

Intramolecular Cation- π Interactions in Protonated Phenylalanine Derivatives

Supporting Information

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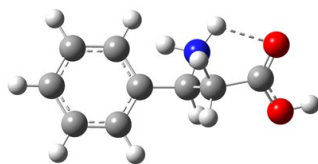
Summary of Gibbs' energies and relative energies at 298 K are given in kJ/mol. Calculations used the B3LYP functional and 6-311++G(d,p) basis set. The XYZ atomic coordinates and calculated IR spectra of isomers with relative energies within 20 kJ/mol are provided.

Phe•H⁺

Table S1 The Gibbs' Energies and Relative energies of Phe•H⁺

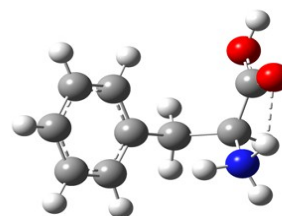
Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-555.1621	0.00
Isomer 2	-555.1602	4.95
Isomer 3	-555.1535	22.78
Isomer 4	-555.1257	95.68
Isomer 5	-555.1253	96.63
Isomer 6	-555.1252	96.86
Isomer 7	-555.1248	98.12
Isomer 8	-555.1162	120.52
Isomer 9	-555.1157	121.93
Isomer 10	-555.1122	130.97
Isomer 11	-555.1111	133.91
Isomer 12	-555.1095	138.06
Isomer 13	-555.1094	138.53
Isomer 14	-555.1094	138.56
Isomer 15	-555.1072	144.17

Phe·H⁺: The XYZ atomic coordinates and structures



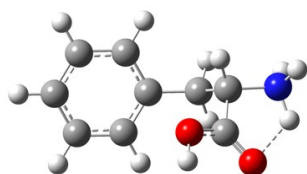
GM, 0.0kJ/mol

N	-1.007741	-1.151757	1.052125
H	-1.142262	-1.144585	2.065677
H	-0.020042	-1.377529	0.851170
H	-1.640283	-1.870094	0.662466
C	-1.368653	0.173450	0.412991
H	-1.226182	0.953359	1.160744
C	-0.459407	0.431546	-0.816569
C	-2.843019	0.051589	0.028115
H	-0.739278	-0.255498	-1.620804
H	-0.683252	1.441695	-1.165121
C	1.005532	0.271000	-0.471551
O	-3.409272	-1.013892	0.009097
C	1.682253	-0.910569	-0.807267
C	1.693943	1.273998	0.223808
H	1.182043	-1.675417	-1.395627
C	3.021431	-1.087083	-0.450500
C	3.029187	1.097109	0.575692
H	1.194825	2.206321	0.469538
H	3.538359	-1.996760	-0.732118
C	3.693273	-0.085202	0.243928
H	3.556207	1.886016	1.099170
H	4.734364	-0.215922	0.513592
O	-3.358615	1.226125	-0.300012
H	-4.284450	1.117828	-0.578123



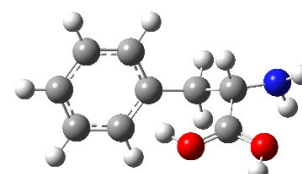
Isomer 2, 5.0kJ/mol

1.145969	1.653908	-0.854047
1.370026	2.648287	-0.795000
0.120231	1.543524	-0.940993
1.626712	0.860396	0.344181
2.445041	1.418729	0.805284
0.481901	0.648992	1.365719
2.234175	-0.413909	-0.258683
0.843874	-0.069088	2.103309
0.321087	1.591790	1.895079
-0.804467	0.185507	0.715551
-1.788910	1.122276	0.364014
-1.022206	-1.166255	0.418971
-1.671679	2.165619	0.646899
-2.959095	0.717427	-0.281992
-2.191501	-1.568716	-0.221415
-0.290124	-1.910722	0.713469
-3.718092	1.449319	-0.531665
-3.157849	-0.628074	-0.579244
-2.354061	-2.619043	-0.432301
-4.068454	-0.946540	-1.072197
2.614259	-1.270272	0.676701
3.043041	-2.039956	0.264813
2.365652	-0.553546	-1.450049
1.585479	1.235404	-1.694201



Isomer 3, 22.8kJ/mol

N	2.967850	-1.234204	0.153791
H	3.574616	-1.451565	-0.641364
H	2.857584	-2.080683	0.717810
H	3.436293	-0.493356	0.708296
C	1.624108	-0.656744	-0.278037

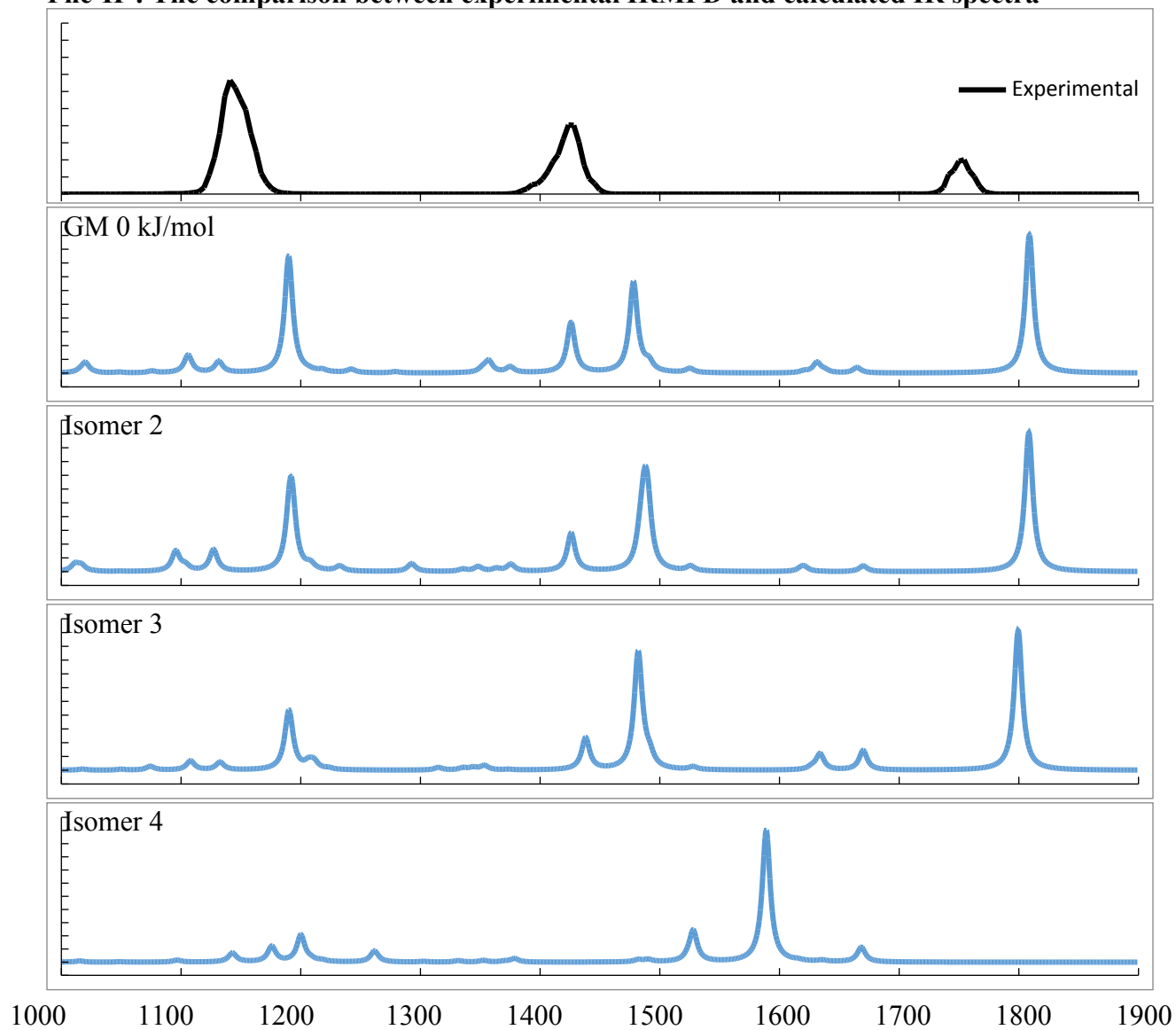


Isomer 4, 95.7kJ/mol

-2.918096	-1.398723	-0.220192
-3.281527	-1.160286	-1.134963
-3.652843	-1.356296	0.474083
-1.706438	-0.721128	0.134937
-1.407074	-1.051539	1.141295

H	1.374084	-1.065061	-1.256633	-0.544250	-1.093334	-0.836350
C	0.553470	-1.035115	0.775145	-1.829636	0.792397	0.300651
C	1.886497	0.851737	-0.359887	-0.553617	-2.183953	-0.871893
H	0.552010	-2.129150	0.854796	-0.792564	-0.742863	-1.842532
H	0.860733	-0.634276	1.746549	0.822585	-0.583447	-0.419443
C	-0.837994	-0.548961	0.430250	1.489619	0.396479	-1.174824
O	2.793793	1.355542	0.261145	1.457587	-1.097057	0.724794
C	-1.401422	0.526966	1.121048	1.039494	0.772619	-2.088914
C	-1.578233	-1.182123	-0.573718	2.752139	0.858921	-0.788749
H	-0.847606	1.012318	1.918773	2.713266	-0.636460	1.104772
C	-2.683678	0.971980	0.804448	0.978358	-1.879466	1.304957
C	-2.857493	-0.735346	-0.892176	3.257158	1.605265	-1.390134
H	-1.167550	-2.038434	-1.101054	3.361566	0.345580	0.351043
H	-3.116111	1.800942	1.352058	3.194402	-1.050371	1.982965
C	-3.410828	0.344246	-0.204436	4.342108	0.697551	0.648147
H	-3.426043	-1.235610	-1.667052	-0.845402	1.605856	0.348625
H	-4.409489	0.687130	-0.447363	0.028775	1.157987	0.137567
O	1.028194	1.471588	-1.144553	-3.008269	1.288393	0.431411
H	1.194067	2.430294	-1.129919	-2.995266	2.256719	0.559491

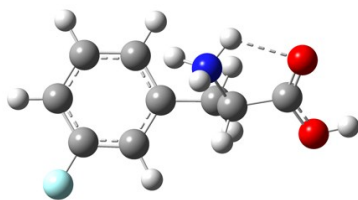
Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra



3-F-Phe•H⁺**Table S2 The Gibbs' Energies and Relative energies of 3F-Phe•H⁺**

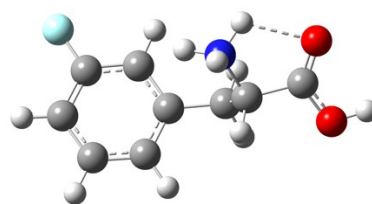
3F-Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-654.4359	0.00
Isomer 2	-654.4356	0.64
Isomer 3	-654.4345	3.53
Isomer 4	-654.4343	4.05
Isomer 5	-654.4306	13.85
Isomer 6	-654.4305	13.96
Isomer 7	-654.4295	16.71
Isomer 8	-654.4293	17.09
Isomer 9	-654.4281	20.36
Isomer 10	-654.4223	35.48
Isomer 11	-654.4220	36.34
Isomer 12	-654.4217	37.14
Isomer 13	-654.4216	37.42
Isomer 14	-654.4212	38.52
Isomer 15	-654.4209	39.30

3-F-Phe·H⁺: The XYZ atomic coordinates and structures



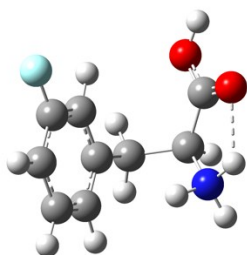
GM, 0.0kJ/mol

C	-0.677902	0.108711	-0.604073
C	-1.491798	-0.943434	-0.167752
C	-2.811995	-0.676996	0.163384
C	-3.359761	0.598250	0.085479
C	-2.548053	1.638853	-0.350229
C	-1.212728	1.401484	-0.692041
H	-1.129989	-1.963894	-0.107580
H	-4.398749	0.753209	0.347480
H	-2.958690	2.637214	-0.440388
H	-0.610226	2.215163	-1.084706
C	0.780766	-0.135620	-0.926123
H	0.919801	-1.066287	-1.479688
H	1.171567	0.672076	-1.551973
C	1.639975	-0.248387	0.359324
H	1.369714	-1.143340	0.919548
C	3.139106	-0.229335	0.056169
N	1.396250	0.950070	1.253834
H	1.459733	0.713298	2.246666
H	0.459998	1.343644	1.067974
O	3.820812	0.738781	0.288490
O	3.536023	-1.361459	-0.502382
H	4.483242	-1.313768	-0.719237
F	-3.586421	-1.693406	0.570773
H	2.137296	1.643119	1.054409



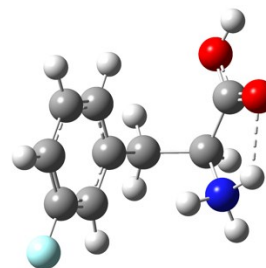
Isomer 2, 0.6kJ/mol

0.667154	0.478064	-0.444546
1.471619	-0.659365	-0.603360
2.801449	-0.608903	-0.195910
3.361216	0.528274	0.363663
2.554969	1.655754	0.513041
1.218157	1.634811	0.119015
1.108645	-1.556946	-1.094145
4.403460	0.527619	0.656671
2.978198	2.560431	0.932565
0.614762	2.529916	0.226217
-0.794117	0.421784	-0.835953
-1.116497	1.352052	-1.307551
-0.966520	-0.381139	-1.558881
-1.710772	0.207138	0.395486
-1.670370	1.074886	1.053602
-3.153648	-0.104663	-0.005758
-1.246589	-0.997595	1.189035
-0.237105	-1.151706	1.040850
-1.415946	-0.890262	2.191895
-3.612184	-1.216588	0.089169
-3.768220	0.967229	-0.480132
-4.670426	0.737824	-0.762862
3.560268	-1.703271	-0.364277
-1.797427	-1.812565	0.870524



Isomer 3, 3.5kJ/mol

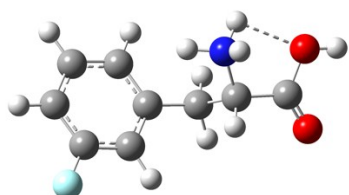
C	-0.492178	-0.591766	-0.727325
C	-0.969462	0.712224	-0.553119



Isomer 4, 4.0kJ/mol

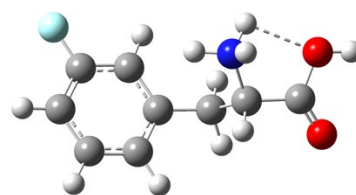
0.454765	0.080523	0.782687
1.549086	-0.762480	0.534565

C	-2.207337	0.900949	0.044174	2.671322	-0.246771	-0.105827
C	-2.995653	-0.155743	0.482658	2.750435	1.076928	-0.507770
C	-2.521991	-1.449965	0.301210	1.663903	1.909948	-0.248709
C	-1.278577	-1.671789	-0.298493	0.522982	1.421010	0.386387
H	-0.414712	1.576602	-0.898226	1.577353	-1.787792	0.890650
H	-3.958577	0.043761	0.935481	3.647322	1.440314	-0.993196
H	-3.130151	-2.291393	0.610465	1.712975	2.952742	-0.537986
H	-0.956265	-2.691007	-0.492154	-0.300296	2.093300	0.598952
C	0.875461	-0.840758	-1.327763	-0.789180	-0.487544	1.433514
H	0.913921	-1.835994	-1.777980	-0.533336	-1.352541	2.050839
H	1.104000	-0.126725	-2.120606	-1.264046	0.240663	2.092899
C	2.015852	-0.737996	-0.286290	-1.859978	-0.927925	0.406049
H	2.942703	-1.136933	-0.705470	-2.626991	-1.529178	0.900248
C	2.326910	0.672287	0.236891	-2.584156	0.203068	-0.338753
N	1.692635	-1.539536	0.958781	-1.251823	-1.775685	-0.693688
H	0.666114	-1.643302	1.038903	-0.244358	-1.557101	-0.776171
H	2.121614	-2.466225	0.963822	-1.361330	-2.778824	-0.536343
O	2.523569	1.532891	-0.749186	-3.089530	1.098585	0.494682
O	2.409696	0.906079	1.417596	-2.688042	0.206457	-1.540774
H	2.022722	-0.986155	1.771101	-1.711359	-1.498847	-1.580866
F	-2.657181	2.155167	0.196757	3.711235	-1.066947	-0.326021
H	2.770537	2.401191	-0.386562	-3.588793	1.768709	-0.003141



Isomer 5, 13.8kJ/mol

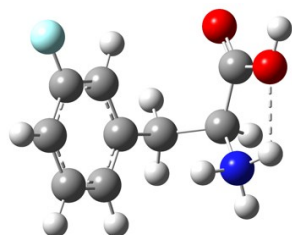
C	-0.685988	0.128041	-0.603208
C	-1.496868	-0.933455	-0.183061
C	-2.815012	-0.674911	0.162378
C	-3.364058	0.601169	0.113375
C	-2.555710	1.651195	-0.305995
C	-1.222547	1.421862	-0.660757
H	-1.134084	-1.954790	-0.147670
H	-4.401548	0.750008	0.384722
H	-2.967753	2.650775	-0.373364
H	-0.623006	2.244252	-1.039498
C	0.769036	-0.115102	-0.944489
H	0.901088	-1.038866	-1.511440
H	1.159957	0.698825	-1.562656
C	1.634485	-0.258254	0.330680



Isomer 6, 14.0kJ/mol

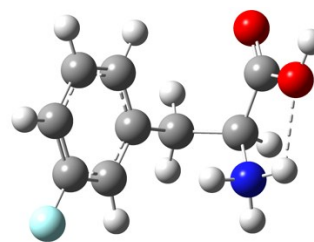
0.676229	0.467288	-0.454180
1.480570	-0.673313	-0.589230
2.807482	-0.618256	-0.173781
3.365294	0.526879	0.371406
2.559554	1.657444	0.498155
1.225461	1.632038	0.095243
1.119896	-1.578517	-1.067410
4.405626	0.529461	0.671158
2.981022	2.568192	0.906107
0.622568	2.529564	0.183379
-0.782333	0.413651	-0.857647
-1.099221	1.342965	-1.335117
-0.956479	-0.391652	-1.577974
-1.705161	0.219131	0.369362

H	1.303748	-1.121101	0.909255	-1.596932	1.062447	1.051793
C	3.111970	-0.444801	-0.009492	-3.173165	0.116697	-0.041151
N	1.428357	0.961969	1.217980	-1.267691	-1.018773	1.140930
H	1.678928	0.779333	2.193037	-1.606113	-1.012958	2.106554
H	2.013500	1.739762	0.893626	-0.235581	-1.060636	1.145488
O	3.537865	-1.450796	-0.486249	-3.793757	1.052900	-0.440207
O	3.825525	0.672856	0.258488	-3.629447	-1.151769	0.069532
H	4.752828	0.542252	-0.003592	-4.551766	-1.198039	-0.235209
F	-3.586169	-1.699639	0.554057	3.565565	-1.716917	-0.319308
H	0.434403	1.241565	1.170716	-1.637219	-1.865562	0.694840



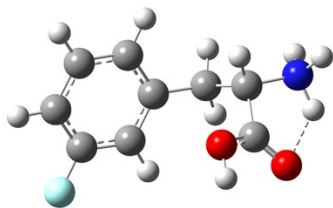
Isomer 7, 16.7kJ/mol

C	0.494095	-0.610240	0.717289
C	0.992194	0.691217	0.578680
C	2.218401	0.876751	-0.043861
C	2.974991	-0.177634	-0.540006
C	2.480468	-1.468699	-0.394057
C	1.248316	-1.688300	0.228590
H	0.460425	1.551432	0.967237
H	3.930723	0.020144	-1.008602
H	3.064352	-2.309629	-0.748256
H	0.911231	-2.707933	0.392897
C	-0.860192	-0.855564	1.352185
H	-0.903486	-1.860821	1.779738
H	-1.055785	-0.153969	2.164795
C	-2.023919	-0.695639	0.350347
H	-2.953523	-1.077265	0.780808
C	-2.295456	0.766172	-0.032929
N	-1.753813	-1.520476	-0.901495
H	-0.740686	-1.480289	-1.110450
H	-2.270120	-1.141228	-1.703283
O	-2.306620	1.651358	0.765483
O	-2.563805	0.889002	-1.351304
H	-2.777254	1.813900	-1.561992
F	2.689698	2.126727	-0.164877
H	-2.006472	-2.502808	-0.769391



Isomer 8, 17.1kJ/mol

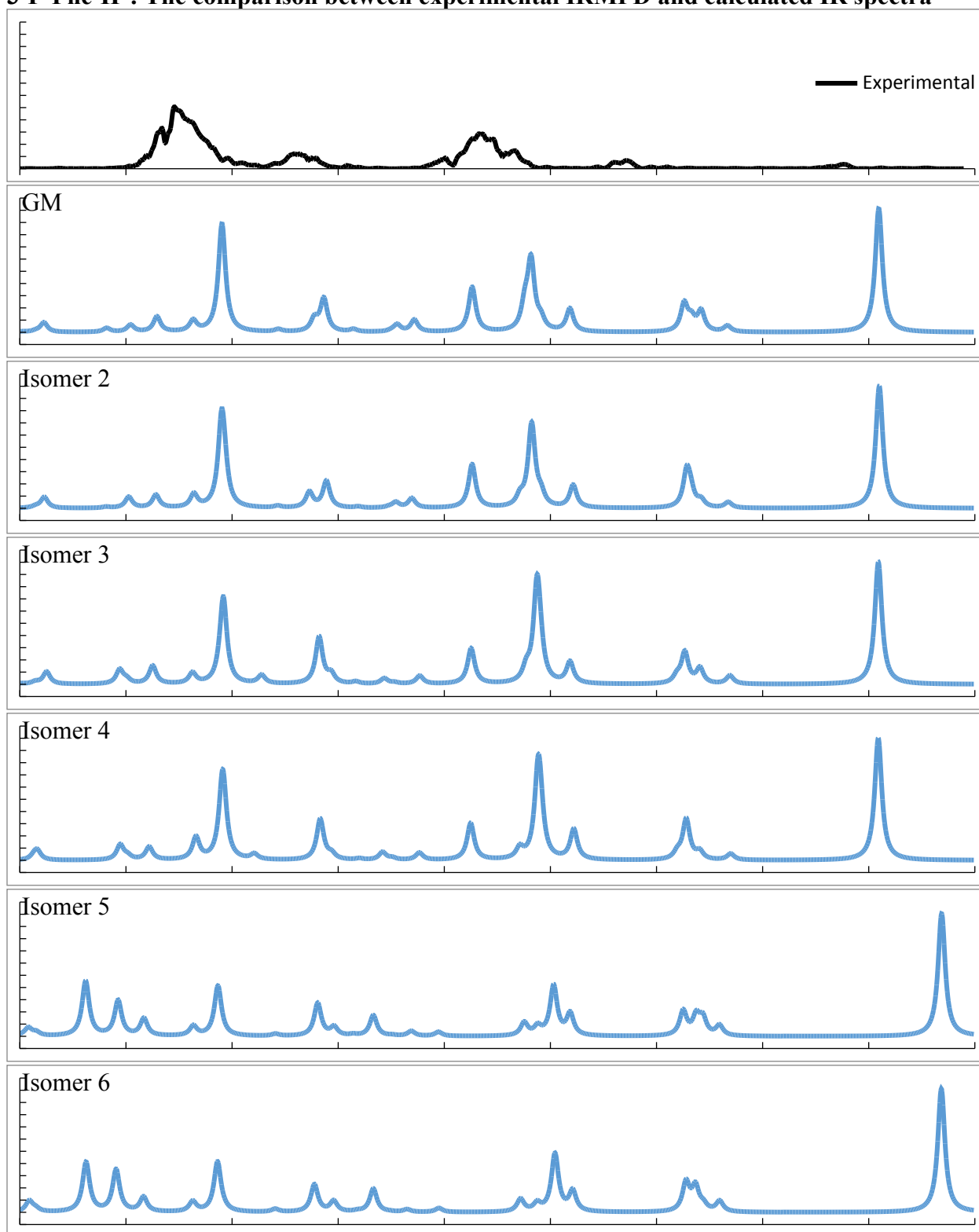
C	0.460656	0.089938	0.799591
C	1.526645	-0.775799	0.507736
C	2.644012	-0.278315	-0.154391
C	2.747235	1.049985	-0.535218
C	1.689789	1.905430	-0.232429
C	0.552618	1.435837	0.424405
H	1.540334	-1.806971	0.847601
H	3.640800	1.399117	-1.037027
H	1.758822	2.952193	-0.502939
H	-0.249178	2.122675	0.668058
C	-0.778047	-0.453648	1.483639
H	-0.525681	-1.316882	2.105523
H	-1.228742	0.291815	2.140803
C	-1.878367	-0.871311	0.484912
H	-2.662306	-1.436546	0.996146
C	-2.575126	0.322579	-0.183174
N	-1.301410	-1.797108	-0.578483
H	-0.352143	-1.468482	-0.825214
H	-1.882151	-1.783350	-1.424457
O	-2.903394	1.298521	0.417531
O	-2.804308	0.088690	-1.494115
H	-3.289938	0.835033	-1.884387
F	3.656104	-1.121775	-0.417047
H	-1.219762	-2.758745	-0.239066

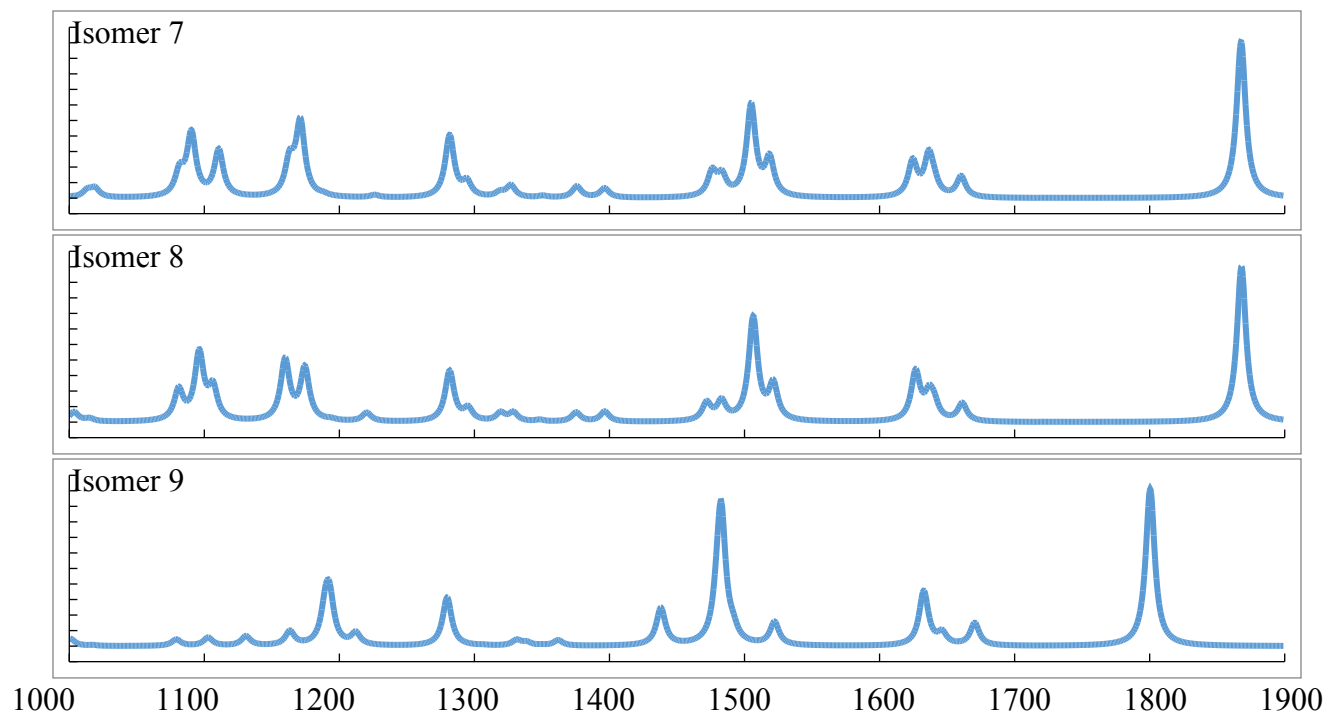


Isomer 9, 20.4kJ/mol

C	0.505105	-0.704620	-0.448320
C	1.228690	0.431498	-0.816932
C	2.519325	0.589405	-0.331851
C	3.118868	-0.340995	0.502748
C	2.391411	-1.474744	0.857534
C	1.093597	-1.660148	0.385838
H	0.819562	1.185365	-1.479921
H	4.130862	-0.178625	0.851365
H	2.844996	-2.221482	1.497770
H	0.552703	-2.561118	0.657078
C	-0.906457	-0.899074	-0.960604
H	-1.033216	-1.935938	-1.293773
H	-1.086435	-0.250911	-1.824248
C	-1.997058	-0.623446	0.104088
H	-1.873185	-1.272975	0.969945
C	-2.076500	0.849533	0.526759
N	-3.366188	-0.896260	-0.508893
H	-3.322325	-1.595050	-1.254966
H	-4.050426	-1.208038	0.185766
O	-1.204177	1.152545	1.466849
O	-2.870564	1.598356	0.006585
H	-3.699529	0.010624	-0.887005
F	3.207487	1.687546	-0.692978
H	-1.251040	2.102383	1.674004

3-F-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra

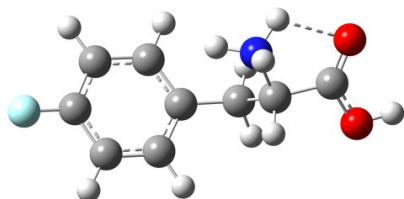




4-F-Phe•H⁺

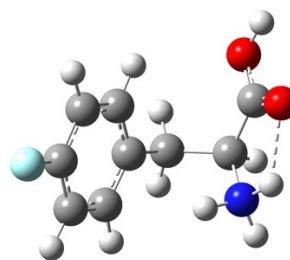
4-F-Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-654.4356	0.00
Isomer 2	-654.4342	3.64
Isomer 3	-654.4304	13.52
Isomer 4	-654.4293	16.64
Isomer 5	-654.4281	19.54
Isomer 6	-654.4221	35.47
Isomer 7	-654.4213	37.45
Isomer 8	-654.4210	38.43
Isomer 9	-654.4123	61.13
Isomer 10	-654.3993	95.32
Isomer 11	-654.3905	118.31
Isomer 12	-654.3900	119.82
Isomer 13	-654.3869	127.74
Isomer 14	-654.3858	130.73
Isomer 15	-654.3838	135.91
Isomer 16	-654.3829	138.21

4-F-Phe·H⁺: The XYZ atomic coordinates and structures



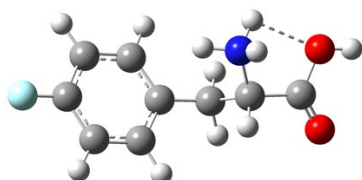
GM, 0.0kJ/mol

C	1.268331	1.293017	0.166314
C	0.578257	0.285685	-0.524072
C	1.275546	-0.869298	-0.906978
C	2.628276	-1.026370	-0.603877
C	3.272255	-0.011209	0.086597
C	2.616531	1.152508	0.473466
H	0.759020	2.209435	0.447068
H	0.777513	-1.638536	-1.490311
H	3.181118	-1.905407	-0.910238
H	3.164697	1.928908	0.992272
C	-0.897607	0.424014	-0.829100
C	-1.777378	0.166650	0.422136
C	-3.259198	0.033663	0.069669
N	-1.396201	-1.153930	1.058989
O	-3.816610	-1.036547	0.065080
O	-3.789879	1.203601	-0.249101
H	-0.411073	-1.372915	0.845376
H	-2.029545	-1.878052	0.680665
H	-4.721062	1.089314	-0.506658
H	-1.188694	-0.271967	-1.621621
H	-1.143299	1.427810	-1.181799
H	-1.623418	0.950618	1.163360
H	-1.516518	-1.145776	2.074530
F	4.571834	-0.149368	0.382408



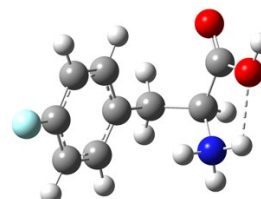
Isomer 2, 3.6kJ/mol

0.710125	-0.948709	-0.655330
0.366502	0.404929	-0.785263
1.313615	1.375849	-0.424173
2.566520	1.013377	0.069804
2.861188	-0.335878	0.194219
1.955850	-1.326517	-0.167347
0.011827	-1.719266	-0.963207
1.098469	2.429930	-0.577401
3.310474	1.754493	0.333395
2.237162	-2.368052	-0.075439
-0.999584	0.825177	-1.285021
-2.085256	0.808500	-0.180320
-2.545900	-0.577526	0.292491
-1.591122	1.492158	1.078576
-2.584109	-0.869131	1.462743
-2.916597	-1.346495	-0.719333
-1.891224	2.465376	1.153586
-1.944612	0.943347	1.883840
-3.256631	-2.193715	-0.383501
-1.354160	0.174250	-2.086043
-0.954595	1.835577	-1.699619
-2.975294	1.343518	-0.520263
-0.558041	1.455330	1.097827
4.062418	-0.697343	0.665017



Isomer 3, 13.5kJ/mol

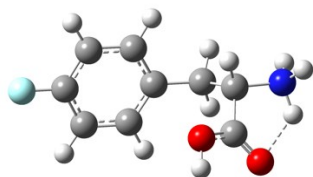
C	1.272670	1.290736	0.116275
C	0.586197	0.257357	-0.539070
C	1.286021	-0.911354	-0.872529



Isomer 4, 16.6kJ/mol

0.737970	-0.927370	-0.723954
0.368962	0.425124	-0.788631
1.284261	1.393181	-0.345853

C	2.636605	-1.056444	-0.555411	2.528889	1.029570	0.167297
C	3.276689	-0.015181	0.099339	2.848850	-0.318573	0.226591
C	2.618839	1.162225	0.437562	1.977096	-1.305100	-0.217999
H	0.761993	2.217829	0.356694	0.064528	-1.691671	-1.094717
H	0.791367	-1.703145	-1.427824	1.053249	2.450034	-0.450312
H	3.191447	-1.946407	-0.824306	3.248780	1.769718	0.493102
H	3.163689	1.958385	0.929179	2.278985	-2.344224	-0.177704
C	-0.886720	0.391632	-0.862440	-0.988746	0.843508	-1.316448
C	-1.772524	0.195017	0.392300	-2.101327	0.769849	-0.248420
C	-3.259127	0.259081	0.049681	-2.520905	-0.666354	0.094814
N	-1.421082	-1.131989	1.050128	-1.659281	1.495312	1.015447
O	-3.807305	1.276879	-0.241225	-2.671609	-1.512171	-0.731797
O	-3.825668	-0.969220	0.078747	-2.740438	-0.811705	1.420326
H	-1.883035	-1.905760	0.559932	-0.654845	1.302419	1.168257
H	-1.717763	-1.171938	2.028527	-1.774046	2.508210	0.930117
H	-4.760010	-0.906979	-0.183439	-3.053587	-1.712755	1.608102
H	-1.179269	-0.330561	-1.631013	-1.313032	0.204421	-2.139611
H	-1.125493	1.383258	-1.252752	-0.948751	1.864836	-1.705059
H	-1.555078	0.970805	1.126745	-3.004139	1.277261	-0.599082
H	-0.397614	-1.260664	1.001449	-2.185374	1.160265	1.830274
F	4.574359	-0.142289	0.407944	4.043252	-0.680855	0.715099

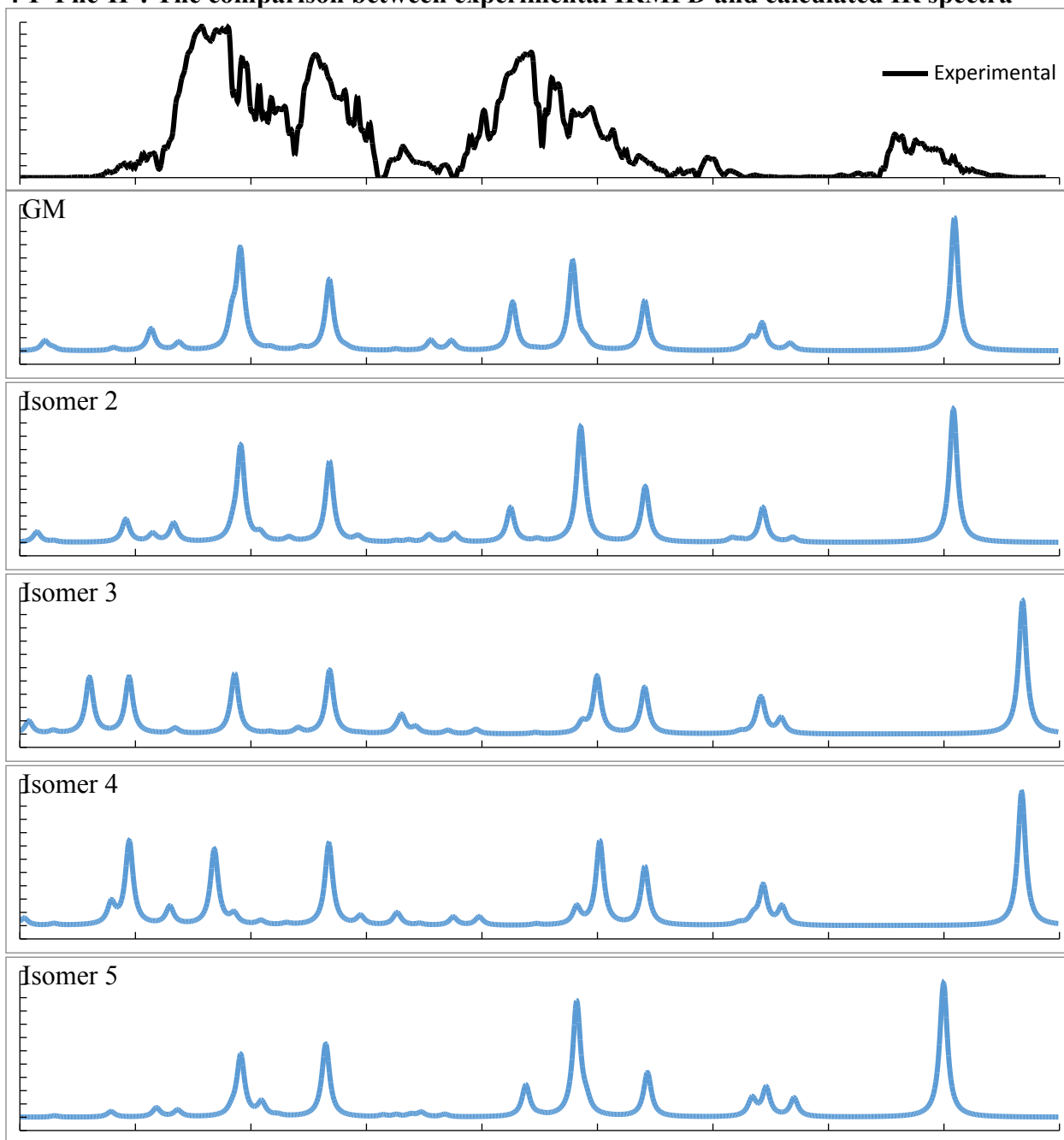


Isomer 5, 19.5kJ/mol

C	-1.005030	0.369551	1.203056
C	-0.408095	-0.653887	0.460956
C	-1.151906	-1.293702	-0.537169
C	-2.461369	-0.911493	-0.805824
C	-3.018559	0.115970	-0.056096
C	-2.316153	0.762500	0.950137
H	-0.453324	0.861175	1.997710
H	-0.720067	-2.111132	-1.106617
H	-3.051671	-1.400554	-1.570182
H	-2.794997	1.546671	1.522658
C	1.016656	-1.075545	0.745099
C	2.035747	-0.601858	-0.322135
C	2.215988	0.920782	-0.356965
N	3.420016	-1.120777	0.051453
O	3.116347	1.450153	0.252403

O	1.299896	1.520872	-1.090347
H	3.867813	-0.372018	0.612744
H	3.372204	-1.987286	0.593535
H	1.419378	2.485924	-1.051458
H	1.077070	-2.170060	0.784133
H	1.331911	-0.695084	1.722162
H	1.779936	-0.988137	-1.308194
H	4.011395	-1.284465	-0.767898
F	-4.283708	0.488700	-0.307953

4-F-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra

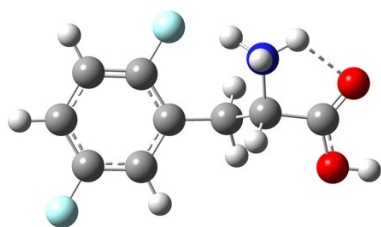


1000 1100 1200 1300 1400 1500 1600 1700 1800 1900

2,5-F₂-Phe•H⁺**Table S4 The Gibbs' Energies and Relative energies of 2,5-F₂-Phe•H⁺**

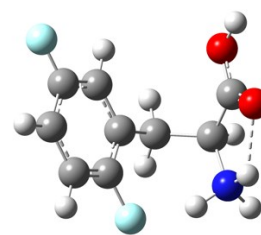
2,5F ₂ -Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-753.7125	0.00
Isomer 2	-753.7121	0.96
Isomer 3	-753.7080	11.66
Isomer 4	-753.7077	12.47
Isomer 5	-753.7048	20.09
Isomer 6	-753.7030	24.88
Isomer 7	-753.7022	26.98
Isomer 8	-753.6982	37.36
Isomer 9	-753.6977	38.77
Isomer 10	-753.6973	39.74
Isomer 11	-753.6849	72.36
Isomer 12	-753.6734	102.62
Isomer 13	-753.6724	105.16
Isomer 14	-753.6704	110.42
Isomer 15	-753.6701	111.16
Isomer 16	-753.6638	127.69
Isomer 17	-753.6615	133.81
Isomer 18	-753.6612	134.69
Isomer 19	-753.6597	138.49
Isomer 20	-753.6593	139.56
Isomer 21	-753.6587	141.26

2,5-F₂-Phe·H⁺: The XYZ atomic coordinates and structures



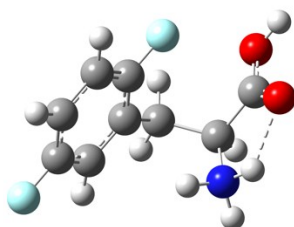
GM, 0.0kJ/mol

C	-2.556510	1.457101	-0.021589
C	-1.229358	1.189150	-0.293654
C	-0.688670	-0.089967	-0.375600
C	-1.563513	-1.158659	-0.152329
C	-2.898326	-0.904723	0.131307
C	-3.414394	0.382508	0.197221
H	-4.464491	0.534254	0.411053
C	0.764328	-0.326658	-0.734413
H	1.068967	0.316417	-1.566553
H	0.882943	-1.355654	-1.075986
C	1.754368	-0.141179	0.436973
H	1.420950	-0.711732	1.304832
N	1.881308	1.315858	0.851259
H	2.824470	1.623841	0.547023
H	1.157132	1.903330	0.409743
F	-0.371628	2.260365	-0.492933
F	-3.717367	-1.946172	0.339155
H	-2.909177	2.479928	0.013131
H	-1.223018	-2.185311	-0.217100
O	4.085523	0.233791	0.001601
C	3.182881	-0.564448	0.065332
O	3.261105	-1.863172	-0.172704
H	4.171529	-2.104947	-0.415973
H	1.824638	1.437427	1.864369



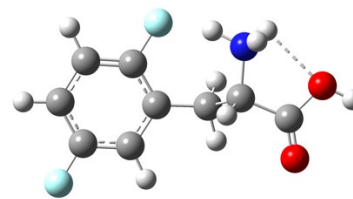
Isomer 2, 1.0kJ/mol

C	-2.101130	1.486706	-0.592284
C	-0.885653	1.393900	0.055795
C	-0.417173	0.245785	0.686558
C	-1.250059	-0.877823	0.643001
C	-2.471400	-0.802590	-0.012038
C	-2.916275	0.358481	-0.628944
H	-3.880170	0.375385	-1.120937
C	0.898920	0.220272	1.439385
H	0.911979	-0.641128	2.108508
H	0.995952	1.105087	2.075607
C	2.174241	0.109530	0.575458
H	3.037653	-0.009974	1.233252
N	2.421567	1.345267	-0.275661
H	3.260045	1.853158	0.010676
H	1.618288	1.992859	-0.243048
F	-0.070776	2.516472	0.080756
F	-3.250222	-1.894840	-0.039140
H	-2.402886	2.419068	-1.051933
H	-0.966461	-1.802625	1.130313
O	2.339110	-0.885241	-1.603496
C	2.170931	-1.057881	-0.421532
O	1.985589	-2.218696	0.185604
H	2.006803	-2.940938	-0.465774
H	2.544814	1.010762	-1.250841



Isomer 3, 11.7kJ/mol

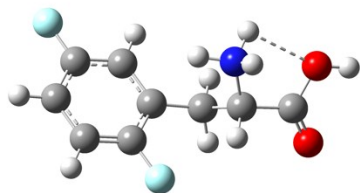
C	-1.677109	1.751035	0.398509
C	-0.559058	1.175632	-0.181628
C	-0.540017	-0.132122	-0.667202



Isomer 4, 12.5kJ/mol

C	-2.568700	1.460846	0.090558
C	-1.246479	1.206807	-0.214094
C	-0.706714	-0.064468	-0.376562

C	-1.719689	-0.882262	-0.541714	-1.581761	-1.142449	-0.203111
C	-2.839850	-0.309394	0.047630	-2.912990	-0.904476	0.110299
C	-2.840630	0.995652	0.518936	-3.426457	0.376809	0.257004
H	-3.737590	1.409393	0.961872	-4.473154	0.517302	0.493792
C	0.693500	-0.725240	-1.312932	0.740330	-0.300536	-0.762496
H	1.155906	-0.021680	-2.007551	1.014782	0.295498	-1.640377
H	0.405694	-1.603439	-1.894335	0.857810	-1.345860	-1.049804
C	1.794938	-1.151226	-0.306941	1.768894	-0.055206	0.364249
H	2.470395	-1.861739	-0.787241	1.367462	-0.410851	1.315220
N	1.201483	-1.827782	0.913946	2.051383	1.432298	0.544187
H	1.350273	-2.837949	0.931645	2.478009	1.630749	1.452640
H	1.657256	-1.385331	1.738134	2.714679	1.754794	-0.167631
F	0.574988	1.911267	-0.294683	-0.391696	2.293126	-0.361778
F	-3.956688	-1.046594	0.150766	-3.730336	-1.955471	0.269128
H	-1.633022	2.776124	0.744112	-2.918041	2.480460	0.190703
H	-1.792471	-1.887438	-0.942878	-1.241541	-2.163904	-0.324849
O	2.751339	0.163123	1.456826	3.108437	-2.000995	-0.026202
C	2.659731	-0.016922	0.266047	3.075708	-0.816681	0.106776
O	3.286755	0.645434	-0.686291	4.136650	0.017212	0.050306
H	3.822666	1.359894	-0.301588	4.947000	-0.494340	-0.115794
H	0.190162	-1.634775	0.966947	1.179912	1.977556	0.442079

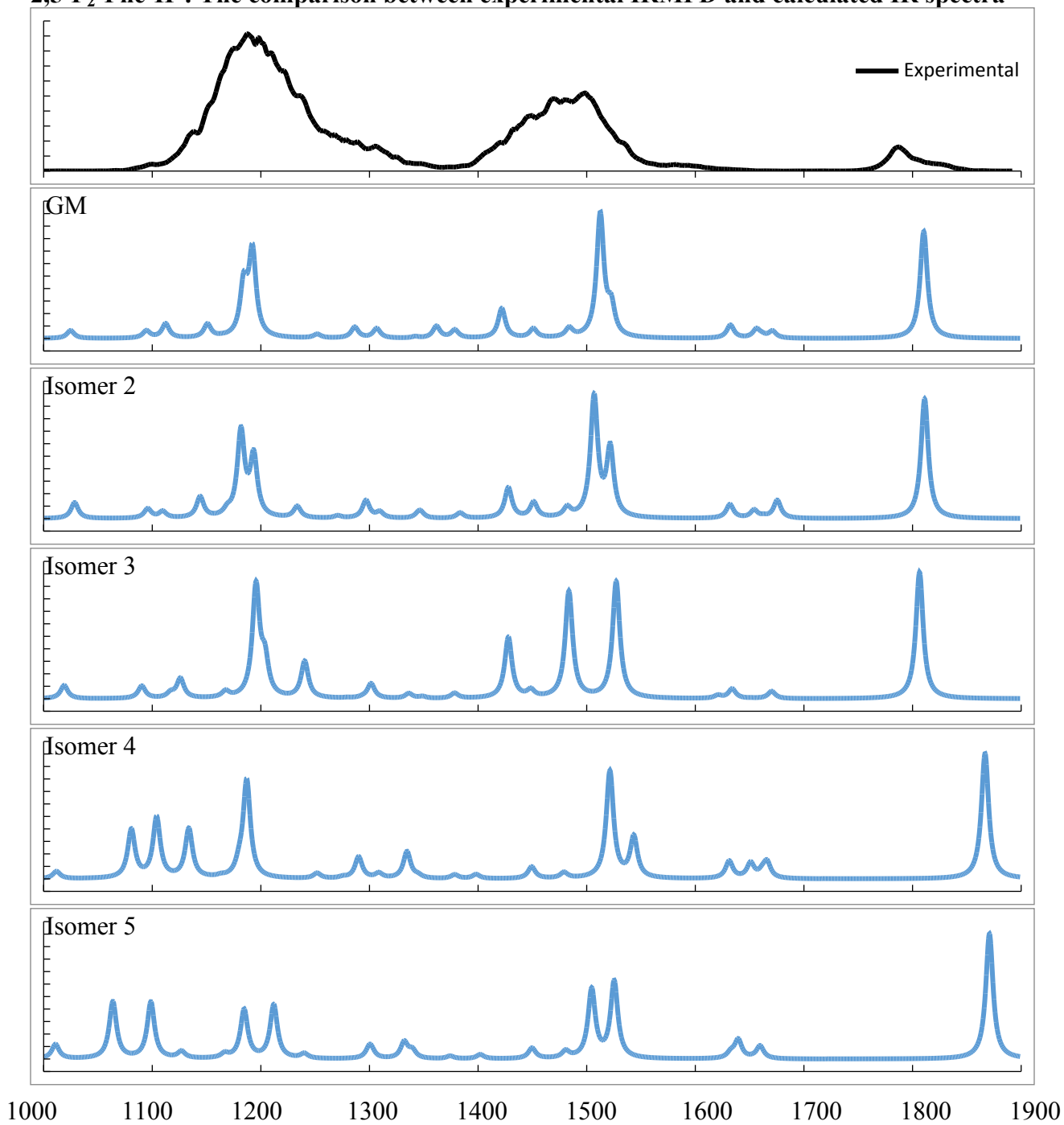


Isomer 5, 20.1kJ/mol

C	2.486652	1.463671	0.415525
C	1.165468	1.298207	0.036205
C	0.658731	0.094212	-0.457490
C	1.544995	-0.987550	-0.554052
C	2.869925	-0.824461	-0.170183
C	3.358079	0.382189	0.310944
H	4.400352	0.469980	0.589989
C	-0.785808	-0.025460	-0.890433
H	-0.945751	-0.985322	-1.389721
H	-1.050126	0.755150	-1.607664
C	-1.776498	0.127005	0.285098
H	-1.686190	1.125147	0.714552
N	-1.413885	-0.854980	1.393310
H	-0.390940	-0.869475	1.508964

H	-1.845665	-0.602015	2.286143
F	0.311426	2.349315	0.141161
F	3.701092	-1.873089	-0.276749
H	2.824189	2.426949	0.776698
H	1.227275	-1.940523	-0.962060
O	-3.766420	0.668098	-0.922809
C	-3.220896	-0.076684	-0.169653
O	-3.752590	-1.201597	0.362433
H	-4.661340	-1.320469	0.037040
H	-1.739079	-1.799377	1.160430

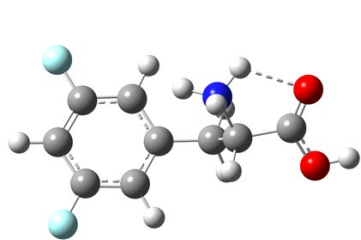
2,5-F₂-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra



3,5-F₂-Phe•H⁺**Table S5 The Gibbs' Energies and Relative energies of 3,5-F₂-Phe•H⁺**

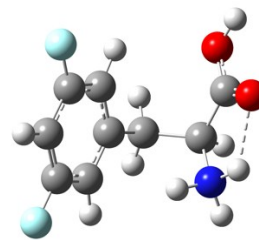
3,5F ₂ -Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-753.7084	0.00
Isomer 2	-753.7072	3.30
Isomer 3	-753.7032	13.61
Isomer 4	-753.7023	16.18
Isomer 5	-753.7015	18.16
Isomer 6	-753.6952	34.73
Isomer 7	-753.6946	36.23
Isomer 8	-753.6934	39.49
Isomer 9	-753.6933	39.69

3,5-F₂-Phe·H⁺: The XYZ atomic coordinates and structures



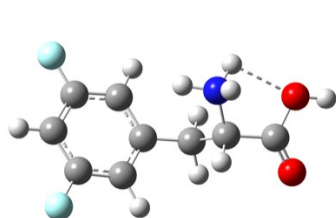
GM, 0.0kJ/mol

C	0.442806	0.131170	-0.564933
C	1.110927	-1.100771	-0.567738
C	2.455301	-1.138344	-0.202047
C	3.159645	-0.006390	0.170936
C	2.465424	1.196760	0.161867
C	1.125493	1.292914	-0.191461
H	0.637493	-2.012445	-0.915916
H	4.206182	-0.053145	0.441988
H	0.651536	2.267356	-0.198376
C	-1.029694	0.184865	-0.912410
H	-1.264916	1.066496	-1.511614
H	-1.313458	-0.690453	-1.503928
C	-1.918146	0.257727	0.354923
H	-1.752302	1.197366	0.881671
C	-3.402435	0.073191	0.029118
N	-1.574517	-0.872876	1.304162
H	-2.240782	-1.643348	1.123506
H	-0.601703	-1.182190	1.155210
O	-3.986820	-0.947678	0.296681
O	-3.898977	1.133259	-0.587119
H	-4.832668	0.982254	-0.815580
F	3.087683	-2.318488	-0.220658
H	-1.682693	-0.602007	2.284570
F	3.117360	2.312808	0.507693



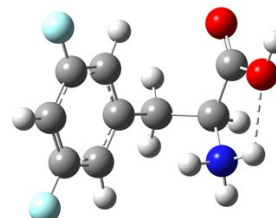
Isomer 2, 3.3kJ/mol

0.281371	-0.278307	0.819315
1.253585	-1.234190	0.488993
2.446259	-0.811243	-0.093831
2.713791	0.519808	-0.365206
1.732211	1.439159	-0.020257
0.523891	1.073725	0.560531
1.142638	-2.281969	0.747868
3.650224	0.831443	-0.808849
-0.186322	1.845831	0.828478
-1.038893	-0.730778	1.407386
-0.909767	-1.673430	1.945220
-1.424253	-0.007161	2.127328
-2.139139	-0.929827	0.338091
-2.997157	-1.442602	0.779555
-2.670830	0.348131	-0.329284
-1.643091	-1.779226	-0.815595
-0.613234	-1.710814	-0.876760
-2.041089	-1.373542	-1.683234
-2.754303	0.447436	-1.528550
-3.044030	1.251940	0.562217
-3.427007	2.024440	0.111409
3.370945	-1.732835	-0.392928
-1.904884	-2.763084	-0.733064
1.960798	2.736344	-0.255133



Isomer 3, 13.6kJ/mol

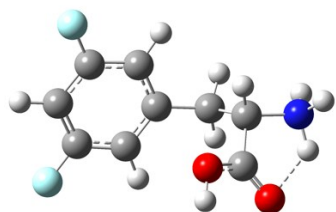
C	0.451478	0.125127	-0.568645
C	1.119201	-1.107092	-0.559216
C	2.460916	-1.143440	-0.184633



Isomer 4, 16.2kJ/mol

0.286127	-0.276682	0.829140
1.230616	-1.247843	0.462879
2.419331	-0.842060	-0.138878

C	3.163758	-0.009787	0.185932	2.709961	0.486999	-0.395597
C	2.470443	1.193786	0.165480	1.755513	1.421517	-0.016315
C	1.132947	1.288645	-0.197464	0.551582	1.074656	0.585131
H	0.647803	-2.020867	-0.904451	1.103321	-2.297001	0.708172
H	4.208504	-0.055637	0.463987	3.643767	0.785551	-0.853559
H	0.659485	2.263269	-0.214378	-0.139362	1.855699	0.876289
C	-1.018012	0.183867	-0.929670	-1.028108	-0.708831	1.448784
H	-1.247968	1.072302	-1.521040	-0.904652	-1.653797	1.984388
H	-1.302225	-0.684046	-1.532371	-1.385780	0.024499	2.173272
C	-1.912699	0.256604	0.330220	-2.155146	-0.874102	0.407584
H	-1.680495	1.157374	0.899088	-3.021429	-1.362199	0.862105
C	-3.396324	0.289758	-0.037125	-2.660272	0.463181	-0.154237
N	-1.603975	-0.922141	1.244331	-1.698256	-1.777990	-0.730806
H	-1.901043	-0.751010	2.208629	-0.704406	-1.580352	-0.937644
H	-2.096414	-1.762190	0.920784	-2.249766	-1.597736	-1.577637
O	-3.905433	1.234831	-0.554680	-2.851179	1.419490	0.531242
O	-4.005169	-0.879640	0.262575	-2.899040	0.380671	-1.480855
H	-4.937215	-0.847187	-0.013398	-3.263179	1.221346	-1.806862
F	3.092198	-2.324787	-0.191403	3.317253	-1.779261	-0.472358
H	-0.586716	-1.099955	1.232632	-1.773895	-2.767668	-0.482505
F	3.120989	2.311076	0.508933	2.008002	2.716514	-0.239244

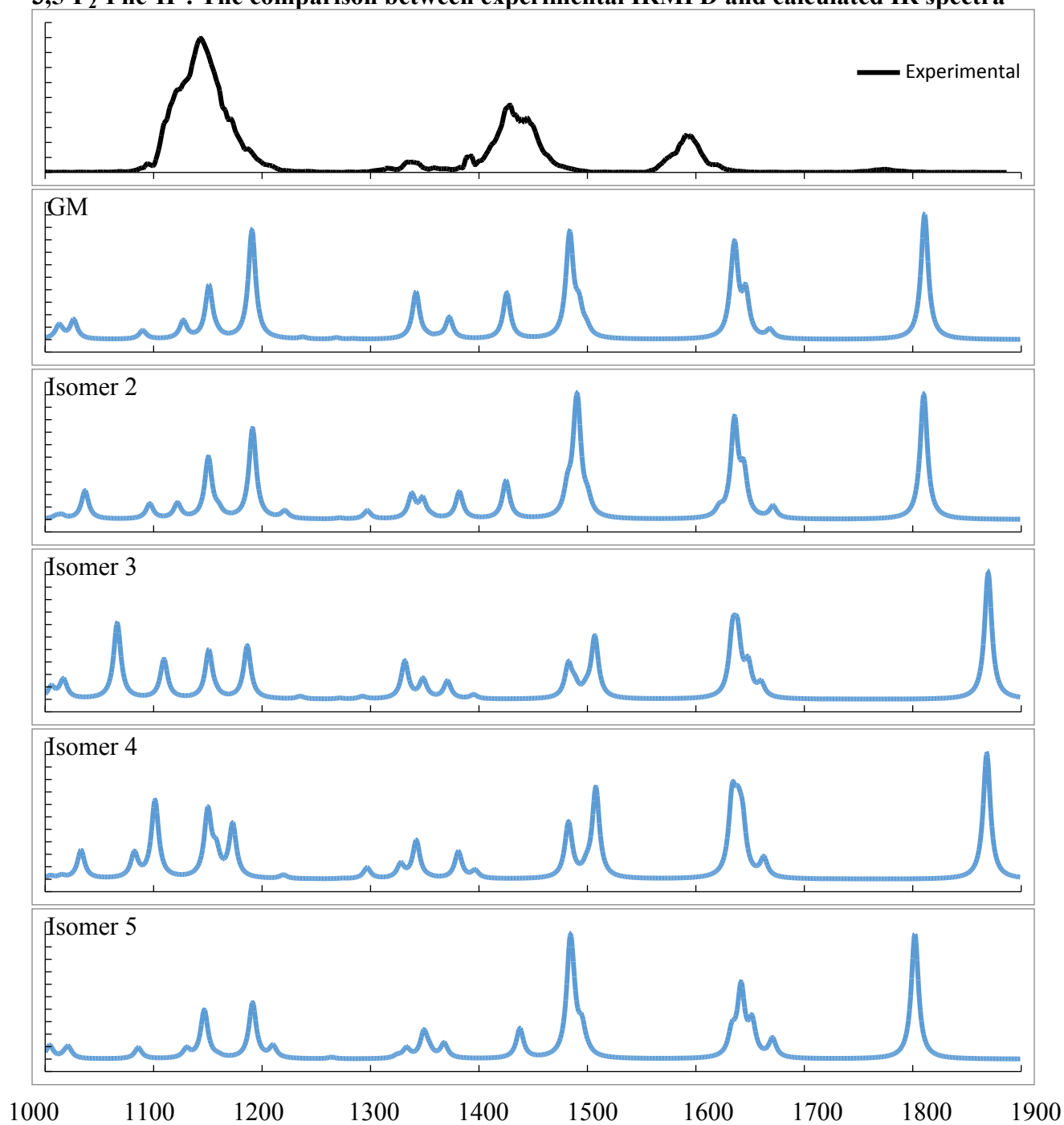


Isomer 5, 18.2kJ/mol

C	0.301145	-0.299655	-0.705094
C	1.037881	-1.351845	-0.154249
C	2.327294	-1.100558	0.293004
C	2.919954	0.151007	0.211144
C	2.161953	1.166970	-0.348487
C	0.865618	0.972298	-0.809763
H	0.646778	-2.359967	-0.081551
H	3.929923	0.322880	0.558919
H	0.332445	1.805871	-1.250595
C	-1.109897	-0.543188	-1.198421
H	-1.429755	0.283663	-1.839977
H	-1.130046	-1.457319	-1.803371
C	-2.143597	-0.721132	-0.059028
H	-1.872190	-1.551741	0.591729

C	-2.379258	0.559867	0.753618
N	-3.508386	-1.017014	-0.669499
H	-3.987365	-0.101429	-0.765778
H	-3.434143	-1.474420	-1.581781
O	-3.306387	1.291397	0.496043
O	-1.475597	0.730670	1.697345
H	-1.629963	1.572065	2.161821
F	3.031823	-2.113522	0.820216
H	-4.088412	-1.602488	-0.062034
F	2.700482	2.391618	-0.451808

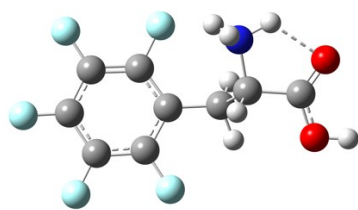
3,5-F₂-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra



F₅-Phe•H⁺**Table S6 The Gibbs' Energies and Relative energies of F₅-Phe•H⁺**

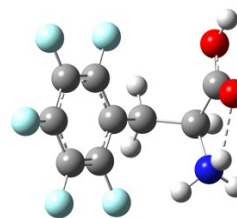
F ₅ -Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-1051.5014	0.00
Isomer 2	-1051.5008	1.52
Isomer 3	-1051.4970	11.40
Isomer 4	-1051.4955	15.45
Isomer 5	-1051.4942	18.91
Isomer 6	-1051.4916	25.72
Isomer 7	-1051.4876	36.22
Isomer 8	-1051.4875	36.39
Isomer 9	-1051.4741	71.61
Isomer 10	-1051.4606	107.00
Isomer 11	-1051.4584	112.68
Isomer 12	-1051.4549	122.02
Isomer 13	-1051.4546	122.88
Isomer 14	-1051.4538	124.99
Isomer 15	-1051.4535	125.72
Isomer 16	-1051.4533	126.28
Isomer 17	-1051.4527	127.74

F₅-Phe·H⁺: The XYZ atomic coordinates and structures



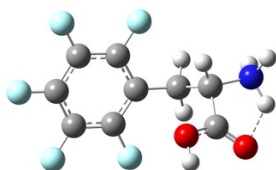
GM, 0.0kJ/mol

C	0.114314	0.143849	-0.378838
C	0.883675	1.282326	-0.136403
C	2.252094	1.211321	0.104018
C	2.885594	-0.029379	0.111712
C	2.146783	-1.189531	-0.116840
C	0.786272	-1.074887	-0.353051
C	-1.356563	0.247040	-0.719133
H	-1.569319	1.259375	-1.063370
H	-1.601881	-0.426820	-1.545643
C	-2.312634	-0.021644	0.462466
H	-2.038501	0.594884	1.319600
C	-3.782756	0.245121	0.097681
N	-2.290165	-1.478503	0.902451
H	-3.227289	-1.862074	0.664830
H	-2.153599	-1.580031	1.910439
O	-4.601627	-0.641340	0.092463
O	-3.988528	1.515315	-0.197377
H	-4.922360	1.662781	-0.428202
F	2.952541	2.313964	0.325334
F	0.296097	2.484814	-0.145835
F	0.067052	-2.217383	-0.558784
F	2.736468	-2.377767	-0.098542
F	4.183895	-0.109835	0.346031
H	-1.559821	-2.019835	0.421008



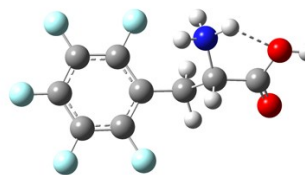
Isomer 2, 1.5kJ/mol

-0.091575	0.121049	-0.741027
0.465615	-1.141865	-0.538126
1.754949	-1.310976	-0.043865
2.525633	-0.193114	0.265945
2.001185	1.085393	0.080795
0.713367	1.209657	-0.414486
-1.460133	0.299382	-1.366036
-1.426555	1.099366	-2.110210
-1.735086	-0.611563	-1.899248
-2.622586	0.596234	-0.391103
-3.541248	0.714339	-0.967366
-2.829777	-0.492380	0.672233
-2.403306	1.873912	0.404972
-3.225172	2.481871	0.391995
-2.240992	1.576930	1.387633
-2.621903	-0.278556	1.841874
-3.239540	-1.623590	0.130986
-3.337935	-2.311714	0.811805
2.250235	-2.527238	0.133511
-0.250391	-2.233150	-0.837711
0.205093	2.466164	-0.581191
2.720923	2.158215	0.381493
3.749000	-0.341746	0.742959
-1.592133	2.410065	0.070195



Isomer 3, 11.4kJ/mol

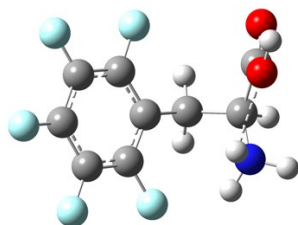
C	0.014312	0.214514	-0.642429
C	-0.596236	-1.036952	-0.639601
C	-1.915862	-1.208693	-0.240840
C	-2.653894	-0.102617	0.174499
C	-2.069324	1.162829	0.189493



Isomer 4, 15.4kJ/mol

0.120166	0.188809	-0.399047
0.918711	1.296276	-0.110879
2.280938	1.176507	0.143391
2.876624	-0.083130	0.117447
2.107388	-1.213032	-0.156820

C	-0.750555	1.298685	-0.217883	0.752196	-1.053386	-0.405378
C	1.430907	0.411466	-1.119366	-1.339851	0.334378	-0.763894
H	1.751440	-0.460546	-1.694046	-1.529563	1.337557	-1.146384
H	1.453846	1.281100	-1.784463	-1.594713	-0.359654	-1.569824
C	2.438065	0.678236	0.028668	-2.312483	0.133756	0.408673
H	2.082576	1.485841	0.667981	-2.104316	0.850409	1.208113
C	2.770223	-0.571548	0.857995	-3.773513	0.348596	-0.015783
N	3.781376	1.094345	-0.555007	-2.148123	-1.246147	1.042047
H	4.222748	1.843010	-0.014389	-2.976303	-1.478348	1.602534
H	3.707763	1.405077	-1.527146	-1.315098	-1.279283	1.636691
O	3.831524	-1.134955	0.733894	-4.106514	1.209087	-0.768632
O	1.781205	-0.918347	1.658570	-4.592198	-0.530294	0.602654
H	2.011734	-1.731535	2.141985	-5.517064	-0.353727	0.358495
F	-2.470622	-2.414861	-0.247163	3.011742	2.248963	0.410139
F	0.108011	-2.112849	-1.024903	0.364586	2.513769	-0.087498
F	-0.181040	2.520281	-0.200363	0.003703	-2.160110	-0.659823
F	-2.768556	2.218057	0.589113	2.663693	-2.417762	-0.170971
F	-3.910217	-0.253790	0.561539	4.168892	-0.209783	0.364973
H	4.394415	0.256000	-0.491826	-2.030980	-1.972612	0.326238

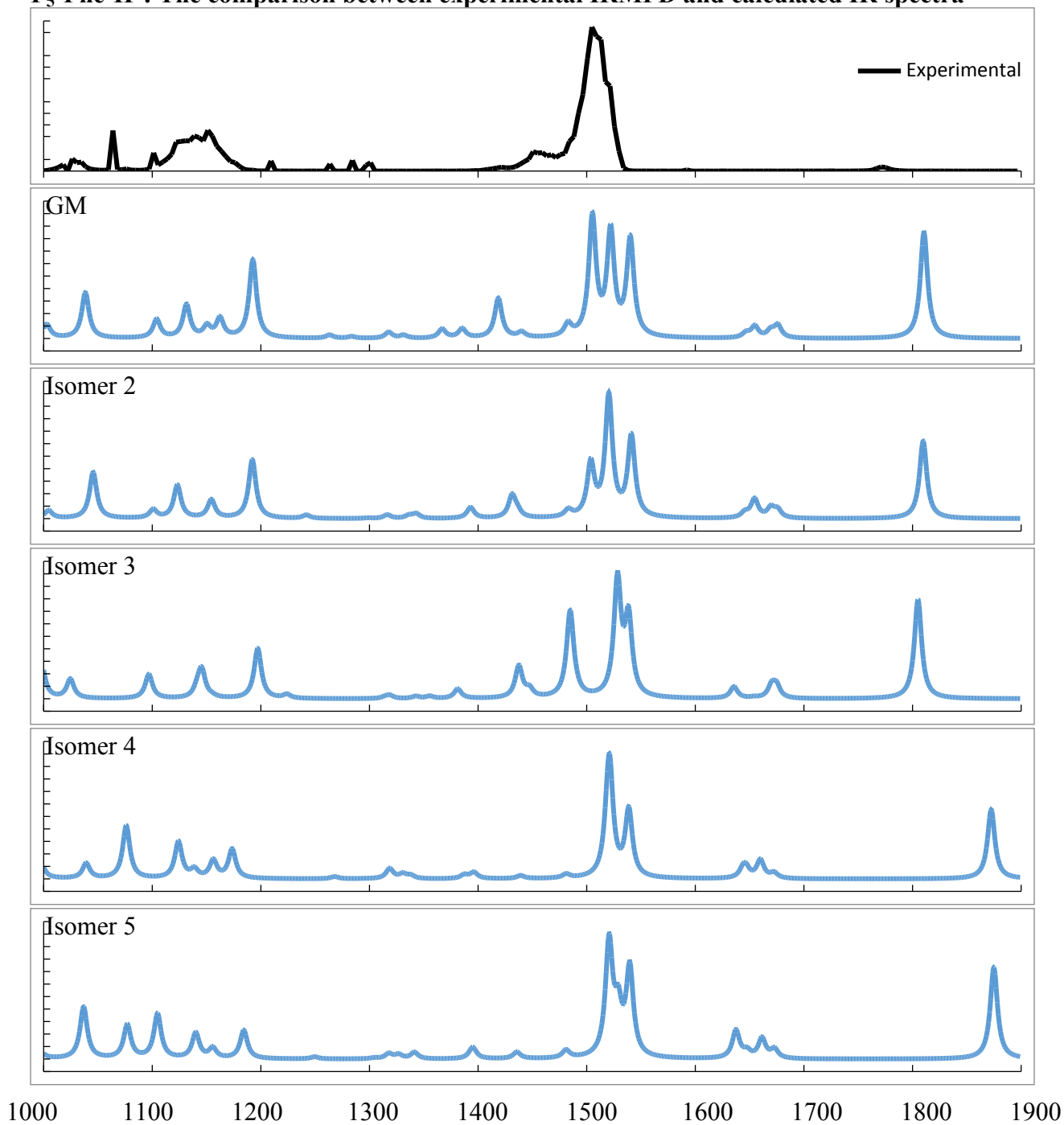


Isomer 5, 18.9kJ/mol

C	-0.073954	0.152463	-0.726360
C	0.432062	-1.132821	-0.527754
C	1.718628	-1.352046	-0.045571
C	2.535734	-0.264726	0.255934
C	2.061656	1.033990	0.075532
C	0.774729	1.211483	-0.408124
C	-1.432881	0.394907	-1.347838
H	-1.366665	1.221448	-2.059699
H	-1.743880	-0.484747	-1.913611
C	-2.585142	0.696489	-0.363246
H	-3.457382	1.017147	-0.934822
C	-3.003447	-0.533948	0.450983
N	-2.226570	1.851066	0.569704
H	-1.660553	1.501988	1.351787
H	-1.683758	2.572858	0.080411
O	-3.534021	-1.474697	-0.050015

O	-2.678605	-0.398827	1.755774
H	-2.938621	-1.198372	2.245081
F	2.168013	-2.586181	0.129599
F	-0.331107	-2.191016	-0.819134
F	0.316221	2.483143	-0.575830
F	2.827834	2.076682	0.369349
F	3.756401	-0.461995	0.722638
H	-3.062704	2.279976	0.975928

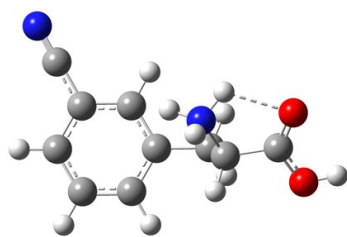
F₅-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra



3-CN-Phe•H⁺**Table S7 The Gibbs' Energies and Relative energies of 3-CN-Phe•H⁺**

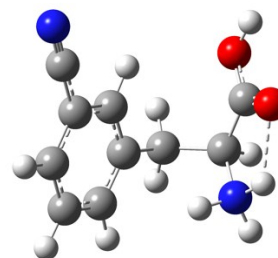
3CN-Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-647.4213	0.00
Isomer 2	-647.4197	4.15
Isomer 3	-647.4164	12.86
Isomer 4	-647.4160	13.93
Isomer 5	-647.4152	15.96
Isomer 6	-647.4075	36.28
Isomer 7	-647.4071	37.42
Isomer 8	-647.4066	38.65
Isomer 9	-647.4057	41.07

3-CN-Phe·H⁺: The XYZ atomic coordinates and structures



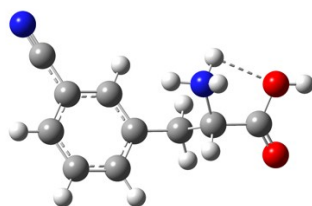
Isomer 1, 0.0kJ/mol

C	0.828636	1.880264	0.061430
C	2.148073	2.081550	0.455901
C	3.076220	1.045703	0.374338
C	2.678237	-0.201323	-0.119576
C	1.348389	-0.401094	-0.528079
C	0.415948	0.635044	-0.433974
H	0.123999	2.703978	0.115752
H	2.459739	3.052386	0.821573
H	4.103605	1.200084	0.679110
H	1.073103	-1.357395	-0.962360
C	-1.024094	0.394948	-0.836358
H	-1.436195	1.256396	-1.365759
H	-1.092930	-0.459773	-1.516080
C	-1.941076	0.148471	0.387645
C	-3.344359	-0.301700	-0.026862
C	3.612688	-1.281079	-0.216765
N	4.349130	-2.167434	-0.286756
O	-4.038556	0.695625	-0.550253
H	-4.912669	0.380760	-0.839442
O	-3.705569	-1.445244	0.102194
H	-1.990084	1.039621	1.013430
N	-1.395452	-0.983272	1.235960
H	-1.612077	-0.862633	2.228528
H	-0.372935	-1.050860	1.131303
H	-1.858270	-1.855370	0.927775



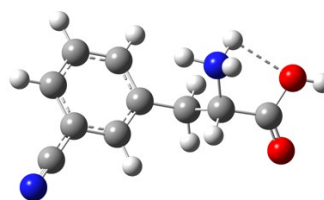
Isomer 2, 4.1kJ/mol

	-0.184179	-0.872393	-0.695920
	-0.907969	0.316886	-0.577798
	-2.190326	0.312685	-0.014769
	-2.761265	-0.888189	0.431695
	-2.049360	-2.074347	0.303605
	-0.770235	-2.069106	-0.256180
	-0.498157	1.251122	-0.943290
	-3.756064	-0.883672	0.858915
	-2.495878	-3.008016	0.623316
	-0.249876	-3.012541	-0.397896
	-2.912009	1.544164	0.097459
	-3.478611	2.545601	0.190429
	1.218390	-0.873672	-1.270095
	1.466453	-1.866575	-1.654086
	1.306890	-0.182345	-2.110061
	2.301256	-0.468919	-0.242888
	3.294253	-0.686716	-0.643732
	2.306513	1.004149	0.196168
	2.153234	-1.244794	1.051840
	1.172652	-1.546081	1.163973
	2.759691	-2.065188	1.101523
	2.341265	1.314754	1.361383
	2.312319	1.828316	-0.838365
	2.371742	2.749560	-0.530378
	2.372378	-0.587299	1.824026



Isomer 3, 12.9kJ/mol

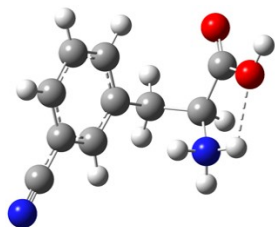
C	0.840367	1.881946	0.055479
C	2.158047	2.078580	0.458475



Isomer 4, 13.9kJ/mol

	-0.888855	1.783905	-0.519045
	-2.214485	2.067996	-0.184919

C	3.082523	1.039007	0.384759	-3.107519	1.035960	0.074242
C	2.682451	-0.207464	-0.109250	-2.671220	-0.295213	-0.008546
C	1.354797	-0.402173	-0.526566	-1.343128	-0.579795	-0.349303
C	0.425512	0.637459	-0.440674	-0.441516	0.458147	-0.603066
H	0.138502	2.708427	0.103161	-0.213283	2.600548	-0.755933
H	2.471011	3.048976	0.824158	-2.551872	3.096339	-0.140450
H	4.108512	1.189679	0.696047	-4.138195	1.247578	0.329510
H	1.079064	-1.358341	-0.960748	-1.034685	-1.616172	-0.436581
C	-1.013713	0.407989	-0.853404	1.001691	0.149995	-0.949655
H	-1.423678	1.280237	-1.366696	1.072163	-0.634407	-1.706609
H	-1.086649	-0.433499	-1.549572	1.492353	1.035496	-1.365259
C	-1.932832	0.152087	0.363813	1.799047	-0.357766	0.273169
C	-3.380920	-0.083775	-0.066525	3.263207	-0.620564	-0.079042
C	3.611307	-1.292897	-0.196687	-3.578374	-1.371295	0.254276
N	4.340870	-2.185565	-0.258446	-4.298706	-2.245357	0.477138
O	-3.737694	-1.377769	0.091869	4.077980	0.302085	0.480717
H	-4.648723	-1.510561	-0.221907	4.998437	0.133597	0.215347
O	-4.063709	0.785020	-0.513007	3.598561	-1.516624	-0.789258
H	-1.911304	1.011471	1.034966	1.365283	-1.286995	0.644286
N	-1.405163	-1.031211	1.165018	1.686050	0.650092	1.410293
H	-0.377472	-0.968833	1.223786	2.315938	1.443570	1.249249
H	-1.790718	-1.058289	2.112837	1.941504	0.242372	2.313805
H	-1.662503	-1.914391	0.710542	0.715543	0.993017	1.460282

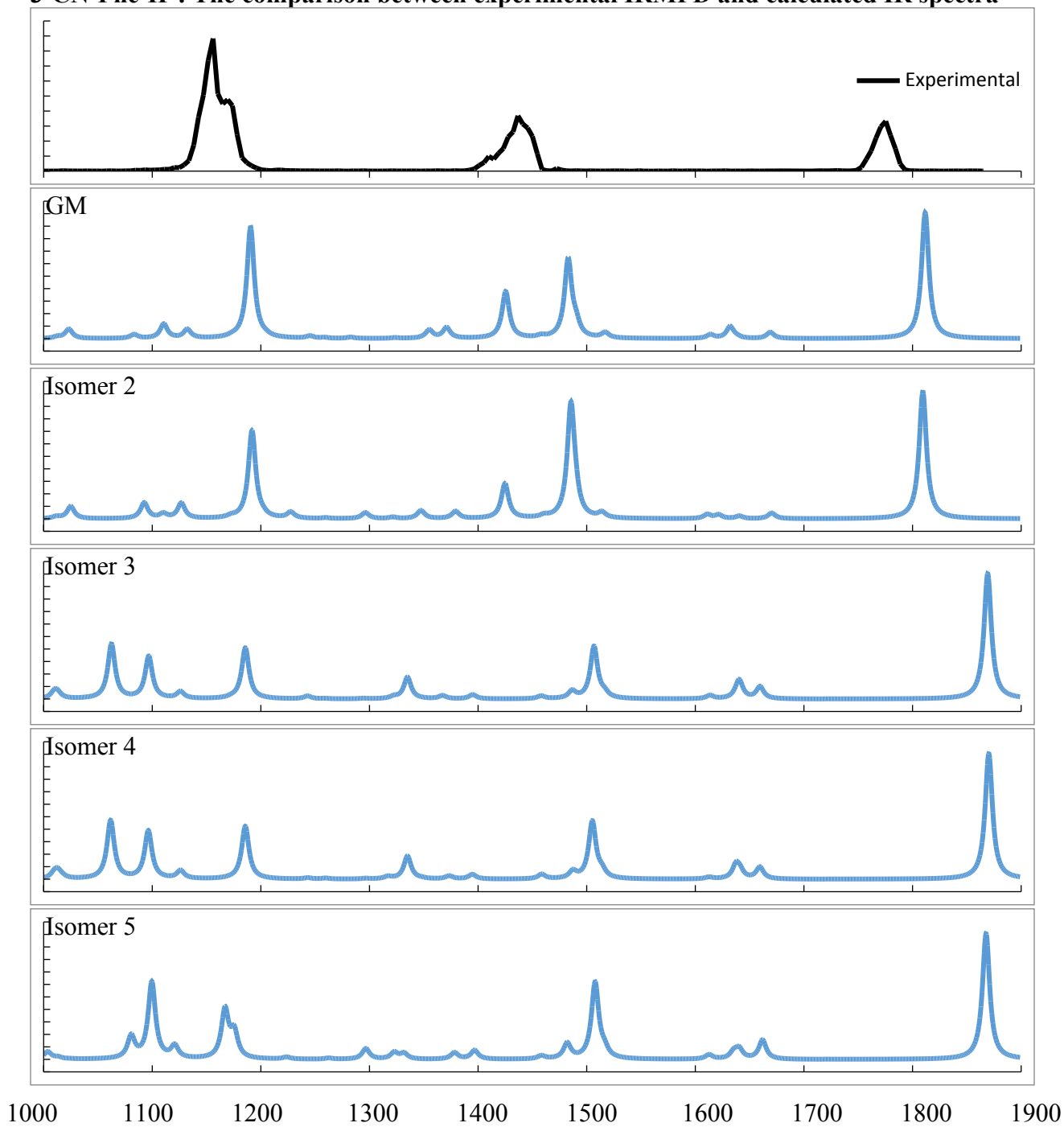


Isomer 5, 16.0kJ/mol

C	0.169805	1.621606	0.352907
C	1.272710	2.159183	-0.305988
C	2.415499	1.392712	-0.519157
C	2.458828	0.074559	-0.051145
C	1.351806	-0.463492	0.625704
C	0.196469	0.299635	0.821837
H	-0.705868	2.237269	0.523629
H	1.245699	3.186467	-0.648674
H	3.273783	1.810089	-1.030445
H	1.433983	-1.463398	1.041935
C	-1.001605	-0.311792	1.521925
H	-0.679398	-1.082449	2.227749

H	-1.546916	0.437313	2.098479
C	-2.024835	-0.933960	0.549422
C	-2.799961	0.109428	-0.268660
C	3.621172	-0.736809	-0.249002
N	4.540805	-1.415076	-0.414231
O	-2.988400	-0.306040	-1.539793
H	-3.526218	0.341828	-2.026182
O	-3.209850	1.125397	0.201362
H	-2.773147	-1.506620	1.104190
N	-1.339903	-1.921142	-0.387713
H	-0.433377	-1.528974	-0.688319
H	-1.154625	-2.815141	0.074773
H	-1.913545	-2.084134	-1.223129

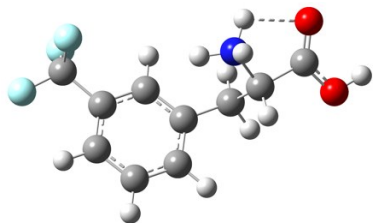
3-CN-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra



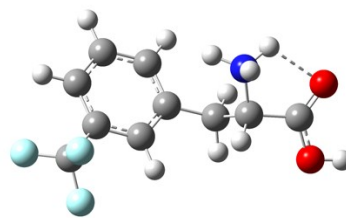
3-CF₃-Phe•H⁺**Table S8 The Gibbs' Energies and Relative energies of 3-CF₃-Phe•H⁺**

3CF ₃ -Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-892.3060	0.00
Isomer 2	-892.3055	1.24
Isomer 3	-892.3051	2.32
Isomer 4	-892.3041	4.98
Isomer 5	-892.3010	13.15
Isomer 6	-892.3004	14.78
Isomer 7	-892.3003	14.96
Isomer 8	-892.2991	18.20
Isomer 9	-892.2990	18.37
Isomer 10	-892.2929	34.30
Isomer 11	-892.2921	36.54
Isomer 12	-892.2915	37.96
Isomer 13	-892.2915	38.12
Isomer 14	-892.2907	40.16
Isomer 15	-892.2901	41.63
Isomer 16	-892.2822	62.51

3-CF₃-Phe·H⁺: The XYZ atomic coordinates and structures

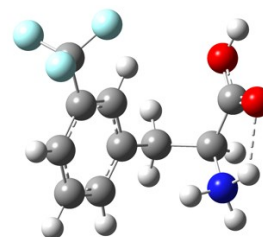
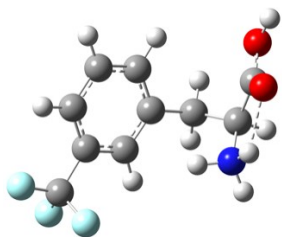


GM, 0.0kJ/mol

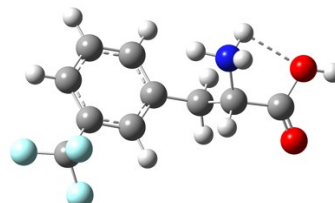
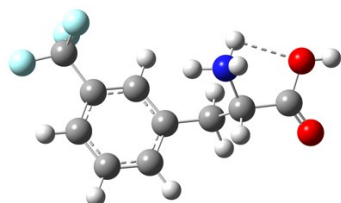


Isomer 2, 1.2kJ/mol

C	0.033473	2.178054	-0.045484	0.004228	2.084672	-0.515758
C	0.307606	0.888658	0.433958	0.291411	0.719117	-0.645565
C	-0.730804	-0.044140	0.499879	-0.736231	-0.211345	-0.456881
C	-2.282541	1.579049	-0.400712	-2.301925	1.580277	-0.005610
C	-1.251504	2.519865	-0.450505	-1.286934	2.511236	-0.201282
H	0.820829	2.924431	-0.077921	0.778480	2.822853	-0.703873
H	-0.559892	-1.027567	0.928395	-0.548948	-1.272113	-0.585008
H	-1.457935	3.523615	-0.801593	-1.502269	3.569919	-0.123142
C	1.710111	0.488287	0.838763	1.699596	0.256484	-0.958346
C	2.590012	0.136219	-0.387681	2.390402	-0.376802	0.275074
C	3.928833	-0.480692	0.023369	3.885644	-0.606397	0.045135
N	1.910208	-0.917488	-1.239182	2.309614	0.564813	1.460645
O	4.150470	-1.659012	-0.108511	4.720370	0.094677	0.562449
O	4.738971	0.424413	0.548684	4.099750	-1.610043	-0.789547
H	1.681661	-0.368018	1.519378	2.302444	1.094780	-1.319893
H	2.219408	1.297769	1.365399	1.705837	-0.502229	-1.743928
H	2.744869	1.017509	-1.010170	1.895477	-1.306632	0.554883
C	-3.096002	-0.758904	0.114416	-3.101070	-0.808259	0.120729
H	-3.283024	1.845550	-0.716115	-3.306950	1.906233	0.230374
C	-2.018861	0.300344	0.076037	-2.021568	0.219365	-0.137630
F	-3.096436	-1.419187	1.290115	-3.068226	-1.213928	1.414201
F	-2.877795	-1.687190	-0.854719	-2.932947	-1.907741	-0.640744
F	-4.320324	-0.253487	-0.080198	-4.328324	-0.322191	-0.116839
H	0.886506	-0.858530	-1.134099	3.185935	1.113678	1.482207
H	2.261143	-1.840985	-0.934152	2.243817	0.063567	2.349986
H	2.140055	-0.821071	-2.231322	1.488455	1.180051	1.371406
H	5.568456	0.004831	0.836074	5.053616	-1.716212	-0.949503

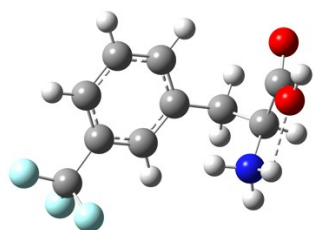


	Isomer 3, 2.3kJ/mol			Isomer 4, 5.0kJ/mol		
C	-0.642484	1.719359	0.340143	-0.258191	2.377311	-0.270422
C	-0.504978	0.416453	0.841685	-0.580380	1.084184	-0.707549
C	0.726590	-0.231197	0.704683	0.377895	0.072271	-0.585051
C	1.644660	1.686792	-0.447728	1.932458	1.633461	0.420669
C	0.424893	2.347964	-0.291018	0.990381	2.648801	0.290837
H	-1.578142	2.252653	0.467870	-0.964936	3.190733	-0.411918
H	0.884887	-1.209289	1.150871	0.166659	-0.928149	-0.943432
H	0.313114	3.360200	-0.660120	1.232240	3.654615	0.612035
C	-1.664872	-0.306887	1.493471	-1.953613	0.787848	-1.275044
C	-2.580243	-1.029744	0.475700	-2.918499	0.164392	-0.239503
C	-3.434811	-0.125243	-0.424546	-2.607579	-1.275518	0.199046
N	-1.775989	-1.875399	-0.492169	-2.924311	0.956178	1.053792
O	-4.125836	0.758878	0.277792	-2.567933	-1.585449	1.364357
O	-3.468038	-0.271224	-1.621504	-2.444510	-2.083575	-0.835438
H	-2.232935	-1.797658	-1.419254	-1.898516	0.091787	-2.113939
H	-2.300034	0.379127	2.056231	-2.409554	1.704810	-1.657441
H	-1.295407	-1.049369	2.205674	-3.938914	0.166904	-0.630549
H	-3.266162	-1.697585	1.002586	2.660860	-0.750236	0.053418
C	3.085197	-0.365987	-0.107444	2.902564	1.838203	0.855581
H	2.474242	2.175908	-0.941559	1.621721	0.347165	-0.022176
C	1.792127	0.398905	0.053452	2.084117	-1.966468	0.180917
F	4.068784	0.386374	-0.614845	3.489476	-0.579890	1.097789
F	2.905514	-1.424174	-0.942943	3.414942	-0.782566	-1.064199
F	3.507791	-0.871195	1.069651	-2.994168	0.269379	1.828139
H	-1.708955	-2.855259	-0.211199	-3.687510	1.632646	1.108919
H	-0.822178	-1.488214	-0.579636	-2.026072	1.454890	1.154795
H	-4.700794	1.274508	-0.313735	-2.299210	-2.994635	-0.525990



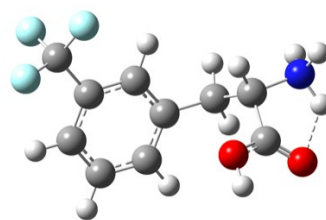
	Isomer 5, 13.2kJ/mol			Isomer 6, 14.8kJ/mol		
C	0.023108	2.184705	-0.038673	-0.011873	2.107276	-0.493025
C	0.299626	0.896600	0.443545	0.285195	0.745655	-0.640189
C	-0.736067	-0.039515	0.504063	-0.735712	-0.194413	-0.459276
C	-2.288615	1.576883	-0.407007	-2.312800	1.580305	0.017477
C	-1.260868	2.521412	-0.451429	-1.304829	2.520797	-0.170407
H	0.808167	2.933638	-0.066949	0.757152	2.853015	-0.671896
H	-0.564532	-1.022058	0.934254	-0.542091	-1.252122	-0.603125

H	-1.468802	3.524250	-0.804172	-1.527637	3.576904	-0.079409
C	1.702963	0.506289	0.856490	1.692961	0.293157	-0.972387
C	2.580076	0.140022	-0.364641	2.383385	-0.380956	0.235723
C	3.989482	-0.271328	0.060336	3.824676	-0.774044	-0.085555
N	1.908341	-0.968866	-1.164031	2.329036	0.553416	1.437785
O	4.778444	0.508050	0.497177	4.094305	-1.656734	-0.839408
O	4.181486	-1.601167	-0.088728	4.708152	0.024806	0.555217
H	1.680750	-0.335413	1.555857	2.296476	1.139571	-1.314194
H	2.213671	1.327471	1.363436	1.697893	-0.444663	-1.777917
H	2.660841	0.996555	-1.034823	1.839558	-1.281295	0.523362
C	-3.094274	-0.765302	0.102933	-3.094238	-0.814980	0.121259
H	-3.288206	1.839225	-0.728710	-3.319409	1.896427	0.260037
C	-2.022666	0.299327	0.071987	-2.023117	0.223180	-0.130056
F	-3.101411	-1.424500	1.279436	-3.054041	-1.232604	1.410935
F	-2.861503	-1.694873	-0.862746	-2.920804	-1.905394	-0.651159
F	-4.319537	-0.268175	-0.103930	-4.325741	-0.335146	-0.107186
H	2.062829	-1.878033	-0.714377	2.494195	0.059450	2.318857
H	0.894121	-0.784373	-1.211777	1.399957	0.998930	1.472245
H	2.278527	-1.037457	-2.115735	3.048829	1.279996	1.359105
H	5.070265	-1.843433	0.223161	5.615548	-0.222267	0.307277



Isomer 7, 15.0kJ/mol

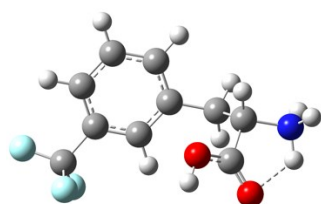
C	-0.628662	1.768265	0.355406
C	-0.506120	0.467436	0.867928
C	0.712000	-0.203190	0.719179
C	1.646497	1.685801	-0.466837
C	0.441587	2.370290	-0.297479
H	-1.554914	2.315688	0.487869
H	0.862120	-1.178032	1.175316
H	0.342556	3.381518	-0.673105
C	-1.668742	-0.223674	1.551982
C	-2.594401	-0.966060	0.565077
C	-3.432241	-0.021126	-0.308630
N	-1.786639	-1.908064	-0.318946
O	-3.954215	0.962080	0.118172
O	-3.531770	-0.482012	-1.574356
H	-2.300021	0.491006	2.082553



Isomer 8, 18.2kJ/mol

-0.309314	1.827215	-0.856452
-0.432855	0.435726	-0.872966
0.660372	-0.352026	-0.507743
1.972972	1.636120	-0.091673
0.888562	2.423029	-0.468562
-1.144621	2.451821	-1.156028
0.597103	-1.434660	-0.532695
0.978247	3.502435	-0.463851
-1.730288	-0.220347	-1.298094
-2.498957	-0.889919	-0.132123
-3.082158	0.115989	0.869490
-3.727610	-1.602115	-0.685812
-4.237541	0.463901	0.794453
-2.191064	0.522016	1.751595
-1.516976	-1.001839	-2.037465

H	-1.305585	-0.939912	2.294292	-2.383648	0.515063	-1.777950
H	-3.306116	-1.591452	1.110928	-1.876919	-1.627348	0.374336
C	3.051441	-0.392592	-0.134398	3.038724	-0.623145	0.235901
H	2.477493	2.155144	-0.977304	2.903758	2.096089	0.215143
C	1.778143	0.399810	0.044405	1.853781	0.246729	-0.112171
F	2.840151	-1.438049	-0.980572	2.646317	-1.801773	0.773800
F	3.471693	-0.922237	1.032857	3.858674	-0.026587	1.118324
F	4.048756	0.340767	-0.642243	3.770521	-0.917092	-0.861335
H	-2.309196	-2.142189	-1.170637	-4.513942	-0.929663	-0.605351
H	-1.539424	-2.770234	0.173794	-3.977072	-2.430787	-0.138823
H	-0.907218	-1.441430	-0.595040	-3.603357	-1.885812	-1.661014
H	-4.107771	0.101713	-2.096744	-2.585102	1.185030	2.345254

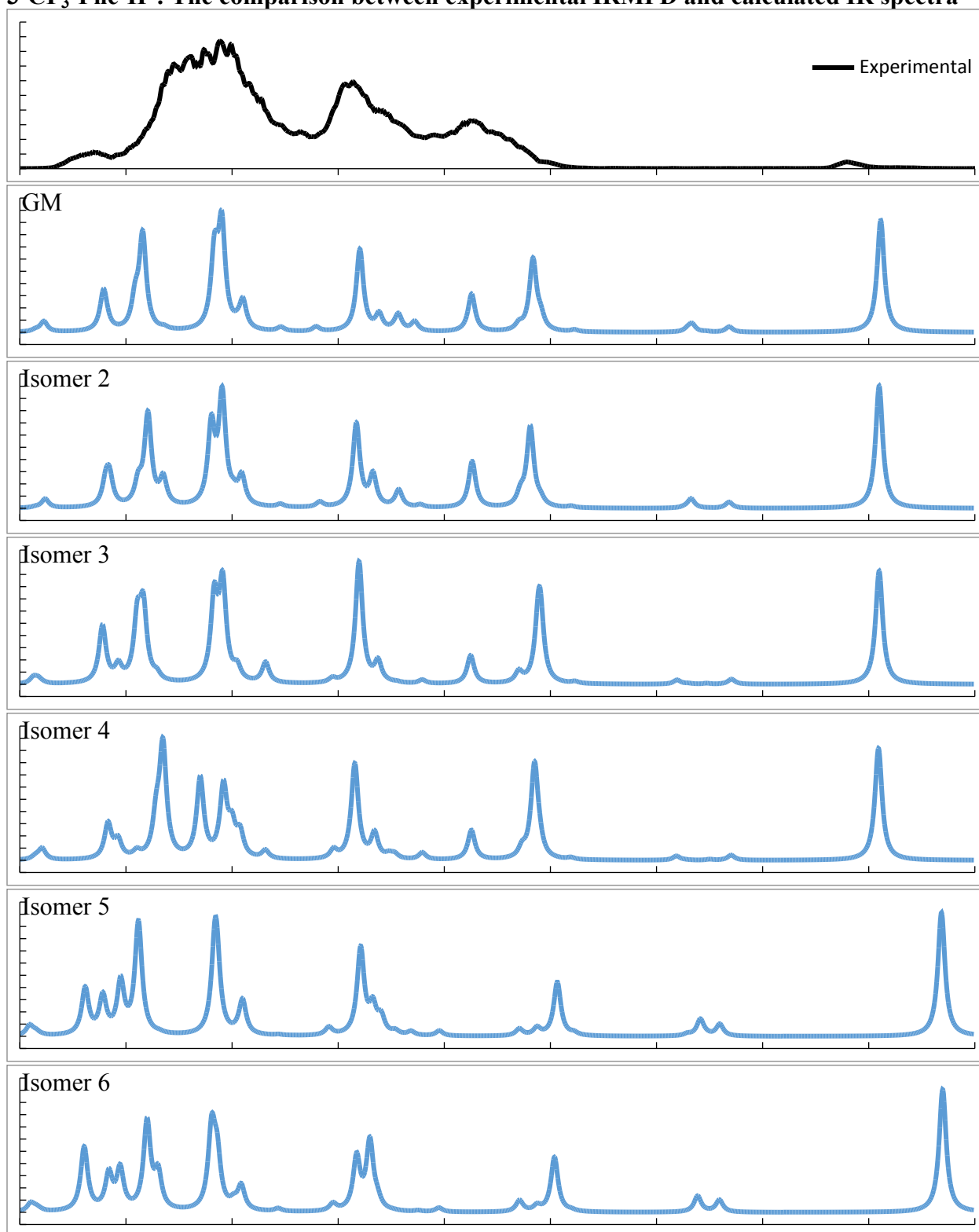


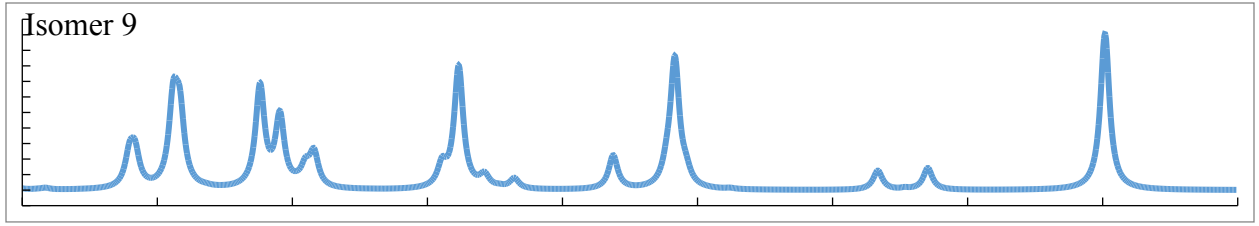
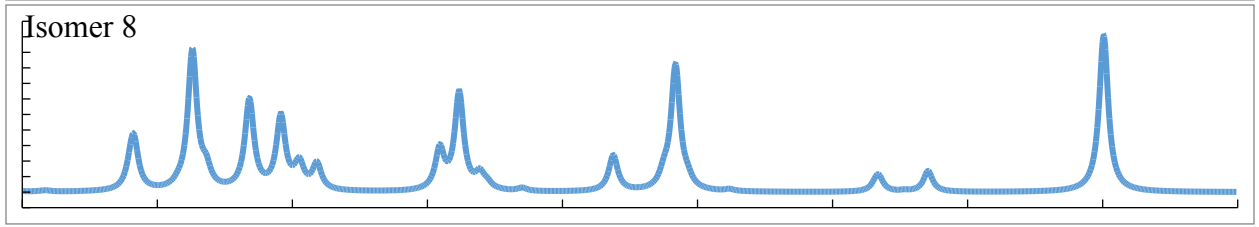
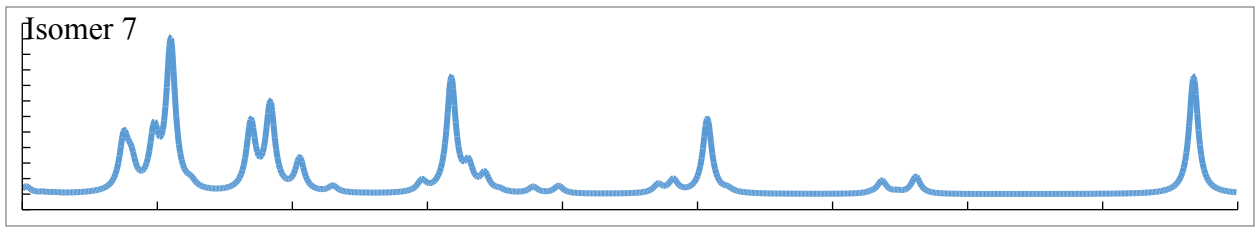
Isomer 9, 18.4kJ/mol

C	-0.220482	2.258150	-0.204925
C	-0.489197	1.064305	0.473860
C	0.525183	0.119645	0.620834
C	2.049892	1.541818	-0.605849
C	1.041388	2.494699	-0.739974
H	-0.990375	3.017529	-0.303236
H	0.346617	-0.798910	1.169238
H	1.244908	3.425334	-1.255306
C	-1.863416	0.798427	1.051138
C	-2.904061	0.344538	-0.003471
C	-2.589055	-1.026225	-0.618845
N	-4.245762	0.129282	0.687211
O	-1.733395	-0.944591	-1.617553
O	-3.098295	-2.030514	-0.179243
H	-4.279181	-0.875382	0.945471
H	-2.248952	1.713408	1.515737
H	-1.799704	0.033790	1.832172
H	-3.034107	1.099821	-0.778000
C	2.845835	-0.712751	0.200002
H	3.034533	1.724999	-1.016358
C	1.788125	0.358097	0.079029
F	4.084699	-0.230669	0.017213
F	2.650753	-1.686802	-0.725388
F	2.808814	-1.313506	1.408637

H	-5.038827	0.311824	0.066092
H	-4.349264	0.711684	1.522078
H	-1.515459	-1.833657	-1.948957

3-CF₃-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra



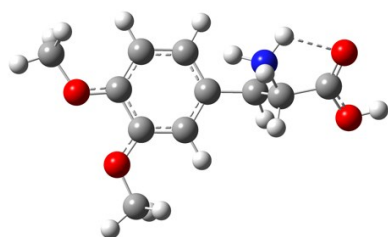


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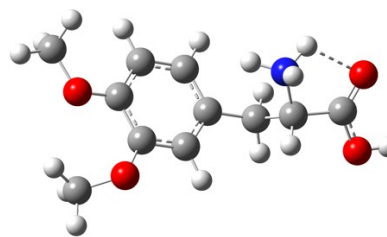
3,4-(OMe)₂-Phe•H⁺**Table S9 The Gibbs' Energies and Relative energies of 3,4-(OMe)₂-Phe•H⁺**

3,4(MeO) ₂ -Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-784.2176	0.00
Isomer 2	-784.2170	1.46
Isomer 3	-784.2169	1.71
Isomer 4	-784.2165	2.89
Isomer 5	-784.2162	3.67
Isomer 6	-784.2157	4.98
Isomer 7	-784.2153	6.04
Isomer 8	-784.2151	6.47
Isomer 9	-784.2143	8.71
Isomer 10	-784.2140	9.44
Isomer 11	-784.2119	15.06
Isomer 12	-784.2118	15.21
Isomer 13	-784.2113	16.54
Isomer 14	-784.2109	17.68
Isomer 15	-784.2106	18.37
Isomer 16	-784.2102	19.31
Isomer 17	-784.2092	22.08
Isomer 18	-784.2072	27.36
Isomer 19	-784.2068	28.43
Isomer 20	-784.2067	28.59
Isomer 21	-784.2067	28.65
Isomer 22	-784.2044	34.56
Isomer 23	-784.2042	35.28
Isomer 24	-784.2013	42.79

3,4-(OMe)₂-Phe·H⁺: The XYZ atomic coordinates and structures

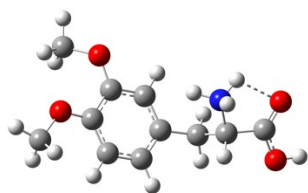


Isomer 1, 0.0kJ/mol

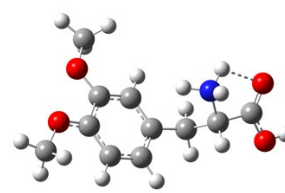


Isomer 2, 1.5kJ/mol

C	-0.240188	-0.139429	-0.696651	-0.353591	-0.060859	-0.693508
C	0.326587	-1.411528	-0.736286	0.230846	-1.320594	-0.844239
C	1.682701	-1.599335	-0.425411	1.581933	-1.517478	-0.539239
C	2.483930	-0.521179	-0.070549	2.370443	-0.467273	-0.068758
C	1.912821	0.788414	-0.033446	1.790849	0.825306	0.066356
C	0.565556	0.957501	-0.334323	0.444461	0.997995	-0.238938
H	-0.255120	-2.263120	-1.077369	-0.342186	-2.149493	-1.248842
H	0.139030	1.952939	-0.325880	0.043881	2.000846	-0.132688
C	-1.713704	0.049647	-0.967693	-1.825806	0.145973	-0.965019
H	-1.915568	0.965015	-1.527366	-2.015060	1.067661	-1.518916
H	-2.099996	-0.783390	-1.562640	-2.220853	-0.678218	-1.566456
C	-2.525927	0.144947	0.356392	-2.634238	0.245198	0.358563
H	-2.293846	1.074885	0.874545	-2.392857	1.171679	0.878769
C	-4.028319	0.008161	0.127367	-4.138756	0.121488	0.134138
N	-2.141311	-1.002249	1.262554	-2.259356	-0.907819	1.263710
H	-2.151279	-0.743355	2.250917	-2.262655	-0.647554	2.251971
H	-2.835244	-1.755532	1.129190	-2.963997	-1.651900	1.133083
O	-4.628411	-1.001413	0.406207	-4.746584	-0.882142	0.418624
O	-4.536935	1.095541	-0.434880	-4.639148	1.211308	-0.429240
H	-5.485071	0.965512	-0.607889	-5.589392	1.090680	-0.597495
H	-1.187196	-1.322014	1.005032	-1.312280	-1.239719	1.007175
H	2.105693	-2.592365	-0.488577	2.012162	-2.500774	-0.670685
O	2.762654	1.775119	0.295003	2.446121	1.903380	0.552806
O	3.788913	-0.587874	0.236209	3.664846	-0.585983	0.295558
C	2.302027	3.126580	0.292337	3.766440	2.241761	0.071434
H	3.167965	3.729351	0.555047	3.900261	3.290251	0.329993
H	1.941402	3.416960	-0.699002	4.527006	1.631851	0.553755
H	1.514762	3.277248	1.038123	3.818568	2.121511	-1.013209
C	4.455489	-1.851279	0.170811	4.318338	-1.852284	0.159591
H	5.488285	-1.648370	0.443196	5.337809	-1.692246	0.502323
H	4.022532	-2.561861	0.881385	3.838139	-2.610019	0.785336
H	4.417212	-2.262154	-0.842194	4.329575	-2.177718	-0.884351

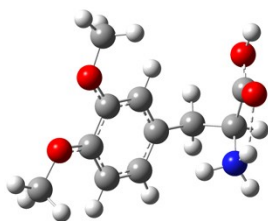


Isomer 3, 1.7kJ/mol

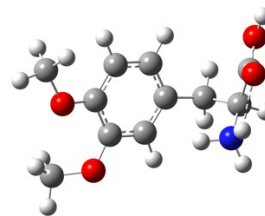


Isomer 4, 2.9kJ/mol

C	0.356088	-0.370532	-0.657425	0.240659	-0.397297	-0.662552
C	-0.273429	-1.601228	-0.476234	-0.378627	-1.625550	-0.466010
C	-1.624127	-1.659754	-0.134961	-1.734528	-1.691357	-0.127831
C	-2.377172	-0.496084	0.051954	-2.493521	-0.533575	0.024276
C	-1.757448	0.762460	-0.154059	-1.874496	0.732617	-0.182214
C	-0.405413	0.799155	-0.500419	-0.518998	0.784226	-0.509493
H	0.274829	-2.526972	-0.615191	0.174932	-2.549420	-0.597548
H	0.016101	1.779060	-0.707277	-0.063274	1.743200	-0.728227
C	1.834615	-0.271053	-0.951119	1.719428	-0.300717	-0.959987
H	2.176266	-1.084397	-1.593753	2.042454	-1.061894	-1.672609
H	2.061573	0.665718	-1.469260	1.960814	0.672105	-1.398856
C	2.679941	-0.348216	0.351330	2.570049	-0.504777	0.325970
H	2.614348	-1.347418	0.781102	2.516158	-1.543838	0.648891
C	4.135419	0.053319	0.123886	4.019881	-0.064178	0.142948
N	2.140903	0.631209	1.371192	2.018760	0.356764	1.441308
H	2.685745	1.504721	1.289735	2.572883	1.228173	1.467707
H	1.136091	0.801589	1.183805	1.019271	0.554307	1.252042
O	4.570956	1.115889	0.495320	4.441764	0.960121	0.623324
O	4.798989	-0.878364	-0.545747	4.694886	-0.911505	-0.619927
H	5.709534	-0.580265	-0.712684	5.601403	-0.586050	-0.754711
H	2.245756	0.293339	2.330037	2.100573	-0.089431	2.357002
H	-2.088773	-2.627183	-0.001698	-2.197616	-2.659850	0.002123
O	-2.367968	1.956446	0.029734	-2.680802	1.801013	-0.051699
O	-3.671726	-0.476757	0.436758	-3.798310	-0.494341	0.339511
C	-3.676339	2.203387	-0.534067	-2.170334	3.102912	-0.333533
H	-3.781947	3.286346	-0.537685	-3.009804	3.780794	-0.199090
H	-3.725426	1.825873	-1.558212	-1.370859	3.375649	0.364047
H	-4.455838	1.747372	0.072092	-1.807871	3.170256	-1.363822
C	-4.363408	-1.714405	0.636674	-4.512359	-1.722372	0.506268
H	-4.396034	-2.299407	-0.286616	-5.534965	-1.433387	0.736128
H	-3.899004	-2.298023	1.436537	-4.496369	-2.312952	-0.414224
H	-5.373912	-1.438822	0.928849	-4.102282	-2.306898	1.335268

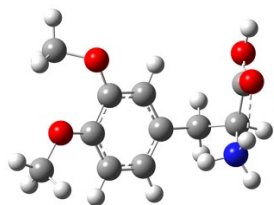


Isomer 5, 3.7kJ/mol

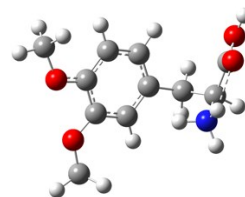


Isomer 6, 5.0kJ/mol

C	0.367453	-0.679780	-0.919337	0.546417	-0.320388	-0.911601
C	-0.467235	-1.777596	-0.714870	0.248869	1.041611	-0.923485
C	-1.780039	-1.603165	-0.250181	-1.001110	1.496029	-0.503879
C	-2.273462	-0.331860	0.015829	-1.981023	0.609822	-0.046805
C	-1.429379	0.800441	-0.198201	-1.706163	-0.781197	-0.059154
C	-0.128011	0.611065	-0.651395	-0.450906	-1.215346	-0.488104
H	-0.137371	-2.776935	-0.985133	0.978618	1.761376	-1.277015
H	0.500665	1.472340	-0.837255	-0.303809	-2.290727	-0.543481
C	1.796945	-0.884545	-1.364746	1.913293	-0.846061	-1.285986
H	1.889111	-1.826757	-1.911017	1.837141	-1.862178	-1.682392
H	2.136789	-0.095303	-2.037352	2.384147	-0.239413	-2.060900
C	2.792948	-0.927407	-0.172727	2.888349	-0.874213	-0.080205
H	3.746157	-1.355638	-0.491042	3.766677	-1.480752	-0.314567
C	3.099924	0.420358	0.488712	3.394961	0.493083	0.395225
N	2.240642	-1.786953	0.942600	2.220399	-1.477163	1.137533
H	2.429361	-1.297898	1.835347	1.192473	-1.367786	1.038369
H	1.209406	-1.853839	0.814993	2.438432	-2.465766	1.268706
O	2.990958	0.591219	1.678497	3.336084	0.829608	1.552740
O	3.524254	1.316762	-0.391365	3.922116	1.197144	-0.595800
H	3.765580	2.138051	0.069471	4.277393	2.033374	-0.249678
H	2.639066	-2.726347	0.963796	2.524298	-0.929080	1.961468
H	-2.415102	-2.469171	-0.124686	-1.204631	2.557978	-0.522031
O	-1.993201	1.991728	0.060282	-2.557201	-1.735966	0.384346
O	-3.511170	-0.052216	0.453384	-3.188769	0.983493	0.428604
C	-1.245891	3.185785	-0.169685	-3.945887	-1.723431	-0.018043
H	-0.361531	3.226969	0.474419	-4.513993	-0.998463	0.560408
H	-0.951916	3.270011	-1.220359	-4.030044	-1.503696	-1.084979
H	-1.916752	4.002403	0.085994	-4.305245	-2.731717	0.177587
C	-4.439631	-1.122335	0.645870	-3.533398	2.372981	0.454443
H	-4.624837	-1.653777	-0.292131	-2.848488	2.934175	1.096266
H	-4.082873	-1.820157	1.409463	-3.536720	2.795407	-0.554197
H	-5.358700	-0.650999	0.985295	-4.537287	2.415830	0.870155

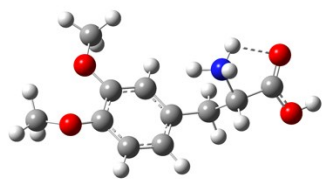


Isomer 7, 6.0kJ/mol

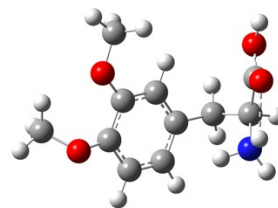


Isomer 8, 6.5kJ/mol

C	0.541602	-0.611905	-0.932581	-0.435173	0.267282	-0.866271
C	-0.244096	-1.755501	-0.759723	-0.218557	-1.104191	-0.814169
C	-1.557880	-1.652063	-0.290683	1.018576	-1.614935	-0.406483
C	-2.111178	-0.410053	0.021840	2.060780	-0.766932	-0.042351
C	-1.332441	0.762585	-0.180983	1.860333	0.642056	-0.104591
C	-0.025230	0.635828	-0.642374	0.618404	1.137409	-0.502405
H	0.133968	-2.732860	-1.046272	-0.996859	-1.796287	-1.115929
H	0.529231	1.554732	-0.796205	0.487789	2.207910	-0.614849
C	1.981171	-0.727456	-1.380224	-1.782168	0.845545	-1.238188
H	2.135724	-1.664422	-1.921824	-1.671453	1.871054	-1.600281
H	2.264930	0.079620	-2.057663	-2.261272	0.279805	-2.038796
C	2.974912	-0.691983	-0.190395	-2.770505	0.863043	-0.041719
H	3.963048	-1.032719	-0.508571	-3.605131	1.538923	-0.243559
C	3.161709	0.671664	0.487654	-3.371398	-0.494206	0.344478
N	2.501565	-1.605398	0.919979	-2.075661	1.341597	1.215623
H	1.477788	-1.742527	0.811980	-1.053150	1.206554	1.095078
H	2.964779	-2.514835	0.920447	-2.262945	2.321073	1.432554
O	3.064884	0.807154	1.683054	-3.338491	-0.908384	1.477851
O	3.473444	1.619352	-0.383337	-3.942617	-1.094231	-0.689091
H	3.625380	2.457911	0.085033	-4.354841	-1.925667	-0.398998
H	2.671900	-1.113607	1.815873	-2.395648	0.734996	1.992303
H	-2.146231	-2.551562	-0.172206	1.164804	-2.686147	-0.388834
O	-1.747863	2.014155	0.114982	2.926110	1.394659	0.223107
O	-3.350269	-0.230358	0.527623	3.281399	-1.159865	0.356189
C	-3.066702	2.466901	-0.264757	2.848239	2.812677	0.096071
H	-3.005213	3.553317	-0.252648	2.624580	3.105520	-0.934376
H	-3.312526	2.124031	-1.272422	2.098485	3.231917	0.776308
H	-3.817568	2.121727	0.442414	3.831304	3.185285	0.373807
C	-4.195825	-1.366674	0.731918	3.583177	-2.557272	0.401093
H	-4.395185	-1.882342	-0.211677	4.615097	-2.619586	0.737747
H	-3.753531	-2.059263	1.453790	2.934107	-3.077203	1.111964
H	-5.125266	-0.969900	1.133363	3.493308	-3.009597	-0.590737

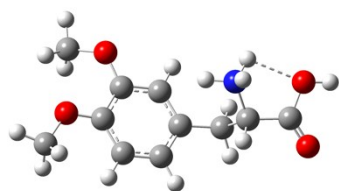


Isomer 9, 8.7kJ/mol

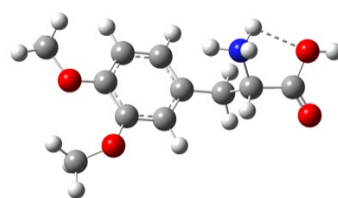


Isomer 10, 9.4kJ/mol

C	0.284013	-0.500389	-0.580444	0.440047	-0.795356	-0.855514
C	-0.203976	-1.766670	-0.257073	-0.217798	-1.985744	-0.528572
C	-1.533804	-1.922786	0.124226	-1.517586	-1.952934	-0.017344
C	-2.406627	-0.838011	0.202174	-2.184842	-0.750373	0.185757
C	-1.918550	0.455906	-0.111008	-1.519887	0.465118	-0.135088
C	-0.580399	0.606242	-0.497546	-0.223104	0.424391	-0.652948
H	0.433516	-2.641529	-0.332748	0.241122	-2.946542	-0.745677
H	-0.218001	1.586814	-0.783334	0.273623	1.349776	-0.914892
C	1.737749	-0.292766	-0.942955	1.869306	-0.834352	-1.346495
H	2.086727	-1.031292	-1.667550	2.066015	-1.782259	-1.853859
H	1.884144	0.692980	-1.394221	2.081089	-0.041503	-2.065463
C	2.654604	-0.424895	0.305122	2.900226	-0.688936	-0.193259
H	2.695753	-1.462859	0.633245	3.890140	-1.005068	-0.530292
C	4.057211	0.125359	0.059181	3.050319	0.720108	0.390793
N	2.086908	0.398131	1.441568	2.508849	-1.554374	0.984609
H	2.574807	1.308809	1.443654	2.669571	-1.000921	1.844654
H	1.069592	0.518103	1.295068	1.491566	-1.761384	0.914019
O	4.418131	1.181362	0.520064	2.963598	0.937061	1.574688
O	4.762267	-0.671312	-0.729987	3.320022	1.617170	-0.547907
H	5.635287	-0.279119	-0.903137	3.471341	2.484884	-0.136419
H	2.239372	-0.036989	2.353735	3.026649	-2.432915	1.029351
H	-1.933235	-2.901094	0.362336	-2.047722	-2.867567	0.218224
O	-2.794527	1.479334	0.008706	-2.203856	1.602457	0.112731
O	-3.658655	-1.087141	0.646744	-3.411997	-0.810322	0.749590
C	-2.394663	2.798830	-0.363440	-1.612617	2.865554	-0.198042
H	-3.272604	3.423620	-0.216771	-2.356287	3.611074	0.073534
H	-1.584146	3.161929	0.276975	-0.704943	3.028730	0.391102
H	-2.090178	2.838127	-1.413471	-1.390145	2.944611	-1.266219
C	-4.804856	-0.550816	-0.049590	-4.518391	-0.083510	0.171420
H	-4.677939	-0.658279	-1.129720	-4.477549	0.970989	0.436181
H	-5.645269	-1.157772	0.280905	-4.522953	-0.201089	-0.915218
H	-4.968108	0.493659	0.207963	-5.409643	-0.544914	0.591646

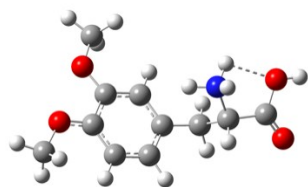


Isomer 11, 15.1kJ/mol

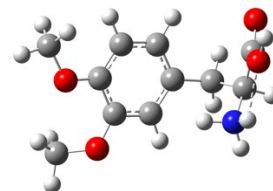


Isomer 12, 15.2kJ/mol

C	0.349783	-0.367338	-0.665041	-0.347499	-0.085017	-0.693034
C	-0.280554	-1.598571	-0.487619	0.243133	-1.343839	-0.826591
C	-1.629453	-1.658086	-0.140255	1.593858	-1.531562	-0.515798
C	-2.380813	-0.494814	0.056381	2.376953	-0.472212	-0.056101
C	-1.760816	0.764229	-0.145220	1.791300	0.818995	0.063866
C	-0.410742	0.801763	-0.497945	0.445509	0.982643	-0.248282
H	0.266570	-2.523713	-0.634624	-0.325778	-2.180497	-1.220845
H	0.009947	1.782781	-0.701190	0.041027	1.985466	-0.157087
C	1.827023	-0.272742	-0.968819	-1.817204	0.120252	-0.982876
H	2.164235	-1.091626	-1.606921	-1.999527	1.030081	-1.558652
H	2.058021	0.659613	-1.493716	-2.213692	-0.715023	-1.568256
C	2.674257	-0.353938	0.329335	-2.630852	0.262203	0.330455
H	2.538009	-1.329897	0.794812	-2.327553	1.167389	0.856014
C	4.159859	-0.154427	0.048294	-4.130024	0.334905	0.065239
N	2.160601	0.677280	1.321831	-2.288536	-0.906098	1.241565
H	1.129443	0.734051	1.222029	-2.448754	-0.693778	2.228825
H	2.395302	0.440150	2.288342	-2.861382	-1.722487	1.002300
O	4.834891	-0.986448	-0.476201	-4.659007	1.300837	-0.392766
O	4.573882	1.079996	0.420065	-4.744240	-0.834594	0.365622
H	5.509969	1.195329	0.184811	-5.688286	-0.774075	0.142133
H	2.568467	1.596965	1.122238	-1.287605	-1.133991	1.095568
H	-2.093971	-2.626007	-0.010278	2.028563	-2.514536	-0.634285
O	-2.370018	1.957848	0.049604	2.441302	1.904190	0.541614
O	-3.673372	-0.476388	0.447050	3.671061	-0.580764	0.311465
C	-3.676113	2.210716	-0.517049	3.754829	2.250508	0.047306
H	-4.457626	1.742795	0.077321	4.523557	1.643015	0.519692
H	-3.784831	3.293291	-0.503643	3.795505	2.133745	-1.038277
H	-3.718505	1.849824	-1.547523	3.886258	3.298893	0.307330
C	-4.365371	-1.714701	0.643603	4.332051	-1.844408	0.187618
H	-4.402615	-2.294665	-0.282628	5.350514	-1.675059	0.528853
H	-3.897783	-2.302807	1.438246	3.856372	-2.598972	0.820619
H	-5.374255	-1.439662	0.941774	4.345277	-2.179652	-0.853183

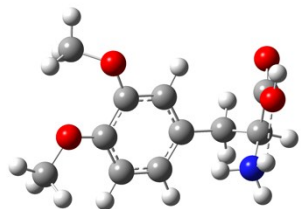


Isomer 13, 16.5kJ/mol

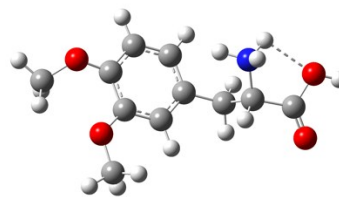


Isomer 14, 17.7kJ/mol

C	0.236186	-0.370721	-0.661591	0.547541	-0.307701	-0.938689
C	-0.372031	-1.606294	-0.470783	0.232907	1.051111	-0.963741
C	-1.726041	-1.686887	-0.129603	-1.015064	1.495142	-0.526956
C	-2.495655	-0.536845	0.029211	-1.975346	0.603594	-0.039373
C	-1.888580	0.736008	-0.171205	-1.682160	-0.783449	-0.034961
C	-0.534593	0.802206	-0.500297	-0.430905	-1.208272	-0.483028
H	0.189020	-2.524284	-0.611752	0.949030	1.773327	-1.338204
H	-0.087269	1.767031	-0.710033	-0.273747	-2.282835	-0.527585
C	1.711902	-0.265335	-0.975299	1.911841	-0.819944	-1.345544
H	2.027883	-1.008213	-1.710383	1.840371	-1.833700	-1.749908
H	1.951846	0.717942	-1.391605	2.362620	-0.197964	-2.120327
C	2.573251	-0.511826	0.292490	2.908665	-0.833918	-0.163809
H	2.451640	-1.542836	0.623017	3.806520	-1.403239	-0.419225
C	4.053541	-0.256624	0.033650	3.384764	0.569294	0.231783
N	2.051626	0.369641	1.416672	2.275535	-1.525228	1.034792
H	2.461616	1.307392	1.351222	1.264541	-1.287275	1.044831
H	1.022020	0.436591	1.312607	2.354971	-2.542647	0.970848
O	4.738762	-1.005121	-0.593195	3.712069	1.392416	-0.566764
O	4.450769	0.929526	0.554297	3.432888	0.717733	1.575344
H	5.383809	1.087298	0.332003	3.780546	1.598011	1.795798
H	2.276491	-0.002033	2.342216	2.701922	-1.204143	1.910380
H	-2.179621	-2.660446	-0.004251	-1.232538	2.554077	-0.558645
O	-2.704807	1.796534	-0.032209	-2.513611	-1.740718	0.442654
O	-3.799927	-0.511500	0.347091	-3.180047	0.968474	0.450803
C	-2.209460	3.103393	-0.315851	-3.901132	-1.766421	0.037041
H	-3.055433	3.772539	-0.178169	-4.480234	-1.019928	0.575951
H	-1.410274	3.384977	0.378749	-3.984092	-1.602799	-1.040202
H	-1.851538	3.174719	-1.347512	-4.249041	-2.767699	0.282864
C	-4.502559	-1.747122	0.507874	-3.547574	2.352355	0.449708
H	-5.527384	-1.468733	0.740852	-4.546262	2.388338	0.878427
H	-4.482501	-2.332158	-0.416019	-2.863560	2.939748	1.068682
H	-4.085839	-2.332505	1.332906	-3.571406	2.751343	-0.568098



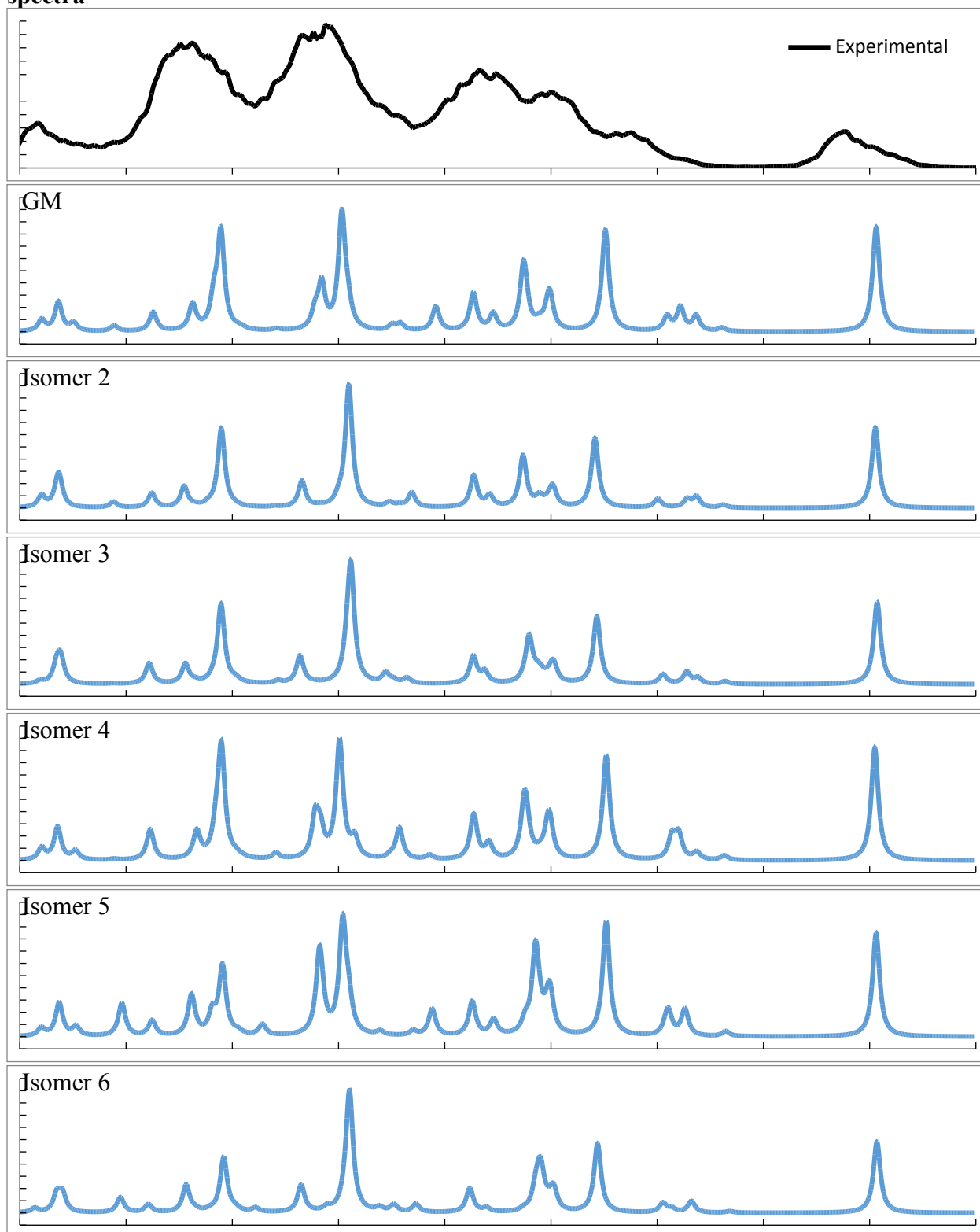
Isomer 15, 18.4kJ/mol

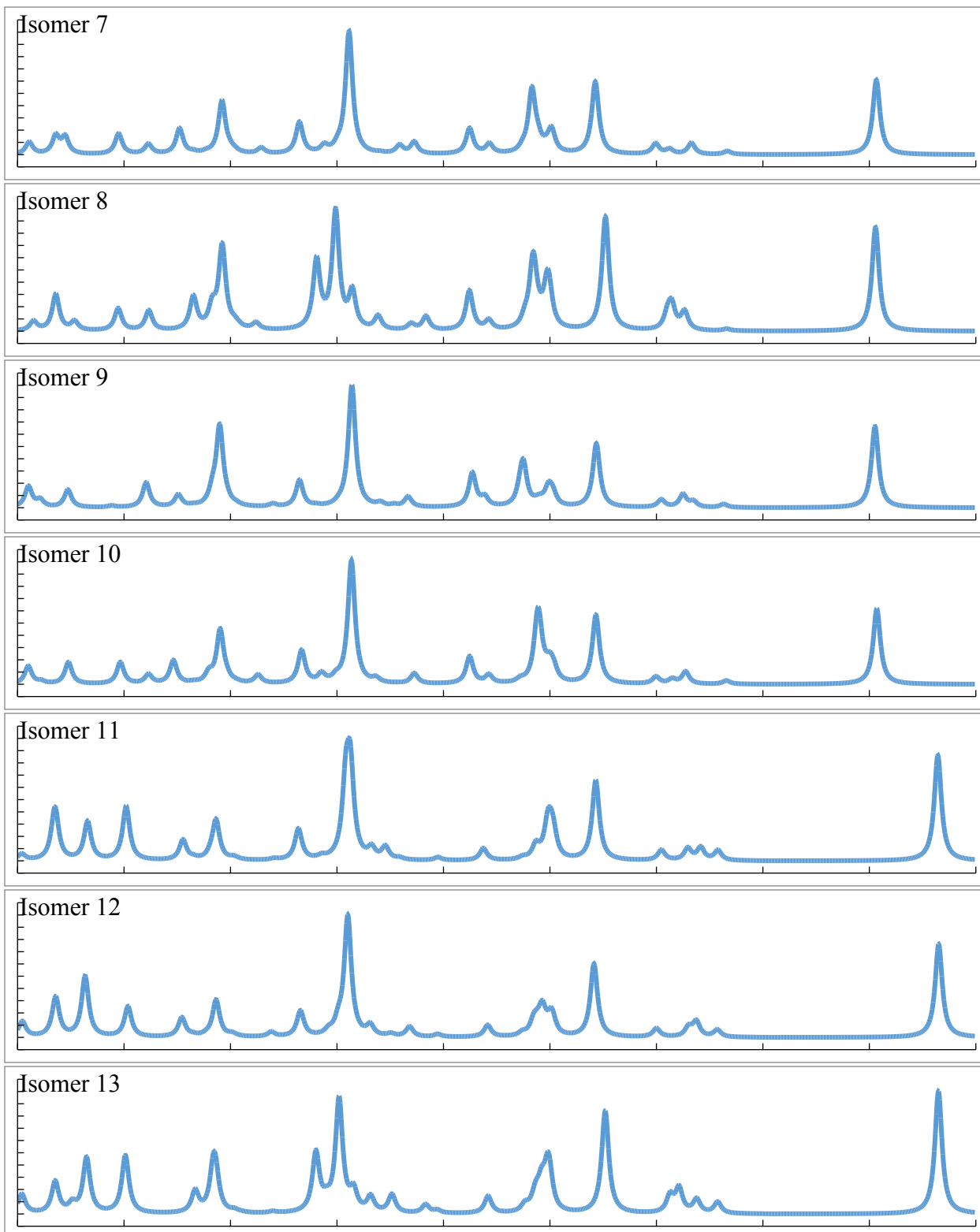


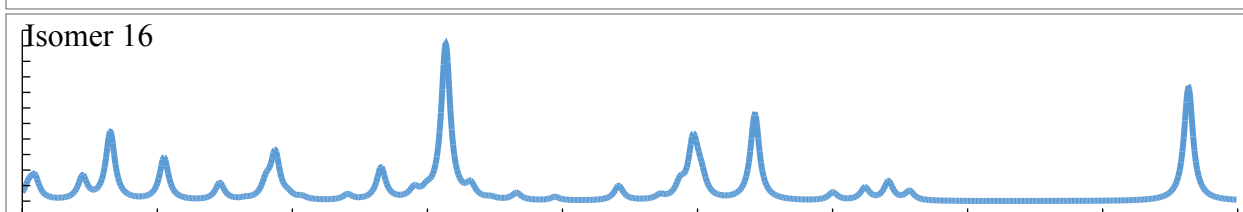
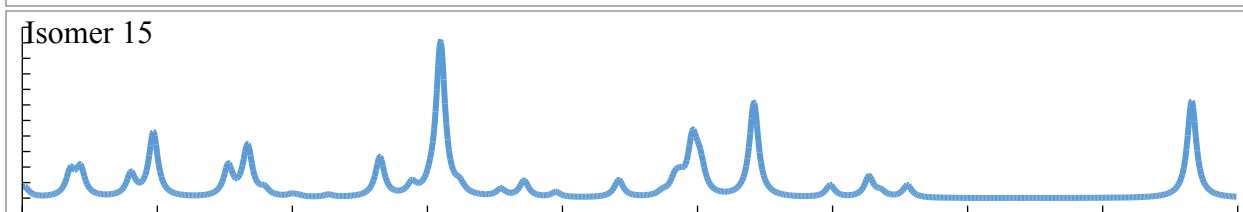
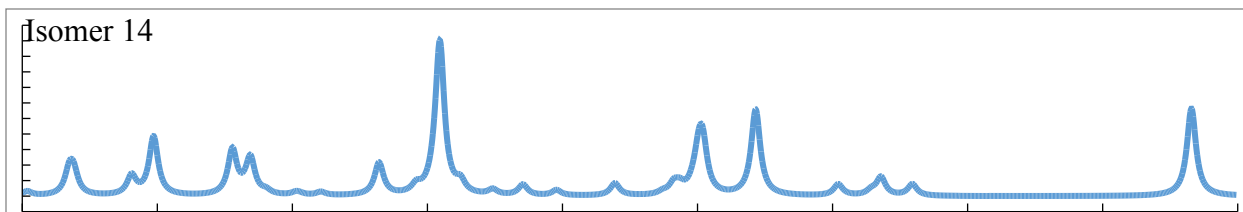
Isomer 16, 19.3kJ/mol

C	0.539141	-0.632889	-0.929323	-0.269118	-0.267678	-0.671707
C	-0.246179	-1.772992	-0.732359	0.180148	-1.590586	-0.617825
C	-1.556302	-1.663716	-0.255201	1.504096	-1.867166	-0.266248
C	-2.106673	-0.416716	0.043281	2.398897	-0.849061	0.043292
C	-1.327218	0.751694	-0.178050	1.946099	0.499241	0.000793
C	-0.025031	0.620697	-0.651399	0.623150	0.768348	-0.356566
H	0.131050	-2.755096	-1.003287	-0.467169	-2.406803	-0.926698
H	0.528790	1.536450	-0.824105	0.282481	1.795349	-0.402293
C	1.972958	-0.754750	-1.399158	-1.716433	0.036502	-0.981851
H	2.125731	-1.706426	-1.915276	-1.830743	0.962288	-1.548844
H	2.242135	0.036702	-2.100832	-2.158546	-0.764862	-1.582059
C	2.981168	-0.664185	-0.228902	-2.542250	0.215010	0.321414
H	3.971415	-1.004246	-0.542226	-2.175682	1.080426	0.872909
C	3.163036	0.764622	0.297895	-4.023754	0.422470	0.026741
N	2.530006	-1.583965	0.896215	-2.321562	-0.996148	1.212465
H	1.491089	-1.597370	0.890036	-1.339770	-1.312055	1.081829
H	2.858449	-2.542246	0.759349	-2.484477	-0.790805	2.200727
O	3.326425	1.701592	-0.421481	-4.457225	1.444350	-0.410611
O	3.165051	0.802165	1.649530	-4.740921	-0.698493	0.274847
H	3.313581	1.713582	1.952660	-5.670890	-0.552751	0.032221
H	2.854998	-1.237046	1.805121	-2.958498	-1.754268	0.944656
H	-2.143608	-2.561602	-0.120252	1.874181	-2.884814	-0.243559
O	-1.743910	2.004702	0.115486	2.848259	1.443453	0.341785
O	-3.342657	-0.227865	0.552600	3.638431	-1.214064	0.439746
C	-3.040062	2.467157	-0.325983	2.481699	2.824485	0.286866
H	-3.830501	2.096377	0.322901	3.372923	3.374931	0.578705
H	-2.984756	3.552678	-0.274997	2.188907	3.113838	-0.726465
H	-3.222409	2.157584	-1.357943	1.673420	3.044912	0.990752
C	-4.191701	-1.359157	0.770243	4.805771	-0.586317	-0.135536
H	-3.751017	-2.045434	1.499146	5.627795	-1.264542	0.083826
H	-5.119440	-0.955051	1.168300	4.689930	-0.489261	-1.217912
H	-4.393633	-1.884434	-0.167446	4.988892	0.388005	0.312582

3,4-(OMe)₂-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra





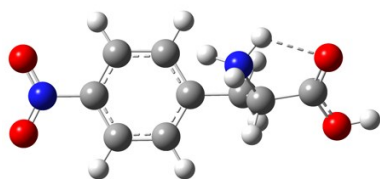


1000 1100 1200 1300 1400 1500 1600 1700 1800 1900

4-NO₂-Phe•H⁺**Table S10 The Gibbs' Energies and Relative energies of 4-NO₂-Phe•H⁺**

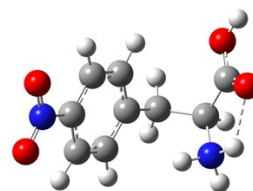
4NO ₂ -Phe Isomer	Gibbs (hartree)	Relative energy (kJ/mol)
Isomer 1	-759.7142	0.00
Isomer 2	-759.7126	3.98
Isomer 3	-759.7091	13.25
Isomer 4	-759.7080	16.16
Isomer 5	-759.7079	16.56
Isomer 6	-759.7018	32.39
Isomer 7	-759.7001	37.00
Isomer 8	-759.6995	38.56
Isomer 9	-759.6988	40.25

4-NO₂-Phe·H⁺: The XYZ atomic coordinates and structures



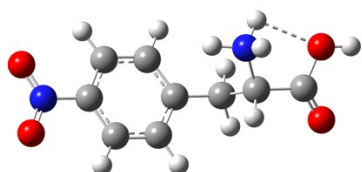
GM, 0.0kJ/mol

C	-0.125317	0.239241	-0.624459
C	0.577275	-0.940596	-0.907831
C	1.942249	-1.039649	-0.638785
C	2.588229	0.055903	-0.085612
C	1.924164	1.245511	0.194335
C	0.562947	1.329838	-0.074880
H	0.073723	-1.775423	-1.386390
H	0.042910	2.261347	0.123279
C	-1.615319	0.317310	-0.883173
H	-1.890662	1.276616	-1.326398
H	-1.920911	-0.460366	-1.589471
C	-2.441918	0.178925	0.419018
H	-2.252076	1.021594	1.083761
C	-3.940291	0.037763	0.136582
N	-2.057219	-1.088828	1.157075
H	-2.723659	-1.827311	0.872448
H	-2.137416	-0.985312	2.171802
O	-4.508805	-1.019295	0.257344
O	-4.466703	1.180837	-0.270020
H	-5.410138	1.062303	-0.477009
H	-1.088990	-1.358192	0.933292
H	2.474914	2.080711	0.606159
H	2.503010	-1.937465	-0.862205
O	4.588674	-1.108207	-0.029342
O	4.584221	0.948412	0.675369
N	4.045517	-0.042310	0.210460



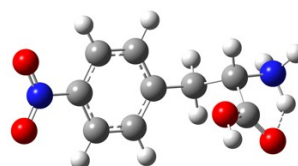
Isomer 2, 4.0kJ/mol

C	-0.355727	0.533871	-0.876381
C	0.524418	1.565312	-0.513702
C	1.833784	1.285501	-0.125199
C	2.249201	-0.037959	-0.109489
C	1.410819	-1.082127	-0.482157
C	0.105573	-0.789517	-0.862786
H	0.209533	2.602677	-0.585748
H	-0.546212	-1.597025	-1.176437
C	-1.786732	0.859924	-1.251717
H	-1.854712	1.885675	-1.623175
H	-2.146517	0.211593	-2.052566
C	-2.778972	0.706531	-0.074810
H	-3.742051	1.147537	-0.343182
C	-3.057236	-0.729828	0.395144
N	-2.283331	1.419910	1.168661
H	-1.254691	1.497352	1.139287
H	-2.681767	2.353600	1.282886
O	-2.992198	-1.037459	1.559718
O	-3.403490	-1.519073	-0.608689
H	-3.632366	-2.403168	-0.272880
H	-2.531650	0.821811	1.979227
H	1.786948	-2.096508	-0.477220
H	2.528304	2.069634	0.145361
O	4.341078	0.592091	0.656128
O	3.986775	-1.518724	0.274826
N	3.645771	-0.348213	0.307790



Isomer 3, 13.3kJ/mol

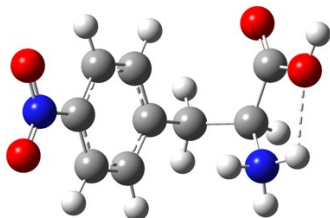
C	-0.117623	0.222183	-0.638025
C	0.588225	-0.960726	-0.899520
C	1.951459	-1.054258	-0.621291



Isomer 4, 16.2kJ/mol

C	0.291033	-0.660126	0.598777
C	-0.440458	-1.450461	-0.294980
C	-1.777465	-1.172839	-0.553831

C	2.593227	0.050033	-0.080232	-2.370553	-0.098564	0.098345
C	1.926465	1.242690	0.178653	-1.676417	0.694197	1.002001
C	0.566742	1.321602	-0.100450	-0.337575	0.405749	1.248668
H	0.088126	-1.803841	-1.366850	0.022454	-2.300769	-0.785710
H	0.044757	2.255821	0.079196	0.210415	1.011912	1.962077
C	-1.605725	0.301888	-0.909586	1.748001	-0.970109	0.874966
H	-1.876236	1.257447	-1.364112	2.073836	-0.456078	1.784700
H	-1.912767	-0.481344	-1.609591	1.862983	-2.047024	1.045802
C	-2.437902	0.191298	0.388382	2.699093	-0.583793	-0.284716
H	-2.182575	1.005970	1.067005	2.423895	-1.095982	-1.206211
C	-3.938346	0.260106	0.101137	2.801784	0.931679	-0.509373
N	-2.083382	-1.099415	1.116901	4.121093	-0.991345	0.082104
H	-2.378623	-1.082115	2.096950	4.681390	-1.233458	-0.739992
H	-2.551796	-1.898832	0.676325	4.558311	-0.157742	0.519224
O	-4.471502	1.258929	-0.270283	3.708554	1.567097	-0.025164
O	-4.531127	-0.940379	0.286693	1.814659	1.397873	-1.247797
H	-5.476549	-0.880083	0.065968	1.889192	2.364267	-1.338232
H	-1.063357	-1.242192	1.078108	4.143351	-1.782498	0.730669
H	2.473631	2.084746	0.581183	-2.182846	1.510810	1.498509
H	2.514647	-1.954463	-0.828296	-2.361669	-1.773337	-1.237790
O	4.593947	-1.111981	0.004498	-4.382755	-0.516552	-0.968562
O	4.584140	0.954302	0.680277	-4.288527	1.161134	0.409324
N	4.048805	-0.043012	0.225988	-3.801294	0.206930	-0.175619



Isomer 5, 16.6kJ/mol

C	-0.354959	0.547216	-0.887713
C	0.502558	1.571573	-0.455803
C	1.807898	1.292085	-0.055159
C	2.243537	-0.024593	-0.097968
C	1.429298	-1.059988	-0.541320
C	0.126593	-0.768978	-0.933742
H	0.174372	2.607055	-0.482702
H	-0.508658	-1.567733	-1.298145
C	-1.782709	0.870498	-1.282654
H	-1.856704	1.903703	-1.632786
H	-2.120968	0.232796	-2.101287
C	-2.792684	0.666806	-0.134569

H	-3.765101	1.084858	-0.408865
C	-3.040581	-0.810633	0.205791
N	-2.342095	1.416686	1.113602
H	-2.547718	2.417021	1.048250
H	-2.796674	1.030818	1.949309
O	-3.155721	-1.654916	-0.627675
O	-3.158971	-0.992655	1.538509
H	-3.367987	-1.922594	1.731676
H	-1.321076	1.311759	1.222234
H	1.820976	-2.067697	-0.582204
H	2.484917	2.071587	0.267918
O	4.310602	0.598191	0.738339
O	3.993725	-1.498021	0.257386
N	3.635500	-0.334727	0.333963

4-NO₂-Phe·H⁺: The comparison between experimental IRMPD and calculated IR spectra

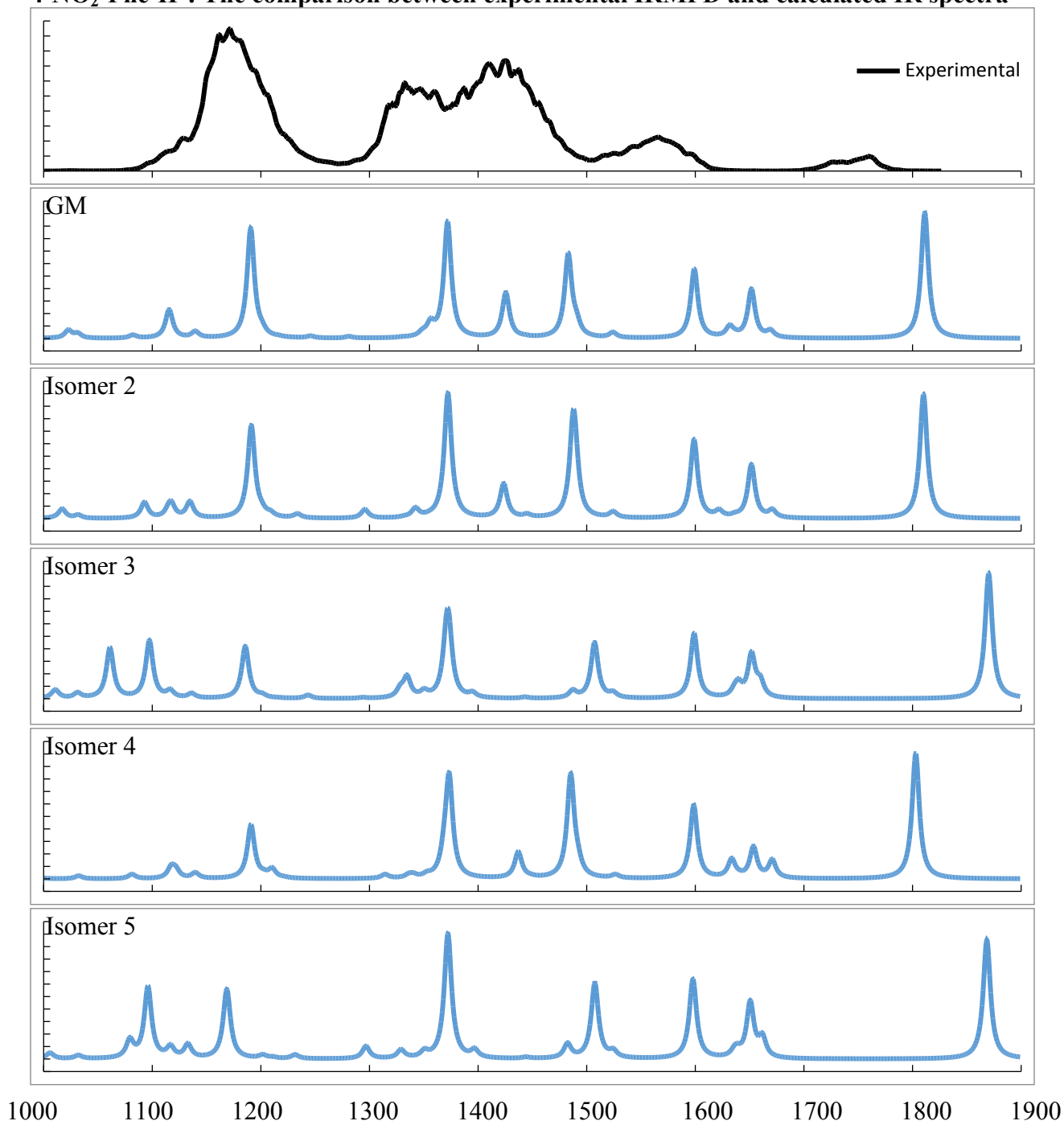


Table S11 Assignments of vibrational modes of fluorinated Phe•H⁺

Structure	Vibrational modes (cm ⁻¹)									
	1780-1730		1460-1380				1190-1100			
	1749		1428		1398		1141			
Phe-H ⁺	C=O Stretch, NH ₂ Scissor		NH ₃ Umbrella		COH Bend, CH & NH ₂ Wag		COH Bend, Ring H Scissor			
IRMPD	1790-1745		1620-1540		1500-1360			1330-1080		
	1774		1609	1593	1488	1452	1397	1260	1166	
3F-Phe-H ⁺	C=O Stretch, NH ₂ Scissor		Ring Stretch		Ring Rock	NH ₃ Umbrella	COH Bend CH Wag	C-F Stretch, Ring Stretch	COH Bend	
IRMPD	1860-1740		1630-1563		1563-1375			1310 – 1063		
	1774		1609		1509		1448	1397	1243	1166
4F-Phe-H ⁺	C=O Stretch, NH ₂ Scissor		Ring Stretch		Ring H Wag		NH ₃ Umbrella	COH Bend, CH & NH ₂ Wag	C-F Stretch, Ring Stretch	COH Bend
IRMPD	1850 – 1750		1650-1375				1375 – 1075			
	1792		1497	1469	1436	1408		1382, 1168	1161	
2,5F ₂ -Phe-H ⁺	C=O Stretch, NH ₂ Scissor		NH ₃ Umbrella	CH ₂ Scissor	Ring Stretch	COH Bend, CH & NH ₂ Wag		COH Bend	Asym. C-F Stretch, Ring Stretch	
IRMPD	1800 – 1740		1650-1550		1500-1300			1230 – 1080		
	1774		1604		1454	1397	1345	1315	1167	1128
3,5F ₂ -Phe-H ⁺	C=O Stretch, NH ₂ Scissor		Ring Stretch		NH ₃ Umbrella , CH ₂ Scissor	COH Bend, CH, NH ₂ & CH ₂ Wag, & C-F Stretch			COH Bend	Asym. C-F Stretch, Ring H Wag
IRMPD	1790 – 1760		1540-1400				1200 – 1090			
	1774		1509		1492		1476		1168	1109
F ₅ -Phe-H ⁺	C=O Stretch, NH ₂ Scissor		Ring Stretch, CH ₂ Twist				NH ₃ Umbrella		COH Bend	Asym. C-F Stretch

Table S12 Assignments of vibrational modes of protonated Phe derivatives (different EWGs/EDGs)

Structure	Vibrational modes (cm ⁻¹)						
IRMPD	1800-1750	1480-1390				1200-1090	
3CN-Phe-H ⁺	1776	1452		1397		1166	
	C=O Stretch, NH ₂ Scissor	NH ₃ Umbrella		COH Bend, CH & NH ₂ Wag		COH Bend	
IRMPD	1810-1700	1510-1270				1270-1040	
3CF ₃ -Phe-H ⁺	1776	1454	1397		1294	1166	
	C=O Stretch, NH ₂ Scissor	NH ₃ Umbrella, CH ₂ Scissor	COH Bend, CH & NH ₂ Wag		Ring Stretch	COH Bend	
IRMPD	1790 – 1700	1630-1500		1500-1270		1270 – 1070	
4NO ₂ -Phe-H ⁺	1758	1602	1552	1439	1383	1331	
	C=O Stretch, NH ₂ Scissor	Asymmetrical N=O Stretch, Ring Stretch		NH ₃ Umbrella, CH ₂ Scissor	COH Bend, CH & NH ₂ Wag	Symmetrical N=O Stretch	COH Bend
IRMPD	1860 – 1700	1670-1000					
3,4(MeO) ₂ -Phe-H ⁺	1770	1521		1445		1278	
	C=O Stretch, NH ₂ Scissor	Ring H Wag		NH ₃ & CH ₃ Umbrella		Ring Stretch	COH Bend

Table S13 The calculated proton affinities and gas phase basicities of Phe and its derivatives at the B3LYP/6-311++G(d,p) level of theory.

Phe Derivatives	$-\Delta H$ (kJ/mol)	$-\Delta G$ (kJ/mol)
3,4(MeO) ₂	951.13	915.31
Phe	926.02	896.32
2,5F ₂	916.28	883.08
3F	914.74	884.65
4F	914.71	884.87
3CF ₃	908.84	875.64
3,5F ₂	903.98	873.96
3CN	897.21	867.76
4NO ₂	891.75	862.61
F ₅	890.37	854.93