
1092.1416	8.5560	1083.9496	0.4941	1057.6170	27.0444	1070.4810	11.7216

— continued on the next page —

$C_{16}H_{10}$		1–$C_{16}H_{11}^+$		2–$C_{16}H_{11}^+$		4–$C_{16}H_{11}^+$	
ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int	ν, cm^{-1}	IR int
1105.3650	0.0000	1127.3516	10.2833	1083.0996	0.2665	1092.7238	1.9344
1144.0798	0.4214	1146.1586	30.9353	1107.5940	2.7481	1100.6467	9.3081
1146.6601	0.0001	1162.9392	10.1137	1131.1866	0.0000	1159.1800	18.6460
1175.9907	0.0001	1174.4712	0.9650	1151.7842	9.8735	1162.8441	1.2149
1182.4068	14.3182	1175.8038	3.1648	1172.8496	8.4850	1179.1170	11.4306
1208.2526	0.0040	1191.7900	3.3840	1186.2498	21.0161	1187.6893	0.7535
1238.0825	0.0008	1204.2396	34.0111	1213.5664	5.3738	1203.7399	18.9939
1240.3292	0.0001	1229.3335	81.7602	1238.2736	3.9808	1234.5776	20.1997
1244.2157	2.1748	1234.6502	83.4711	1245.7966	5.0913	1237.7360	18.5845
1317.7591	5.2586	1252.4066	26.7257	1251.1884	12.2932	1252.9277	9.3160
1325.5821	0.0007	1322.5934	11.0836	1293.6961	158.2851	1325.6396	112.2704
1373.1458	0.0003	1357.3778	78.4578	1346.0674	103.5324	1334.6865	11.1933
1399.1937	0.0018	1362.0484	55.3707	1346.5580	7.5443	1335.4976	24.6094
1407.3476	0.0008	1364.3560	70.0057	1355.3209	23.3295	1370.0729	9.2170
1429.4404	3.2860	1383.6554	87.0799	1407.3655	1.3157	1380.6631	154.5740
1431.5310	6.9852	1410.7907	27.1735	1407.5246	18.1018	1407.1274	12.5503
1454.9869	1.2825	1420.8215	4.2517	1425.5012	80.1772	1424.0572	65.6510
1485.0450	3.1353	1432.8487	4.7756	1427.3118	6.4131	1429.4466	4.6571
1504.9519	0.0003	1450.7626	0.2849	1442.4997	14.6186	1440.0267	15.5180
1563.0586	0.0005	1487.1203	54.2065	1472.8360	58.1742	1479.1663	48.3764
1593.7654	0.0003	1504.2297	2.0058	1513.0355	46.2821	1513.1456	51.4439
1602.4305	12.1115	1538.2747	153.1500	1562.9437	115.5723	1549.9078	4.2840
1611.9029	1.5195	1572.0022	84.3038	1564.1022	3.3750	1565.5552	23.6833
1637.0552	0.0007	1584.9714	116.3863	1607.1853	4.0784	1595.0864	75.7052
3036.7044	2.6658	1610.7141	266.9465	1607.7609	33.5238	1604.1307	36.8072
3037.0646	0.0445	1633.3277	33.9505	1624.1268	87.4592	1629.3258	159.0258
3039.5478	0.0097	2874.3037	21.0480	2848.5199	7.9957	2859.6963	30.1848
3040.1169	0.0993	2883.7229	1.4680	2849.8495	44.5904	2864.3705	4.3288
3046.7735	16.0856	3056.6725	0.0690	3060.6343	0.1379	3048.3867	0.1898
3047.5586	0.0445	3058.2026	0.0572	3060.8045	0.0862	3053.8725	1.4159
3055.2178	12.3247	3059.2597	0.4489	3062.1924	0.0519	3056.2523	0.5670
3055.2749	52.6730	3060.9412	0.0809	3062.7257	0.6191	3060.3166	0.3360
3063.0471	53.4440	3064.5143	0.1818	3063.6648	2.1822	3064.0593	1.0369
3063.6080	2.7379	3069.8436	0.6518	3069.4393	1.0050	3067.5172	0.4729
		3073.0496	0.1959	3076.0615	1.1421	3074.8974	1.5060
		3075.1417	1.1855	3076.1686	1.1011	3079.7530	1.2761
		3084.0800	0.3097	3079.4115	0.7470	3086.2294	0.0157

A.3 Vibrational Spectra

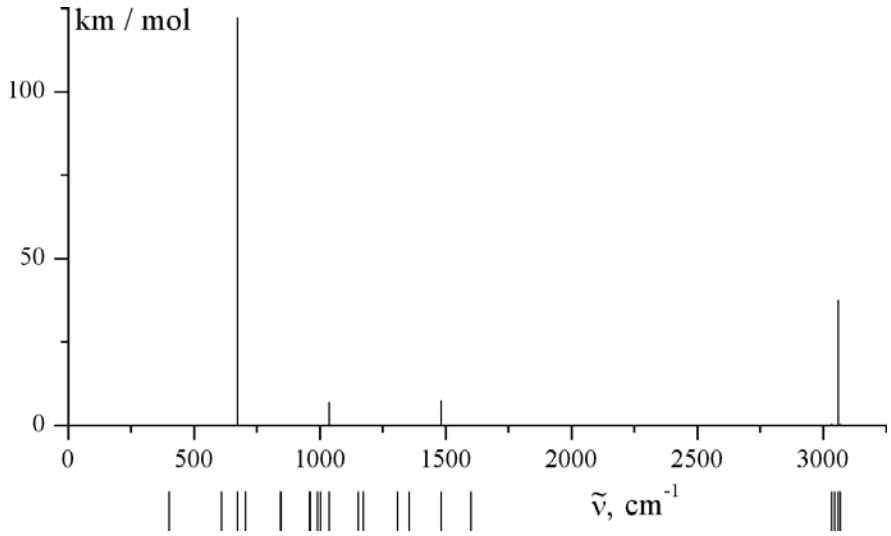


Figure A.1: Calculated benzene C_6H_6 IR vibrational spectrum.

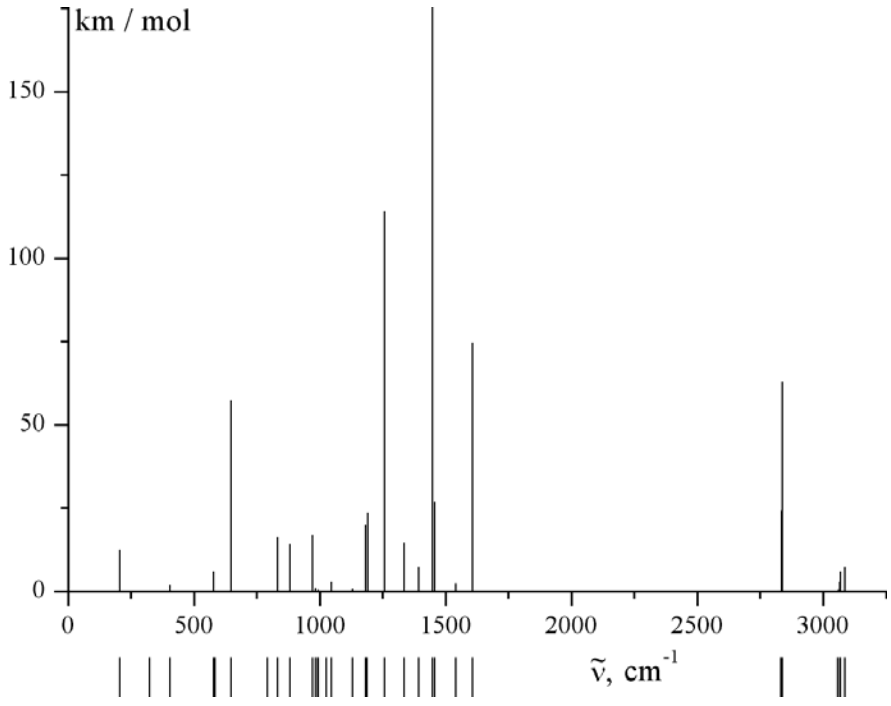


Figure A.2: Calculated protonated benzene $C_6H_7^+$ IR vibrational spectrum.

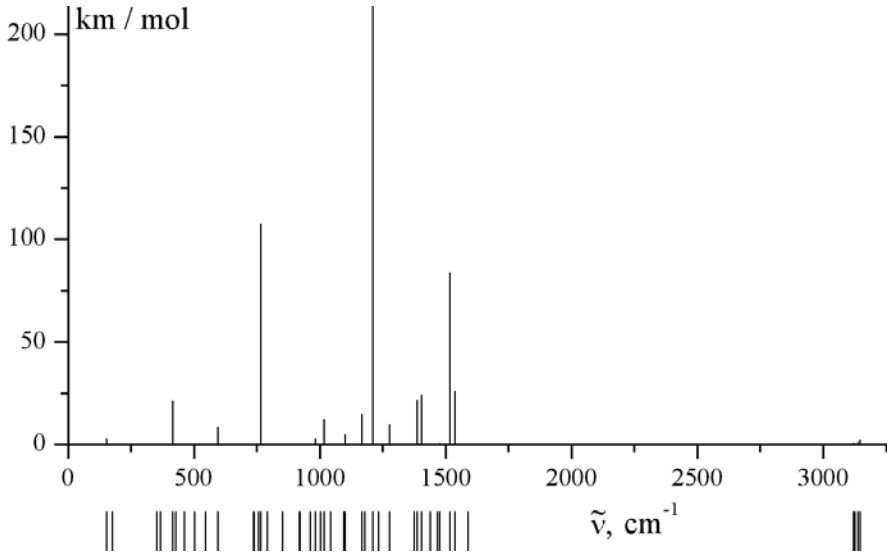


Figure A.3: Calculated naphthalene $C_{10}H_8$ IR vibrational spectrum.

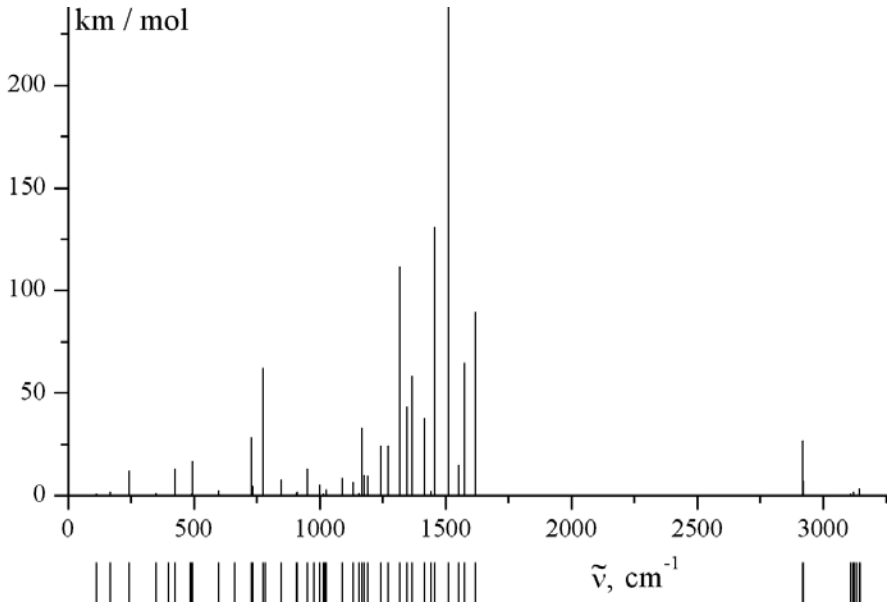


Figure A.4: Calculated protonated naphthalene 1–$C_{10}H_9^+$ IR vibrational spectrum.

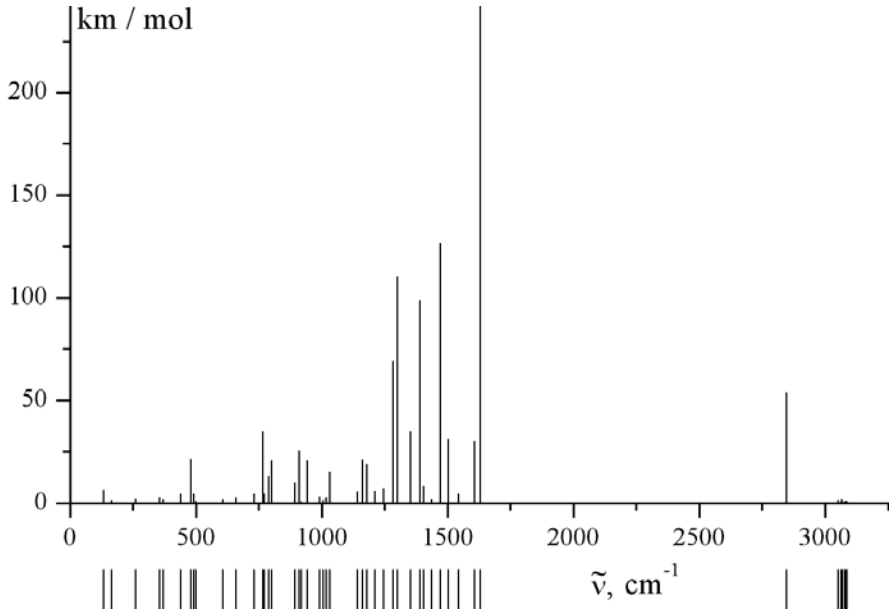


Figure A.5: Calculated protonated naphthalene 2–$C_{10}H_9^+$ IR vibrational spectrum.

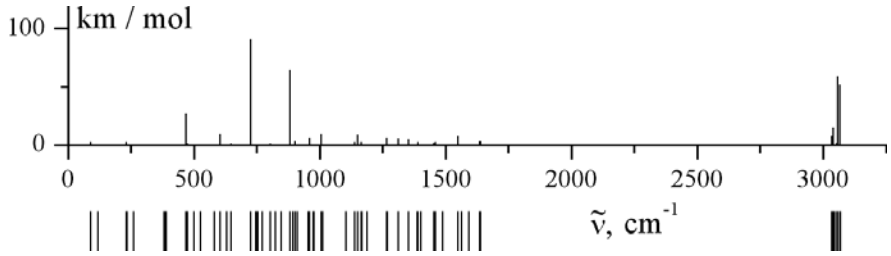


Figure A.6: Calculated anthracene $C_{14}H_{10}$ IR vibrational spectrum.

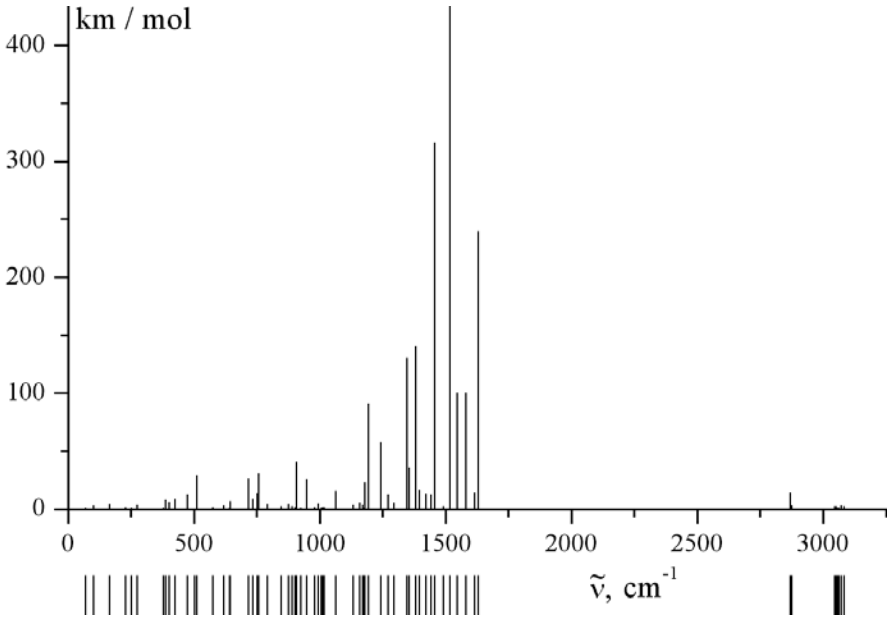


Figure A.7: Calculated protonated anthracene 1–$C_{14}H_{11}^{+}$ IR vibrational spectrum.

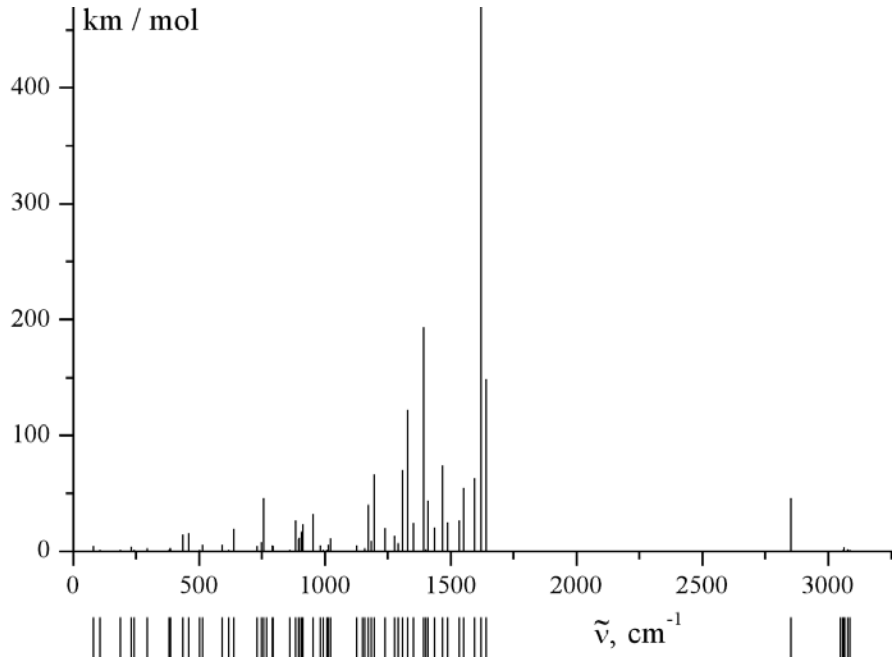


Figure A.8: Calculated protonated anthracene 2–$C_{14}H_{11}^{+}$ IR vibrational spectrum.

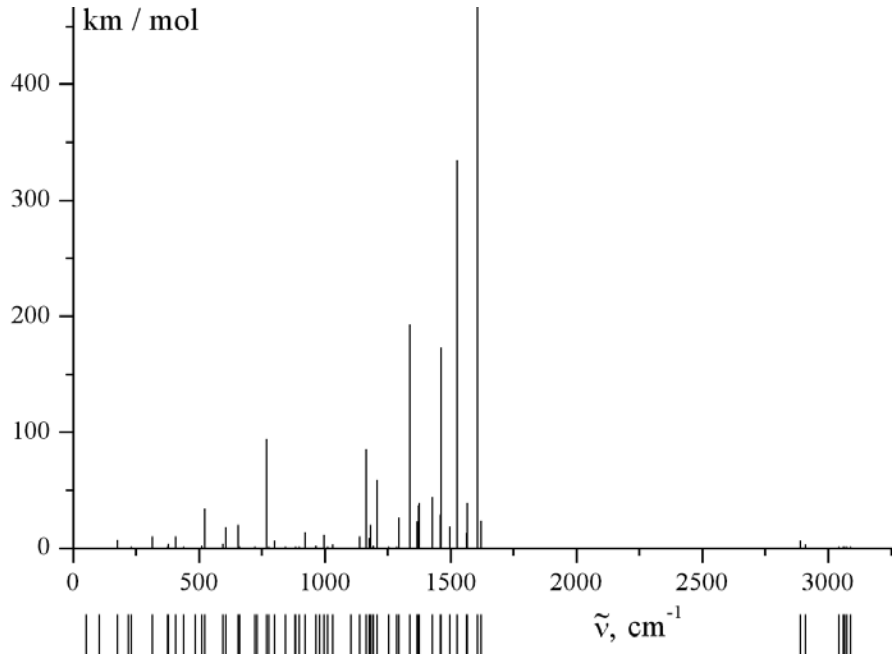


Figure A.9: Calculated protonated anthracene 9–$C_{14}H_{11}^{+}$ IR vibrational spectrum.

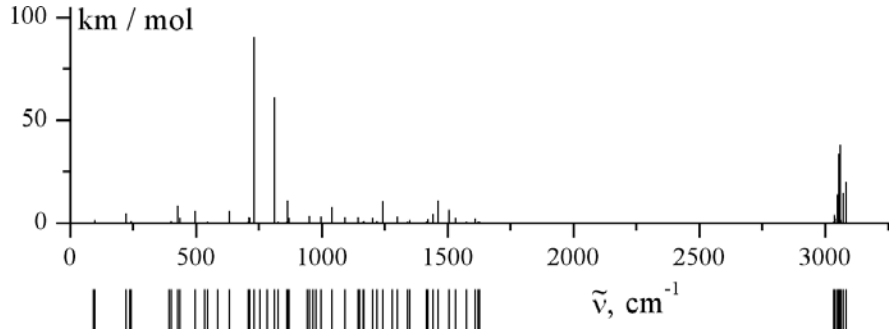


Figure A.10: Calculated phenanthrene $C_{14}H_{10}$ IR vibrational spectrum.

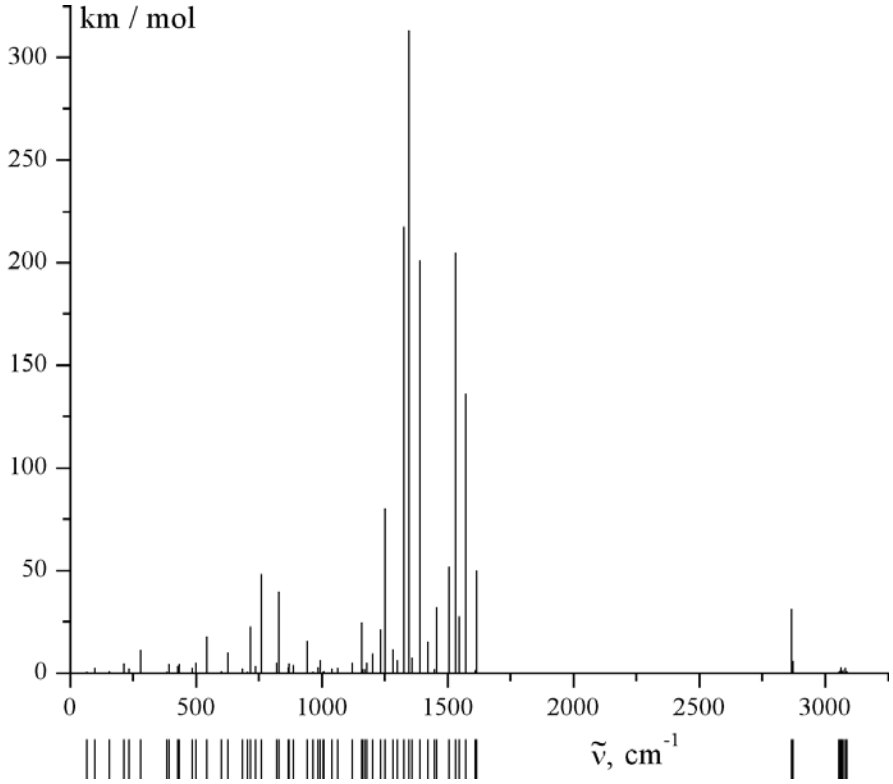


Figure A.11: Calculated protonated phenanthrene 1–$C_{14}H_{11}^{+}$ IR vibrational spectrum.

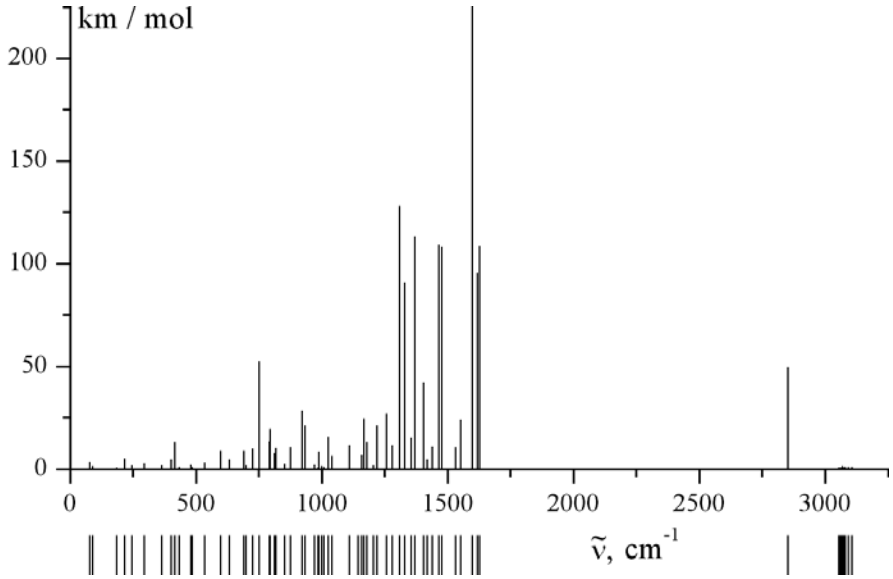


Figure A.12: Calculated protonated phenanthrene 2–$C_{14}H_{11}^{+}$ IR vibrational spectrum.

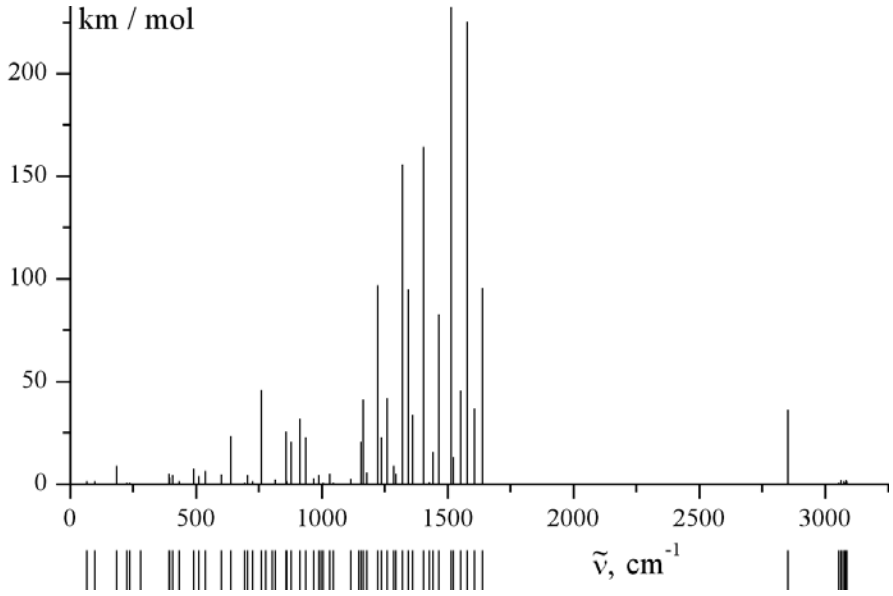


Figure A.13: Calculated protonated phenanthrene 3–$C_{14}H_{11}^{+}$ IR vibrational spectrum.

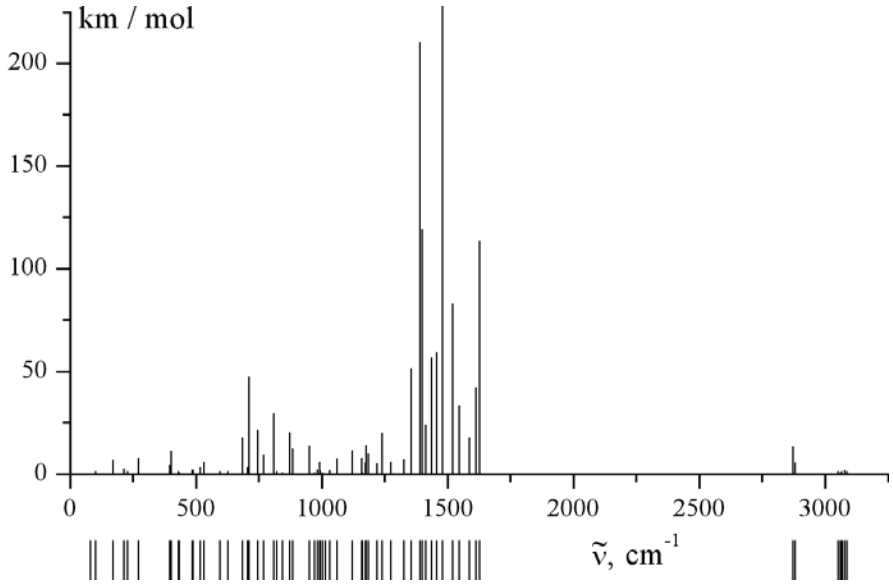


Figure A.14: Calculated protonated phenanthrene 4–$C_{14}H_{11}^{+}$ IR vibrational spectrum.

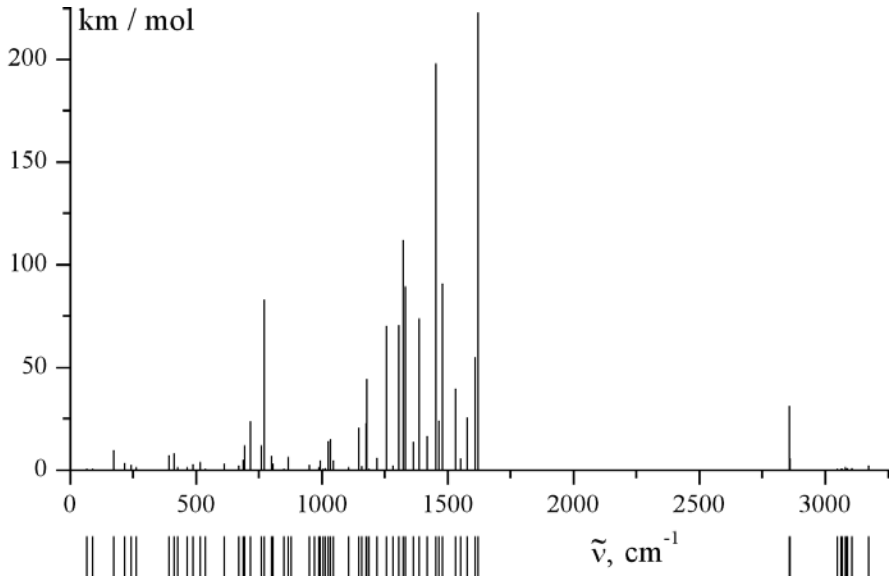


Figure A.15: Calculated protonated phenanthrene 9–$C_{14}H_{11}^{+}$ IR vibrational spectrum.

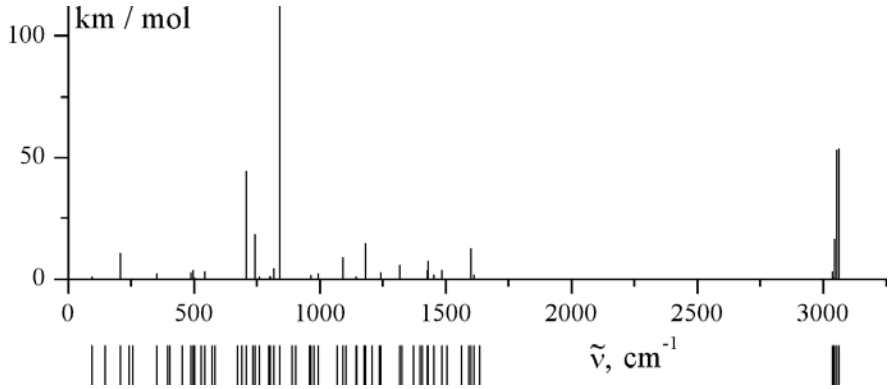


Figure A.16: Calculated pyrene $C_{16}H_{10}$ IR vibrational spectrum.

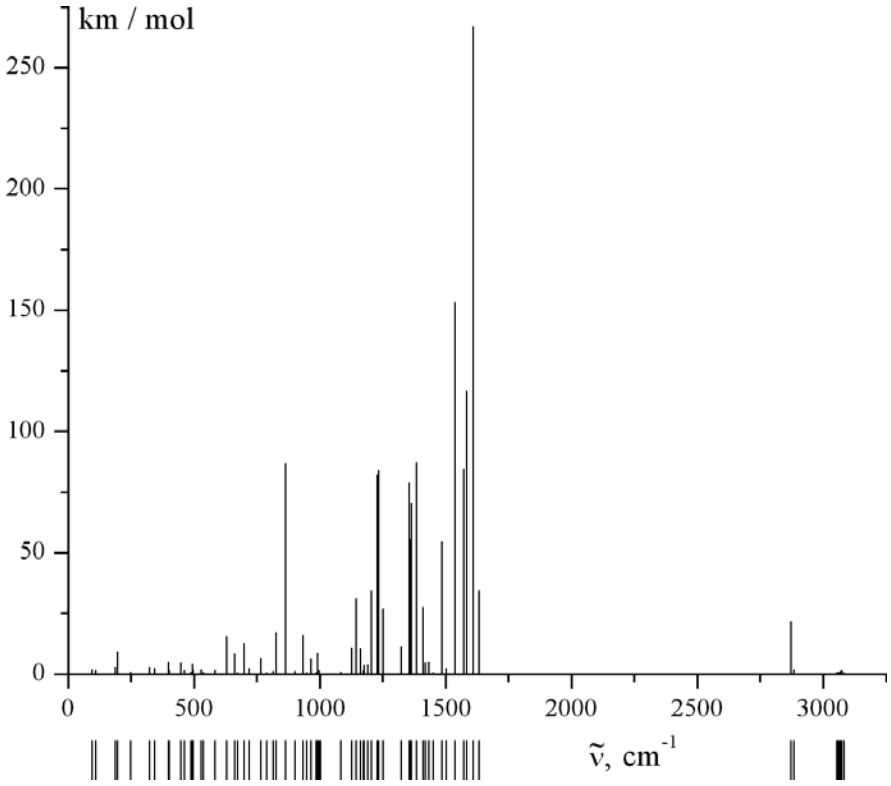


Figure A.17: Calculated protonated pyrene 1–$C_{16}H_{11}^{+}$ IR vibrational spectrum.

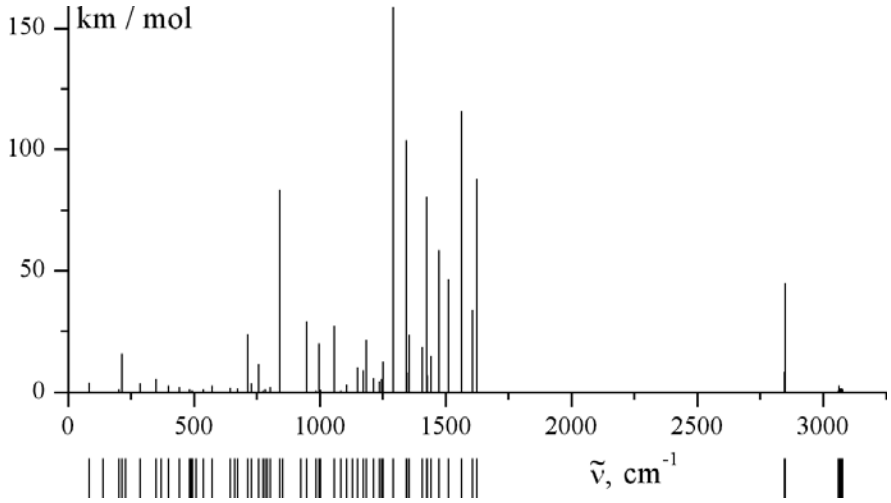


Figure A.18: Calculated protonated pyrene 2–$C_{16}H_{11}^{+}$ IR vibrational spectrum.

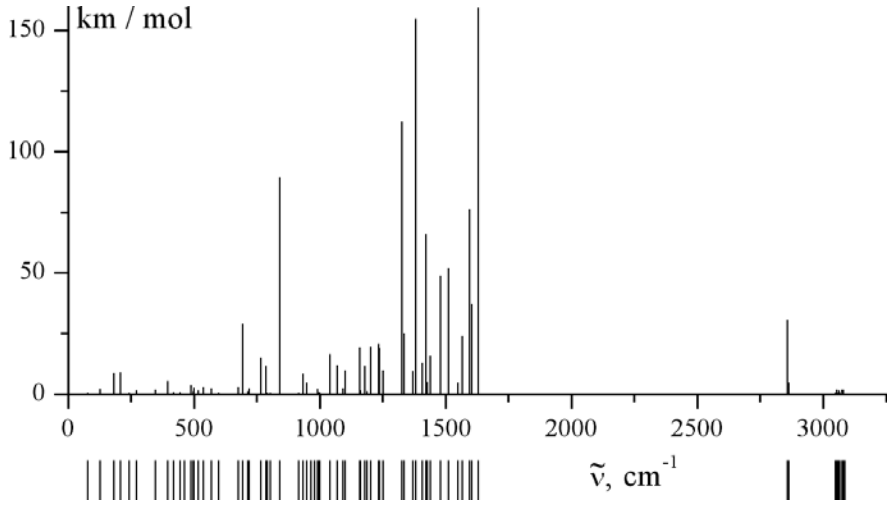


Figure A.19: Calculated protonated pyrene 4–$C_{16}H_{11}^{+}$ IR vibrational spectrum.

A.4 Energy Landscapes for Protonated PAHs

Table A.28: Protonated benzene energy landscape.

	Energy (kcal/mol)	Description
$C_6H_7^+$	-63.22	Stable isomer
1–2 $C_6H_7^+$	-51.90	1–2 isomerization transition state
$C_6H_5^+ + H_2$	0.00	Dissociation via H_2 loss from CH_2 site
$C_6H_6^+ + H$	12.63	Dissociation via H loss from CH_2 site
$C_6H_5^+ + 2H$	103.55	Dissociation via 2 H atoms loss, one from CH_2 site
$C_6H_6 + H^+$	118.97	Dissociation via H^+ loss from CH_2 site

Table A.29: Protonated naphthalene energy landscape.

	Energy (kcal/mol)	Description
1–$C_{10}H_9^+$	-62.41	Stable isomer (C 1)
2–$C_{10}H_9^+$	-59.51	Stable isomer (C 2)
9–$C_{10}H_9^+$	-43.47	Unstable isomer (C 9)
1–2 $C_{10}H_9^+$	-47.35	1–2 isomerization transition state
2–3 $C_{10}H_9^+$	-42.43	2–3 isomerization transition state
1–9 $C_{10}H_9^+$	-38.78	1–9 isomerization transition state
9–10 $C_{10}H_9^+$	-35.79	9–10 isomerization transition state
$C_{10}H_8^+ + H$	0.00	Dissociation via H loss from CH_2 site
1–$C_{10}H_7^+ + H_2$	7.28	Dissociation via H_2 loss from CH_2 site (C 1)
2–$C_{10}H_7^+ + H_2$	8.58	Dissociation via H_2 loss from CH_2 site (C 2)
1–$C_{10}H_7^+ + 2H$	110.84	Dissociation via 2 H atoms loss, one from CH_2 site (C 1)
2–$C_{10}H_7^+ + 2H$	112.14	Dissociation via 2 H atoms loss, one from CH_2 site (C 2)
$C_{10}H_8 + H^+$	133.79	Dissociation via H^+ loss from CH_2 site
2→1 $C_{10}H_8^+ + H$	48.34	Dissociation via H loss from C 2 in isomer 1
3→1 $C_{10}H_8^+ + H$	50.23	Dissociation via H loss from C 3 in isomer 1
4→1 $C_{10}H_8^+ + H$	47.75	Dissociation via H loss from C 4 in isomer 1
5→1 $C_{10}H_8^+ + H$	49.53	Dissociation via H loss from C 5 in isomer 1
6→1 $C_{10}H_8^+ + H$	49.97	Dissociation via H loss from C 6 in isomer 1
7→1 $C_{10}H_8^+ + H$	48.78	Dissociation via H loss from C 7 in isomer 1
8→1 $C_{10}H_8^+ + H$	49.17	Dissociation via H loss from C 8 in isomer 1
1→2 $C_{10}H_8^+ + H$	50.70	Dissociation via H loss from C 1 in isomer 2
3→2 $C_{10}H_8^+ + H$	52.34	Dissociation via H loss from C 3 in isomer 2
4→2 $C_{10}H_8^+ + H$	52.05	Dissociation via H loss from C 4 in isomer 2
5→2 $C_{10}H_8^+ + H$	52.76	Dissociation via H loss from C 5 in isomer 2
6→2 $C_{10}H_8^+ + H$	51.44	Dissociation via H loss from C 6 in isomer 2
7→2 $C_{10}H_8^+ + H$	52.98	Dissociation via H loss from C 7 in isomer 2
8→2 $C_{10}H_8^+ + H$	52.40	Dissociation via H loss from C 8 in isomer 2

Table A.30: Protonated anthracene energy landscape.

	Energy (kcal/mol)	Description
1–$C_{14}H_{11}^+$	-52.41	Stable isomer (C 1)
2–$C_{14}H_{11}^+$	-49.36	Stable isomer (C 2)
9–$C_{14}H_{11}^+$	-61.06	Stable isomer (C 9)
11–$C_{14}H_{11}^+$	-31.70	Unstable isomer (C 11)
1–2 $C_{14}H_{11}^+$	-34.87	1–2 isomerization transition state
2–3 $C_{14}H_{11}^+$	-28.16	2–3 isomerization transition state
1–11 $C_{14}H_{11}^+$	-24.57	1–11 isomerization transition state
9–11 $C_{14}H_{11}^+$	-29.33	9–11 isomerization transition state
11–12 $C_{14}H_{11}^+$	-21.23	11–12 isomerization transition state
$C_{14}H_{10}^+ + H$	0.00	Dissociation via H loss from CH_2 site
1–$C_{14}H_9^+ + H_2$	19.17	Dissociation via H_2 loss from CH_2 site (C 1)
2–$C_{14}H_9^+ + H_2$	18.58	Dissociation via H_2 loss from CH_2 site (C 2)
9–$C_{14}H_9^+ + H_2$	19.67	Dissociation via H_2 loss from CH_2 site (C 9)
1–$C_{14}H_9^+ + 2H$	122.73	Dissociation via 2 H atoms loss, one from CH_2 site (C 1)
2–$C_{14}H_9^+ + 2H$	122.14	Dissociation via 2 H atoms loss, one from CH_2 site (C 2)
9–$C_{14}H_9^+ + 2H$	123.23	Dissociation via 2 H atoms loss, one from CH_2 site (C 9)
$C_{14}H_{10} + H^+$	151.44	Dissociation via H^+ loss from CH_2 site

Table A.31: Protonated phenanthrene energy landscape.

	Energy (kcal/mol)	Description
1–$C_{14}H_{11}^+$	-59.53	Stable isomer (C 1)
2–$C_{14}H_{11}^+$	-57.53	Stable isomer (C 2)
3–$C_{14}H_{11}^+$	-58.98	Stable isomer (C 3)
4–$C_{14}H_{11}^+$	-58.46	Stable isomer (C 4)
9–$C_{14}H_{11}^+$	-59.33	Stable isomer (C 9)
$C_{14}H_{10}^+ + H$	0.00	Dissociation via H loss from CH_2 site
$C_{14}H_{10} + H^+$	140.27	Dissociation via H^+ loss from CH_2 site

Table A.32: Protonated pyrene energy landscape.

	Energy (kcal/mol)	Description
1–$C_{16}H_{11}^+$	-60.78	Stable isomer (C 1)
2–$C_{16}H_{11}^+$	-46.57	Stable isomer (C 2)
4–$C_{16}H_{11}^+$	-50.52	Stable isomer (C 4)
$C_{16}H_{10}^+ + H$	0.00	Dissociation via H loss from CH_2 site
$C_{16}H_{10} + H^+$	150.46	Dissociation via H^+ loss from CH_2 site

A.5 Energy Landscapes for Hydrogenated PAHs

Table A.33: Hydrogenated benzene energy landscape.

	Energy (kcal/mol)	Description
C_6H_7	-22.53	Stable isomer
C_6H_7 fr	-19.68	Stable isomer, frozen $C_6H_7^+$ geometry
C_6H_6 + H	0.00	Dissociation via H loss from CH_2 site
C_6H_5 + H_2	5.57	Dissociation via H_2 loss from CH_2 site
C_6H_5 + 2H	109.12	Dissociation via 2 H atoms loss, one from CH_2 site
$C_6H_7^+$ + e^-	132.99	Ionization

Table A.34: Hydrogenated naphthalene energy landscape.

	Energy (kcal/mol)	Description
1–$C_{10}H_9$	-30.26	Stable isomer (C 1)
2–$C_{10}H_9$	-25.49	Stable isomer (C 2)
1–$C_{10}H_9$ fr	-27.31	Stable isomer (C 1), frozen 1–$C_{10}H_9^+$ geometry
2–$C_{10}H_9$ fr	-22.45	Stable isomer (C 2), frozen 2–$C_{10}H_9^+$ geometry
$C_{10}H_8$ + H	0.00	Dissociation via H loss from CH_2 site
1–$C_{10}H_7$ + H_2	5.69	Dissociation via H_2 loss from CH_2 site (C 1)
2–$C_{10}H_7$ + H_2	5.65	Dissociation via H_2 loss from CH_2 site (C 2)
1–$C_{10}H_7$ + 2H	109.25	Dissociation via 2 H atoms loss, one from CH_2 site (C 1)
2–$C_{10}H_7$ + 2H	109.21	Dissociation via 2 H atoms loss, one from CH_2 site (C 2)
1–$C_{10}H_9^+$ + e^-	118.97	Ionization (C 1)
2–$C_{10}H_9^+$ + e^-	121.87	Ionization (C 2)

Table A.35: Hydrogenated anthracene energy landscape.

	Energy (kcal/mol)	Description
1–$C_{14}H_{11}$	-34.13	Stable isomer (C 1)
2–$C_{14}H_{11}$	-29.91	Stable isomer (C 2)
9–$C_{14}H_{11}$	-40.63	Stable isomer (C 9)
1–$C_{14}H_{11}$ fr	-31.00	Stable isomer (C 1), frozen 1–$C_{14}H_{11}^{+}$ geometry
2–$C_{14}H_{11}$ fr	-26.67	Stable isomer (C 2), frozen 2–$C_{14}H_{11}^{+}$ geometry
9–$C_{14}H_{11}$ fr	-38.04	Stable isomer (C 9), frozen 9–$C_{14}H_{11}^{+}$ geometry
$C_{14}H_{10}$ + H	0.00	Dissociation via H loss from CH_2 site
1–$C_{14}H_9$ + H_2	5.66	Dissociation via H_2 loss from CH_2 site (C 1)
2–$C_{14}H_9$ + H_2	5.65	Dissociation via H_2 loss from CH_2 site (C 2)
9–$C_{14}H_9$ + H_2	5.93	Dissociation via H_2 loss from CH_2 site (C 9)
1–$C_{14}H_9$ + 2H	109.22	Dissociation via 2 H atoms loss, one from CH_2 site (C 1)
2–$C_{14}H_9$ + 2H	109.21	Dissociation via 2 H atoms loss, one from CH_2 site (C 2)
9–$C_{14}H_9$ + 2H	109.49	Dissociation via 2 H atoms loss, one from CH_2 site (C 9)
1–$C_{14}H_{11}^{+}$ + e^-	111.33	Ionization (C 1)
2–$C_{14}H_{11}^{+}$ + e^-	114.37	Ionization (C 2)
9–$C_{14}H_{11}^{+}$ + e^-	102.68	Ionization (C 9)

A.6 Ionization Energies

Table A.36: Ionization energies for PAHs, hydrogenated and dehydrogenated PAHs.

Molecule	Calculated (eV)	Experimental (eV)
C_6H_6	9.0562	9.24378
$C_{10}H_8$	7.8655	8.1442
$C_{14}H_{10}$ anthracene	7.1002	7.4233
$C_{14}H_{10}$ phenanthrene	7.5845	7.891
$C_{16}H_{10}$ pyrene	7.1427	7.426
Hydrogenated		
C_6H_7	6.7439	
1–$C_{10}H_9$	6.4713	
2–$C_{10}H_9$	6.3900	
1–$C_{14}H_{11}$ anthracene	6.3078	
2–$C_{14}H_{11}$ anthracene	6.2568	
9–$C_{14}H_{11}$ anthracene	6.2144	
Dehydrogenated		
C_6H_5	8.2670	
1–$C_{10}H_7$	7.9347	
2–$C_{10}H_7$	7.9927	
1–$C_{14}H_9$ anthracene	7.6861	
2–$C_{14}H_9$ anthracene	7.6607	
9–$C_{14}H_9$ anthracene	7.6960	

A.7 Excited States

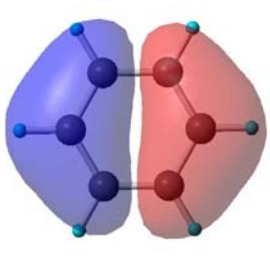
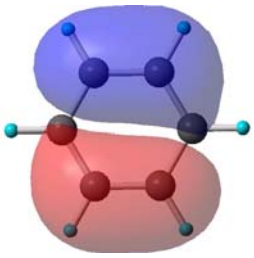
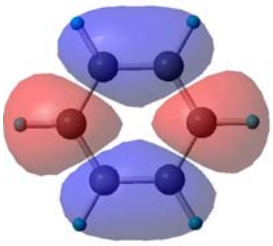
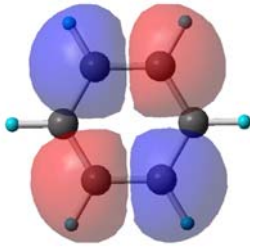
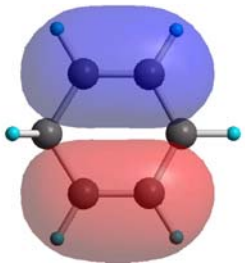
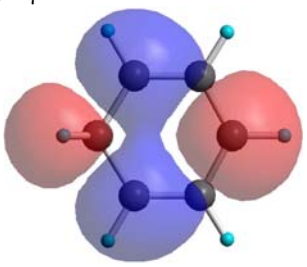
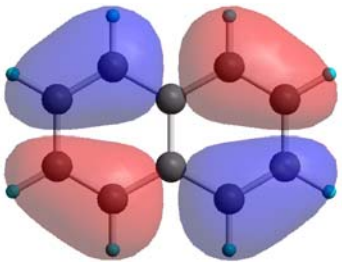
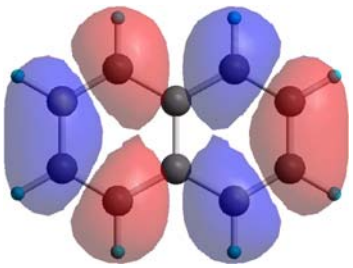
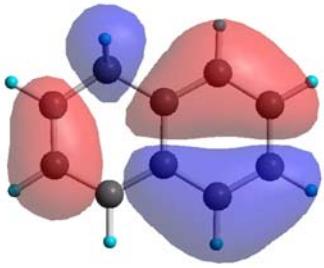
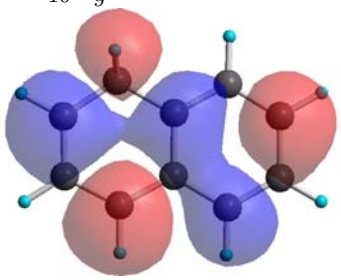
Table A.37: Calculated first singlet excited states of neutral and protonated PAHs. S_1 state energies, $S_1 \leftarrow S_0$ wavelengths, red shifts, oscillator strengths.

Molecule	S_1 (eV)	$S_1 \leftarrow S_0$ wavelength (nm)			Red shift (nm)	Oscillator strength
	Calculated		Scaled	Scaled range		
Benzene						
C_6H_6	6.0122	206.22	**262.56**			0.0000
$C_6H_7^+$	4.5130	274.72	**349.77**	323.20 – 366.29	87.21	0.1737
Naphthalene						
$C_{10}H_8$	5.0429	243.98	**312.30**			0.0825
1–$C_{10}H_9^+$	4.1253	298.84	**382.53**	351.58 – 398.45	70.22	0.4090
2–$C_{10}H_9^+$	3.5890	342.88	**438.90**	403.39 – 457.17	126.60	0.1714
Anthracene						
$C_{14}H_{10}$	4.0598	305.39	**361.17**			0.1399
1–$C_{14}H_{11}^+$	3.3092	374.66	**443.09**	440.78 – 499.55	81.92	0.3459
2–$C_{14}H_{11}^+$	2.9899	414.67	**490.41**	487.85 – 552.89	129.24	0.1862
9–$C_{14}H_{11}^+$	3.8949	318.33	**376.47**	374.51 – 424.44	15.30	0.7120
Phenanthrene						
$C_{14}H_{10}$	4.8007	258.26	**340.99**			0.0318
1–$C_{14}H_{11}^+$	3.4305	361.42	**477.20**	425.20 – 481.89	136.21	0.4661
2–$C_{14}H_{11}^+$	3.2886	377.01	**497.78**	443.54 – 502.68	156.79	0.1205
3–$C_{14}H_{11}^+$	3.5525	349.01	**460.81**	410.60 – 465.35	119.82	0.3068
4–$C_{14}H_{11}^+$	3.3196	373.49	**493.13**	439.40 – 497.99	152.14	0.1984
9–$C_{14}H_{11}^+$	3.4149	363.06	**479.36**	427.13 – 484.08	138.37	0.2854
Pyrene						
$C_{16}H_{10}$	4.3936	282.19	**367.43**			0.3643
1–$C_{16}H_{11}^+$	3.6456	340.09	**442.82**	400.11 – 453.45	75.39	0.3338
2–$C_{16}H_{11}^+$	2.8356	437.23	**569.30**	514.39 – 582.97	201.87	0.1419
4–$C_{16}H_{11}^+$	3.2337	383.41	**499.23**	451.07 – 511.21	131.80	0.1464

Table A.38: Symmetry and S_0, S_1 electronic states assignment for neutral and protonated PAHs.

Molecule	Symm group	State Symbol S_0	State Symbol S_1	Orbital Symmetry and Electronic Configuration. (x,y) = (2,0) for S_0, (1,1) for S_1
Benzene				
C_6H_6	D_{6h}	$\widetilde{X}\ ^1A_{1g}$	$\widetilde{A}\ ^1E_{1u}$	$(1a_{2u})^2(1e_{1g})^x(1e_{2u})^y(1b_{2g})^0$, here (x,y) = (4,0) for S_0, (3,1) for S_1
$C_6H_7^+$	C_{2v}	$\widetilde{X}\ ^1A_1$	$\widetilde{A}\ ^1B_1$	$(1b_2)^2(2b_2)^2(1a_2)^x(3b_2)^y(2a_2)^0(4b_2)^0$
Naphthalene				
$C_{10}H_8$	D_{2h}	$\widetilde{X}\ ^1A_g$	$\widetilde{A}\ ^1B_{2u}$	$(1b_{1u})^2(1b_{3g})^2(1b_{2g})^2(2b_{1u})^2(1a_u)^x(2b_{2g})^y(2b_{3g})^0(3b_{1u})^0(2a_u)^0(3b_{3g})^0$
1–$C_{10}H_9^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^x(6a'')^y(7a'')^0(8a'')^0(9a'')^0(10a'')^0$
2–$C_{10}H_9^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^x(6a'')^y(7a'')^0(8a'')^0(9a'')^0(10a'')^0$
Anthracene				
$C_{14}H_{10}$	D_{2h}	$\widetilde{X}\ ^1A_g$	$\widetilde{A}\ ^1B_{2u}$	$(1b_{1u})^2(1b_{2g})^2(1b_{3g})^2(2b_{1u})^2(2b_{2g})^2(1a_u)^2(2b_{3g})^x(3b_{1u})^y(2a_u)^0(3b_{2g})^0(3b_{3g})^0(4b_{1u})^0(3a_u)^0...$
1–$C_{14}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^x(8a'')^y(9a'')^0(10a'')^0(11a'')^0(12a'')^0(13a'')^0(14a'')^0$
2–$C_{14}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^x(8a'')^y(9a'')^0(10a'')^0(11a'')^0(12a'')^0(13a'')^0(14a'')^0$
9–$C_{14}H_{11}^+$	C_{2v}	$\widetilde{X}\ ^1A_1$	$\widetilde{A}\ ^1B_1$	$(1b_2)^2(2b_2)^2(1a_2)^2(3b_2)^2(2a_2)^2(4b_2)^2(3a_2)^x(5b_2)^y(4a_2)^0(6b_2)^0(5a_2)^0(7b_2)^0(6a_2)^0(8b_2)^0$
Phenanthrene				
$C_{14}H_{10}$	C_{2v}	$\widetilde{X}\ ^1A_1$	$\widetilde{A}\ ^1B_1$	$(1b_2)^2(1a_2)^2(2b_2)^2(3b_2)^2(2a_2)^2(3a_2)^2(4b_2)^x(4a_2)^y(5b_2)^0(6b_2)^0(5a_2)^0(6a_2)^0(7b_2)^0(7a_2)^0$
1–$C_{14}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^x(8a'')^y(9a'')^0(10a'')^0(11a'')^0(12a'')^0(13a'')^0(14a'')^0$
2–$C_{14}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^x(8a'')^y(9a'')^0(10a'')^0(11a'')^0(12a'')^0(13a'')^0(14a'')^0$
3–$C_{14}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^x(8a'')^y(9a'')^0(10a'')^0(11a'')^0(12a'')^0(13a'')^0(14a'')^0$
4–$C_{14}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^x(8a'')^y(9a'')^0(10a'')^0(11a'')^0(12a'')^0(13a'')^0(14a'')^0$
9–$C_{14}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^x(8a'')^y(9a'')^0(10a'')^0(11a'')^0(12a'')^0(13a'')^0(14a'')^0$
Pyrene				
$C_{16}H_{10}$	D_{2h}	$\widetilde{X}\ ^1A_g$	$\widetilde{A}\ ^1B_{3u}$	$(1b_{1u})^2(2b_{2g})^2(1b_{3g})^2(2b_{1u})^2(1a_u)^2(3b_{1u})^2(2b_{2g})^2(2b_{3g})^x(2a_u)^y(4b_{1u})^0(3b_{2g})^0(3b_{3g})^0(4b_{2g})^0...$
1–$C_{16}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^2(8a'')^x(9a'')^y(10a'')^0(11a'')^0(12a'')^0(13a'')^0...$
2–$C_{16}H_{11}^+$	C_{2v}	$\widetilde{X}\ ^1A_1$	$\widetilde{A}\ ^1B_1$	$(1b_2)^2(2b_2)^2(1a_2)^2(3b_2)^2(2a_2)^2(4b_2)^2(5b_2)^2(3a_2)^x(6b_2)^y(4a_2)^0(7b_2)^0(8b_2)^0(5a_2)^0(9b_2)^0(6a_2)^0...$
4–$C_{16}H_{11}^+$	C_s	$\widetilde{X}\ ^1A'$	$\widetilde{A}\ ^1A'$	$(1a'')^2(2a'')^2(3a'')^2(4a'')^2(5a'')^2(6a'')^2(7a'')^2(8a'')^x(9a'')^y(10a'')^0(11a'')^0(12a'')^0(13a'')^0...$

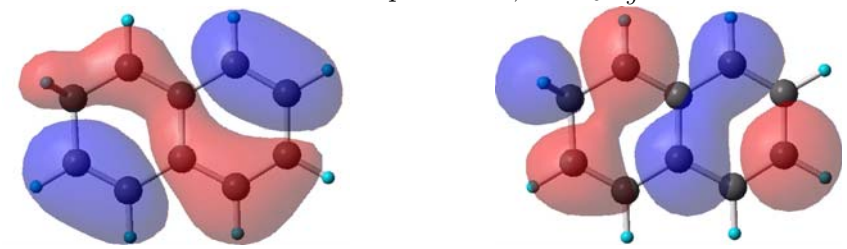
Table A.39: Highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of neutral and protonated PAHs.

HOMO	LUMO
Benzene, C_6H_6	
	
	
Protonated Benzene, $C_6H_7^+$	
	
Naphthalene, $C_{10}H_8$	
	
Protonated Naphthalene, 1–$C_{10}H_9^+$	
	

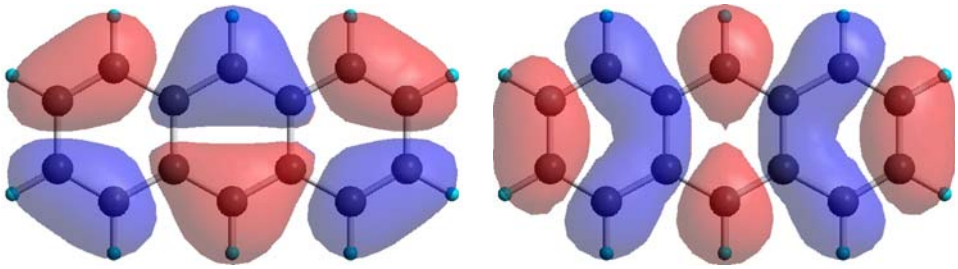
— continued on the next page —

HOMO	LUMO

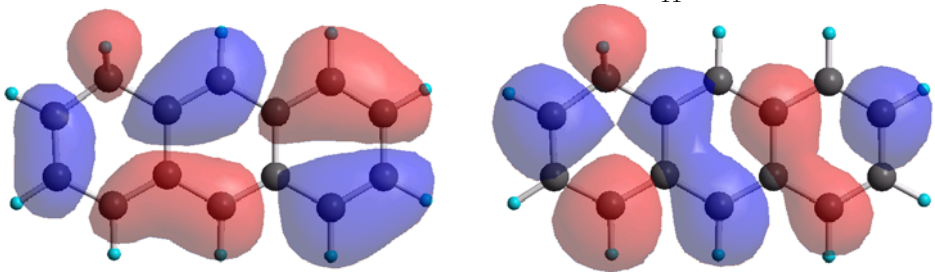
Protonated Naphthalene, 2–$C_{10}H_9^+$



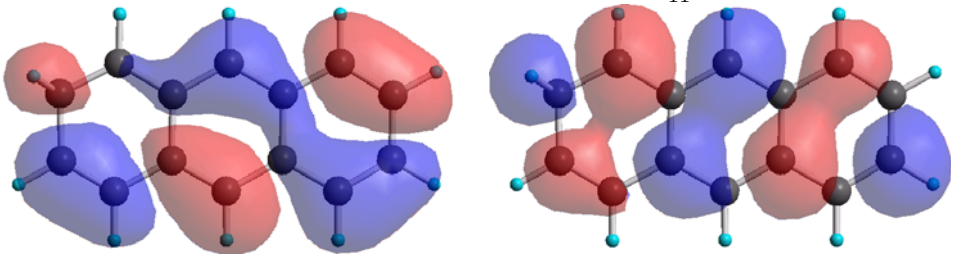
Anthracene, $C_{14}H_{10}$



Protonated Anthracene, 1–$C_{14}H_{11}^+$



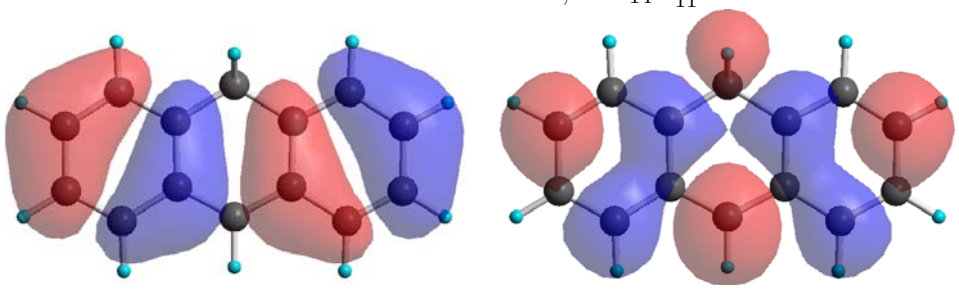
Protonated Anthracene, 2–$C_{14}H_{11}^+$



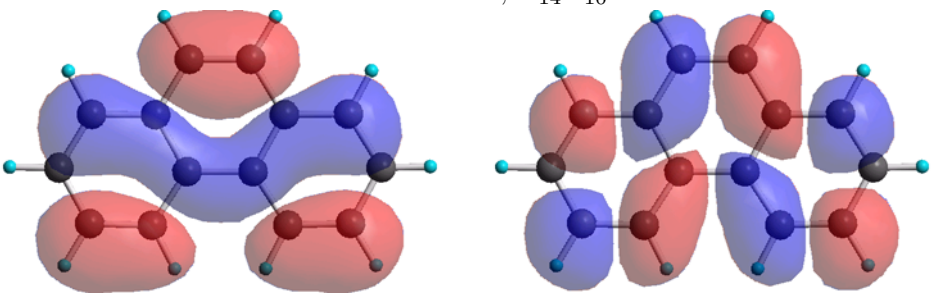
— continued on the next page —

HOMO	LUMO

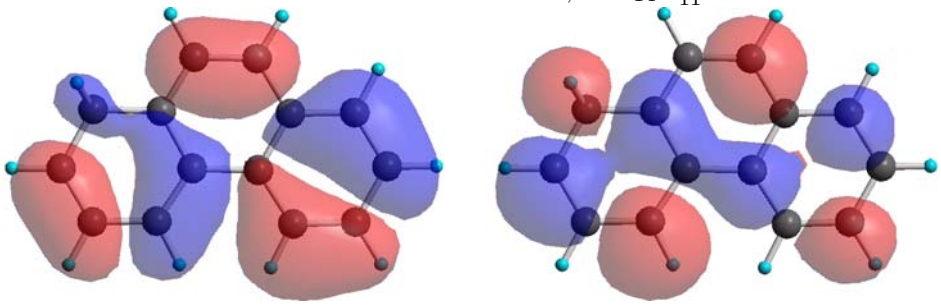
Protonated Anthracene, 9–$C_{14}H_{11}^{+}$



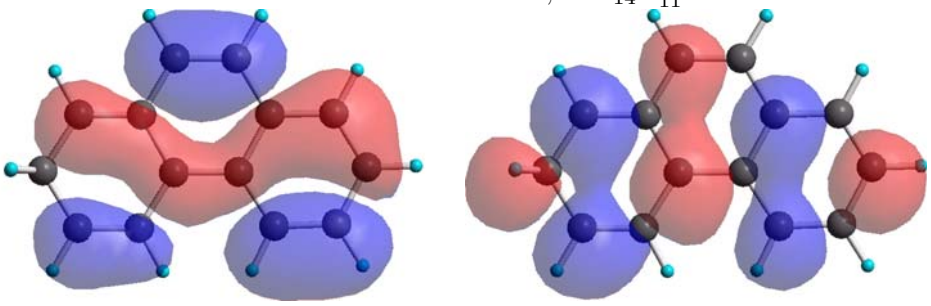
Phenanthrene, $C_{14}H_{10}$



Protonated Phenanthrene, 1–$C_{14}H_{11}^{+}$



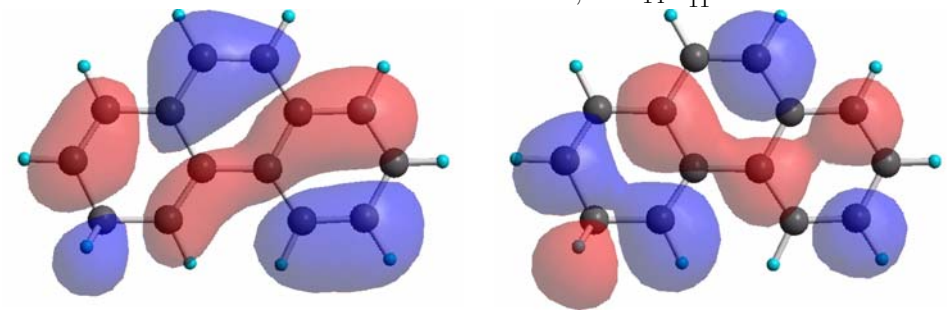
Protonated Phenanthrene, 2–$C_{14}H_{11}^{+}$



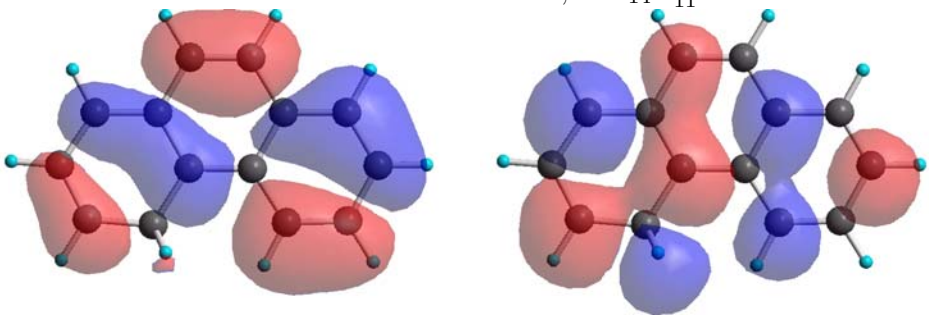
— continued on the next page —

HOMO	LUMO

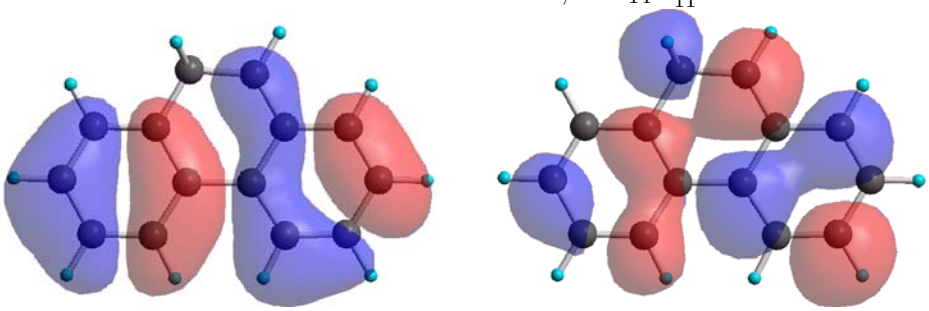
Protonated Phenanthrene, 3–$C_{14}H_{11}^{+}$



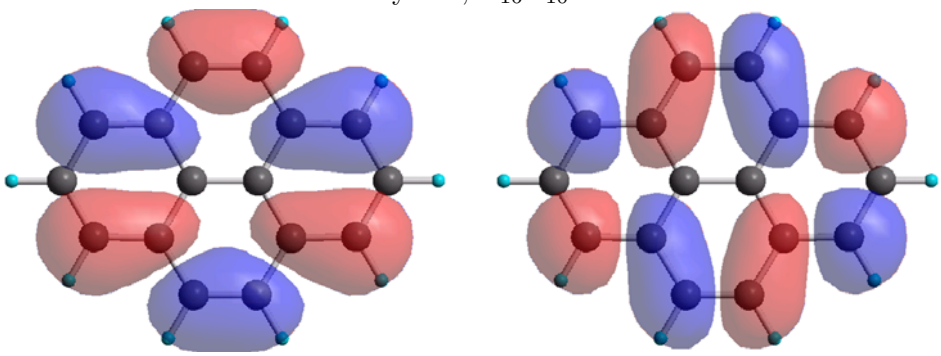
Protonated Phenanthrene, 4–$C_{14}H_{11}^{+}$



Protonated Phenanthrene, 9–$C_{14}H_{11}^{+}$



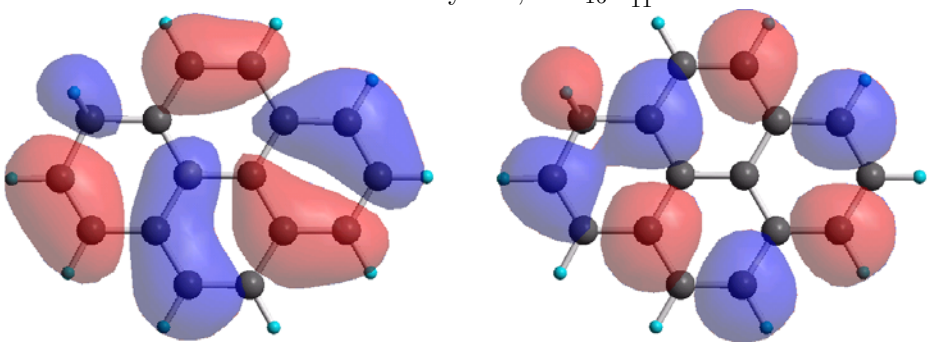
Pyrene, $C_{16}H_{10}$



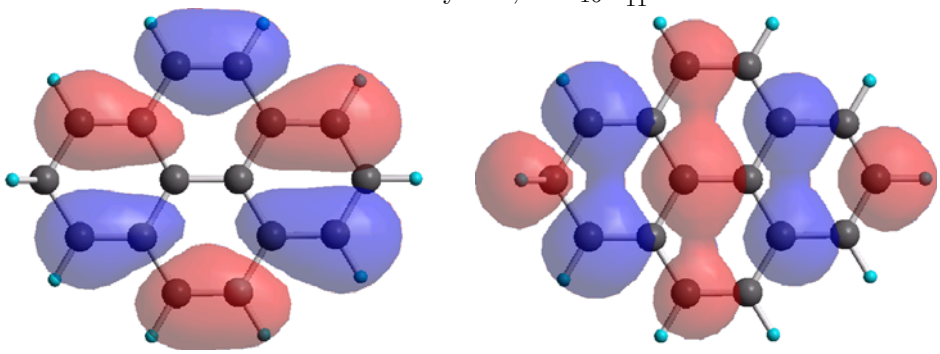
— continued on the next page —

HOMO	LUMO

Protonated Pyrene, 1–$C_{16}H_{11}^{+}$



Protonated Pyrene, 2–$C_{16}H_{11}^{+}$



Protonated Pyrene, 4–$C_{16}H_{11}^{+}$