

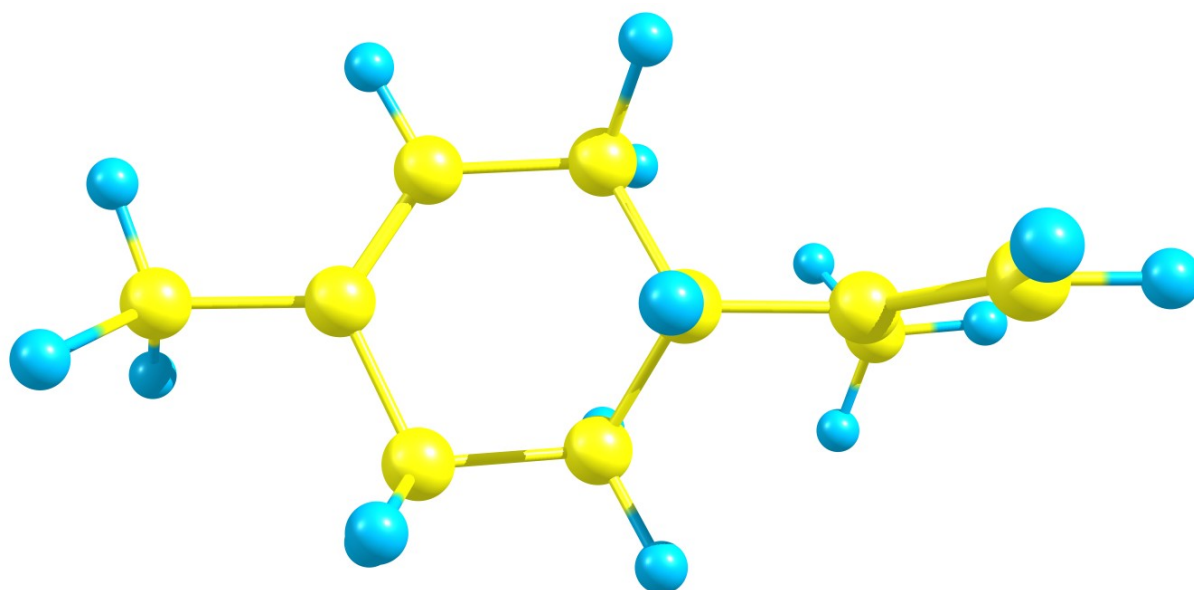
SUPPLEMENTARY INFORMATION

Limonene: electronic state spectroscopy by high-resolution vacuum ultraviolet photoabsorption, electron scattering, He(I) photoelectron spectroscopy and *ab initio* calculations

M. A. Śmialek, M.-J. Hubin-Franskin, J. Delwiche, D. Duflot, N. J. Mason, S. Vrønning-Hoffmann, G. G. B. de Souza, A. M. Ferreira Rodrigues, F. N. Rodrigues and P. Limão-Vieira

Calculated geometries MP2/cc-pVDZ : neutral species

Down-I

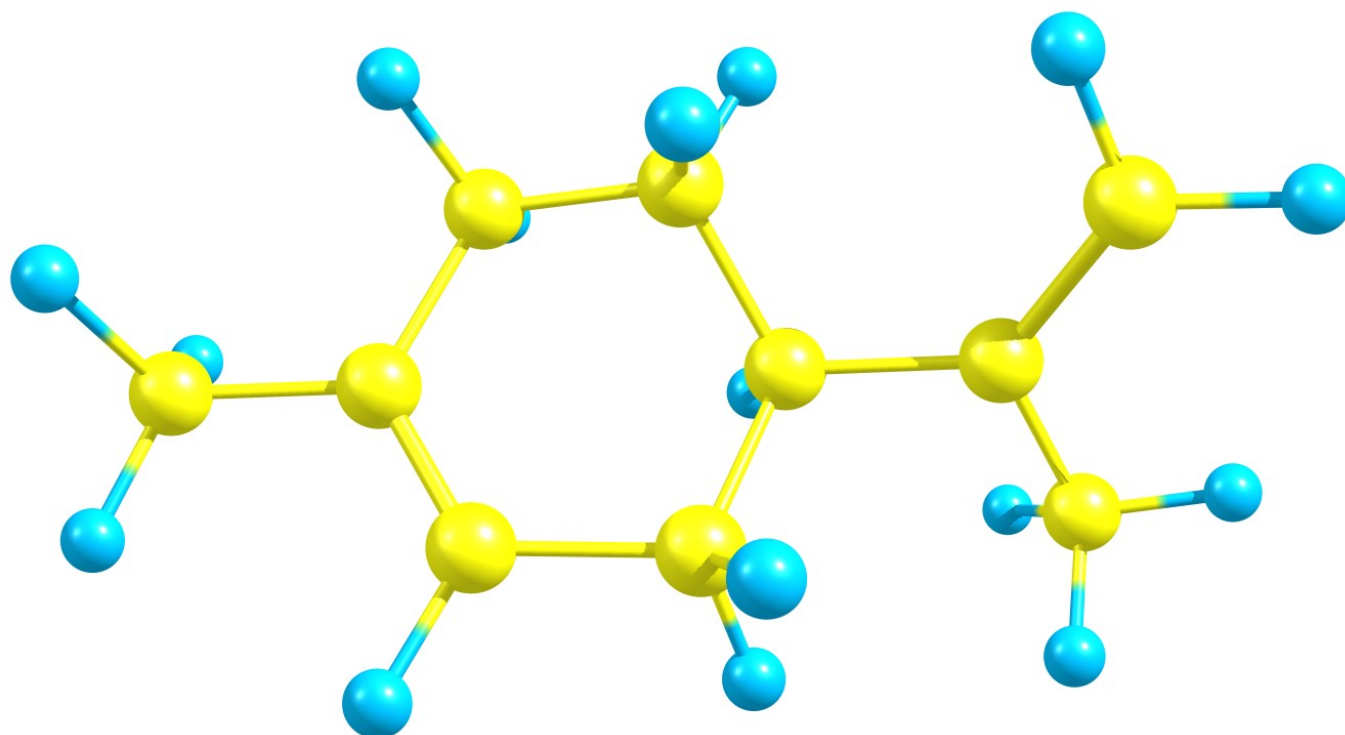


Cartesian coordinates

MP2/VDZ ENERGY=-389.38723619

C	-2.1510955516	0.0788398623	0.0165837542
C	-1.4560400451	-1.2563363434	0.1836362970
C	0.0126816473	-1.2072674474	-0.2492246235
C	0.7062840980	0.0193983826	0.3653115768
C	0.0583236945	1.2946754316	-0.2050616122
C	-1.4498523262	1.2216723984	-0.1750142787
C	2.2102456862	0.0105474557	0.1782325321
C	3.0375343808	0.1778543052	1.2344550415
C	-3.6569708988	0.0619473638	0.0849973539
C	2.7477791992	-0.1930664506	-1.2196391735
H	2.3325023774	0.5459771072	-1.9267378199
H	3.8457145497	-0.1036606869	-1.2366882858
H	2.4801774138	-1.1925605746	-1.6049872871
H	4.1259254325	0.1853745689	1.1112430859
H	2.6405273276	0.3115135486	2.2465483340
H	0.5011619355	0.0059854028	1.4542666965
H	0.0628185115	-1.1399381571	-1.3526228223
H	0.5340888103	-2.1346740628	0.0490243089
H	0.4029866375	2.1715671124	0.3739874741
H	0.4013356968	1.4629022253	-1.2454497931
H	-2.0009635064	-2.0239438337	-0.3981946291
H	-1.5294645372	-1.5733847514	1.2436847657
H	-2.0026862489	2.1617122241	-0.3101484532
H	-4.0801987690	1.0755317673	-0.0035901592
H	-4.0809499953	-0.5652733236	-0.7202557163
H	-3.9984255202	-0.3739435247	1.0418734335

Down-II

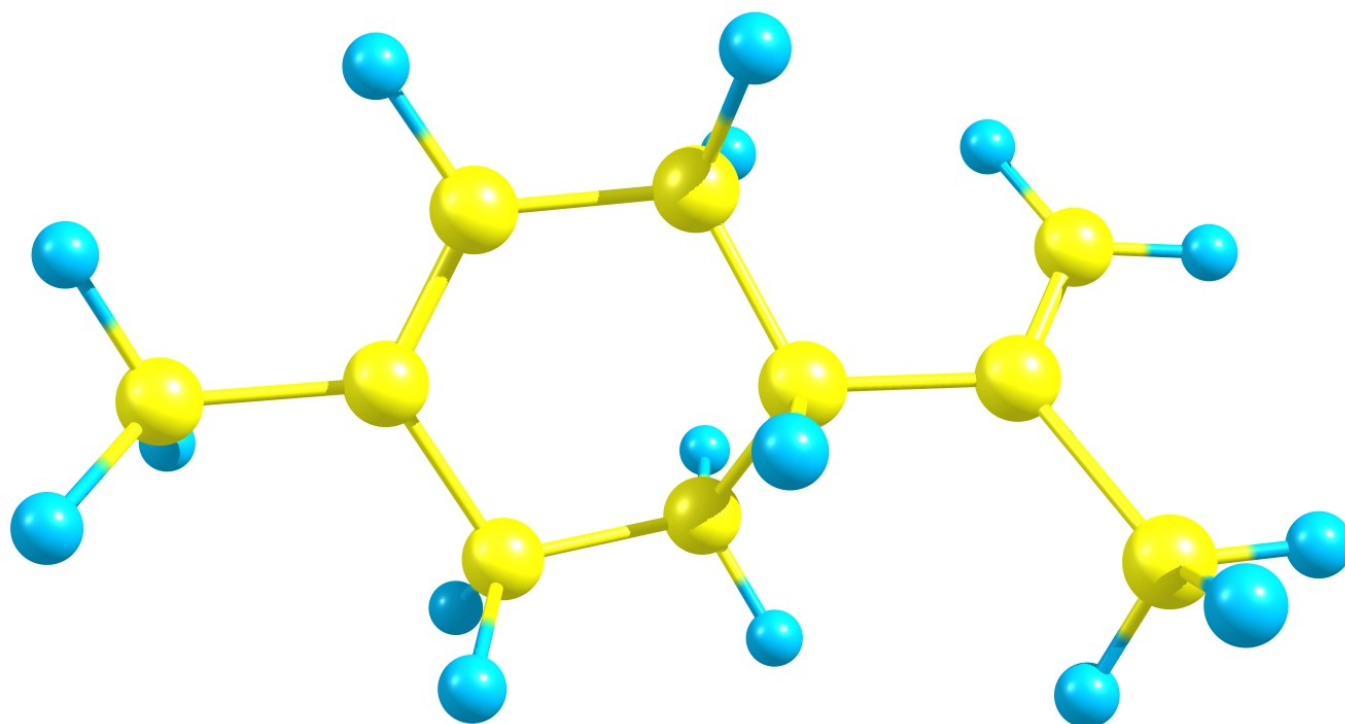


Cartesian coordinates

MP2/VDZ ENERGY=-389.38669214

C	-2.9056570838	-0.8242167403	1.2167848033
C	-2.2067694628	0.0086464805	0.1662521764
C	-2.9011954745	0.5957871453	-0.8342673736
C	-0.6990008954	0.1131935919	0.3019655021
C	-0.0351013066	1.1507946916	-0.6086015996
C	-0.0305613515	-1.2574911677	0.0641852281
C	1.4408354099	1.3239750294	-0.2367889262
C	1.4757391149	-1.1619171434	0.0211619168
C	2.1607003266	0.0000793645	-0.0945686123
C	3.6670909955	0.0518080151	-0.0826306529
H	-2.6378299367	-0.4779140556	2.2312148936
H	-2.6099605769	-1.8859305587	1.1502895204
H	-4.0006532955	-0.7697715016	1.1081705602
H	-3.9884579264	0.4822850397	-0.8995645854
H	-2.4148646003	1.1973827700	-1.6065514458
H	-0.4800902090	0.4034981584	1.3519346045
H	-0.1083223264	0.8093459309	-1.6587323722
H	-0.5613609226	2.1186461992	-0.5393681325
H	-0.3223642007	-1.9692928602	0.8576746215
H	-0.4151742489	-1.6825396130	-0.8856849172
H	1.9560671825	1.9355560235	-1.0016253885
H	1.5305136313	1.8908447782	0.7119553242
H	2.0404575933	-2.1013193251	0.0995191433
H	4.1082456298	-0.9472992102	0.0638371402
H	4.0540857742	0.4693297398	-1.0299774079
H	4.0274381599	0.7121092178	0.7275159796

Down-III



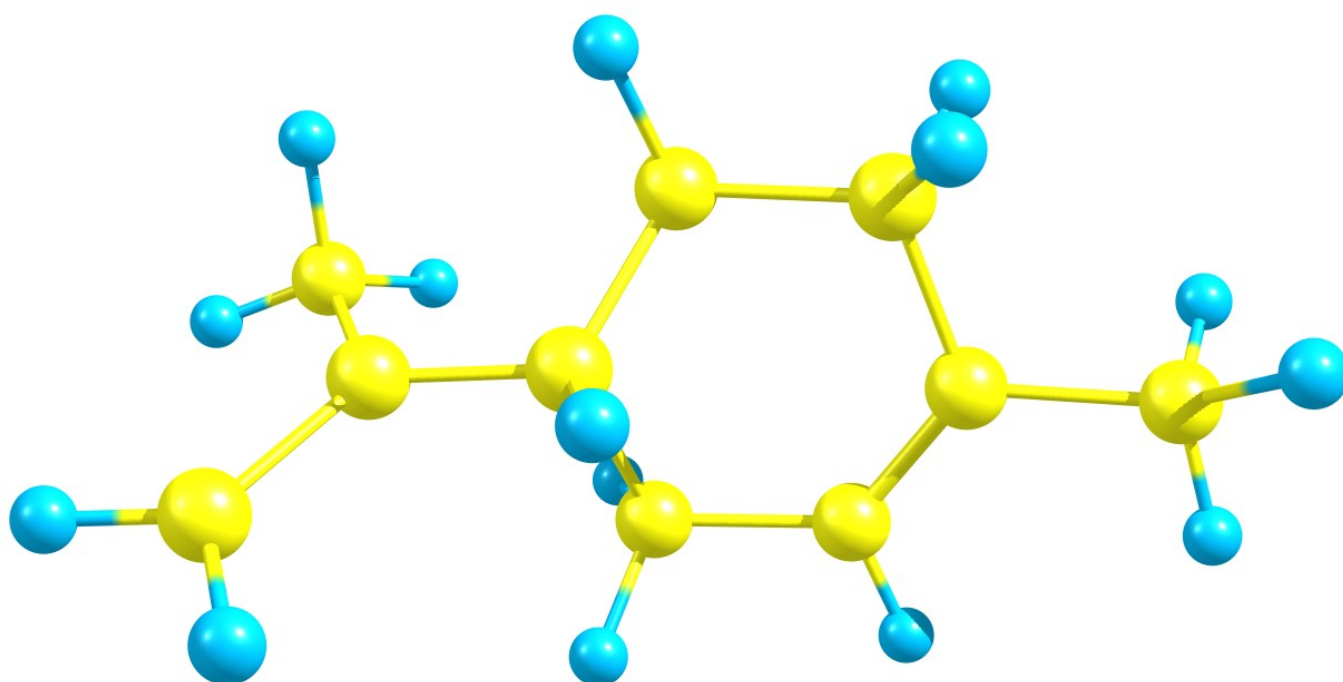
Cartesian coordinates

MP2/VDZ ENERGY=-389.38603653

C	-2.9784475654	-1.0914994037	-0.6454420737
C	-2.2100762797	0.0748459772	-0.0672154593
C	-2.8471729826	1.0797200896	0.5747232070
C	-0.7058104731	0.0183256634	-0.2596371010
C	-0.0407965723	-0.9734084159	0.7156064312
C	0.0157510347	1.3651966064	-0.1388587095
C	1.4106527530	-1.2414080711	0.3029971654
C	1.5146786528	1.2014064920	-0.2317305012
C	2.1617502335	0.0266463002	-0.0435180223
C	3.6581126263	-0.0981375124	-0.1768485422
H	-2.8459866994	-1.1330920770	-1.7416813836
H	-2.6148012181	-2.0528274355	-0.2422956371
H	-4.0558435143	-1.0143669133	-0.4286886936
H	-3.9348713781	1.0583243247	0.7003812955
H	-2.3161319393	1.9428145786	0.9842540555
H	-0.5205004008	-0.3646614206	-1.2857689689
H	-0.0701377747	-0.5280027976	1.7285828443
H	-0.6006811571	-1.9233391437	0.7636184836
H	-0.3404944618	2.0567871064	-0.9240439172
H	-0.2368976406	1.8413706497	0.8287351547
H	1.9465412356	-1.7713019065	1.1136834299
H	1.4362413219	-1.9246630514	-0.5703680405
H	2.1071211860	2.0973018604	-0.4630267329
H	4.1219852842	0.8577598078	-0.4691143999
H	4.1119154729	-0.4295199633	0.7749121329
H	3.9201842565	-0.8574433447	-0.9364380173

Calculated geometries MP2-ZAPT/cc-pVDZ : ionic species

Down-I

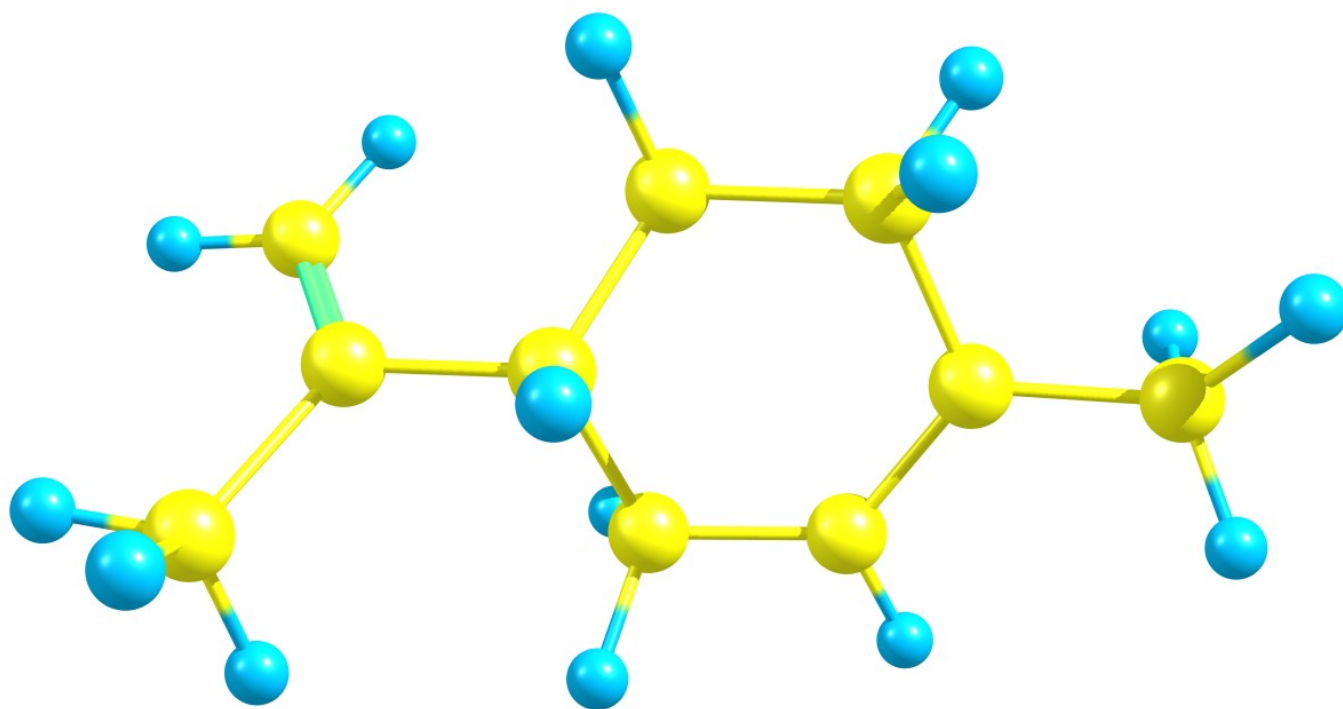


Cartesian coordinates

E(MP2/ZAPT)= -389.0649494778

6	-2.122935028	0.086175508	0.039128811
6	-1.489575160	-1.287188606	0.005536137
6	-0.021809460	-1.252573713	-0.425503835
6	0.703414774	-0.147831502	0.353582832
6	0.127293272	1.259943627	-0.143138704
6	-1.378978313	1.214572165	-0.033254118
6	2.141304503	-0.004306266	0.146326945
6	2.937181761	0.532722007	1.203308519
6	-3.621609181	0.127020020	0.176567890
6	2.772935959	-0.368776176	-1.142731468
1	2.128904094	-0.098429006	-1.995083223
1	3.783763817	0.042359132	-1.266611655
1	2.833843028	-1.478678426	-1.159508460
1	4.022579814	0.628187106	1.097481403
1	2.470371578	0.847053732	2.142460723
1	0.467625091	-0.195404594	1.431961004
1	0.042189540	-1.044304462	-1.508041285
1	0.458807258	-2.229102375	-0.241019066
1	0.530632511	2.078280680	0.478827721
1	0.460400804	1.435216349	-1.182801492
1	-2.057921435	-1.933118766	-0.686999738
1	-1.587059564	-1.756072741	1.003945226
1	-1.870198718	2.195306058	0.003906563
1	-3.997406602	1.158890648	0.247543648
1	-4.100646407	-0.363759325	-0.688299420
1	-3.939667939	-0.424731071	1.078645044

Down-II

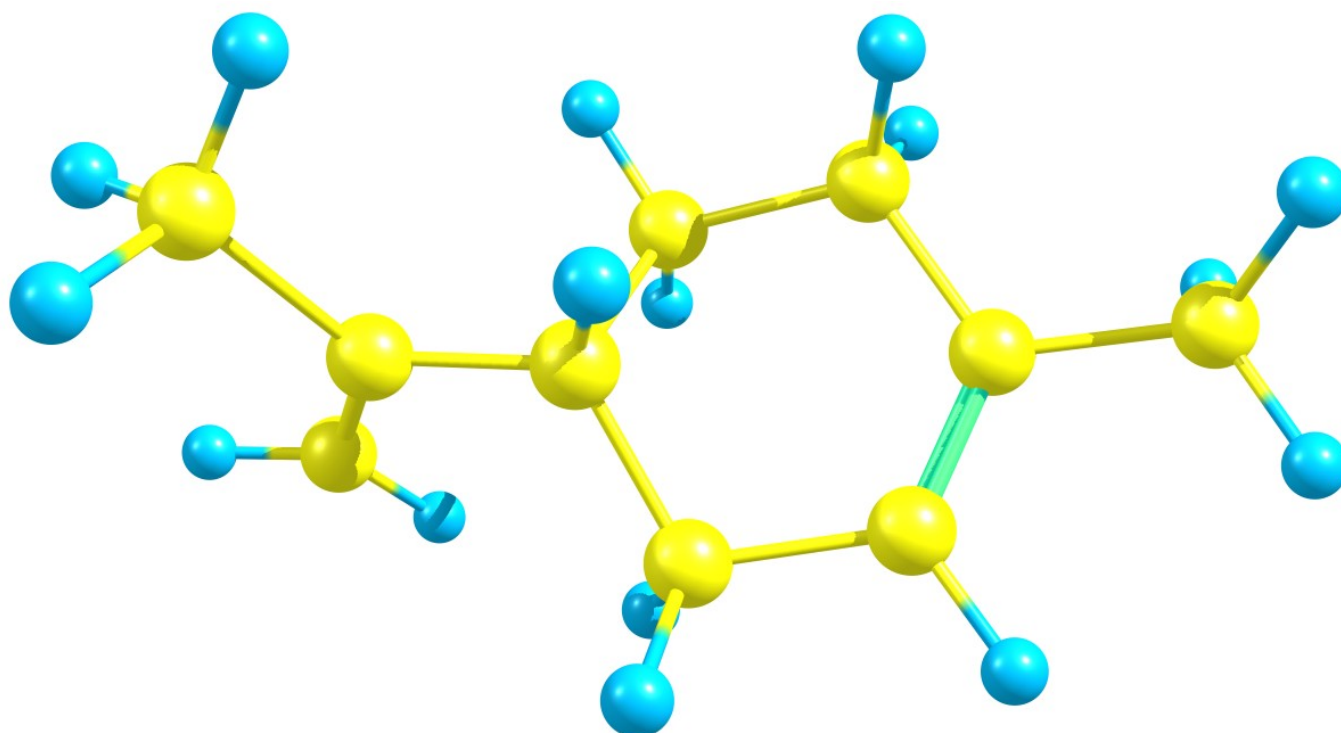


Cartesian coordinates

E(MP2/ZAPT)= -389.0751095779

6	-3.039580638	1.031477316	-0.639812436
6	-2.214786273	-0.079851520	-0.034406562
6	-2.764015396	-1.049464148	0.729951275
6	-0.725634987	-0.027586973	-0.335948812
6	0.056980696	-1.300076093	0.004416543
6	-0.082007572	1.161915544	0.403657783
6	1.512721640	-1.172920356	-0.459242866
6	1.388731266	1.174101488	0.424558425
6	2.187271420	0.073487234	-0.020681503
6	3.665338655	0.169816078	-0.029637048
1	-2.744061106	2.022865211	-0.251262304
1	-4.108703639	0.896086060	-0.417380108
1	-2.915305659	1.058489507	-1.736743223
1	-3.835773895	-1.038808734	0.950951153
1	-2.185142175	-1.882799221	1.138226335
1	-0.610620600	0.161387581	-1.423564253
1	0.036235908	-1.480415878	1.094630100
1	-0.403646289	-2.174609194	-0.480611585
1	-0.441582082	2.151987490	0.062031075
1	-0.377501032	1.142939053	1.484679646
1	2.141020362	-2.041112296	-0.187840906
1	1.561687451	-1.132573841	-1.573869923
1	1.909807830	2.058445786	0.817974222
1	4.033494096	1.205776355	-0.047614506
1	4.019688570	-0.300806090	0.913381332
1	4.098780716	-0.419414325	-0.853251823

Down-III



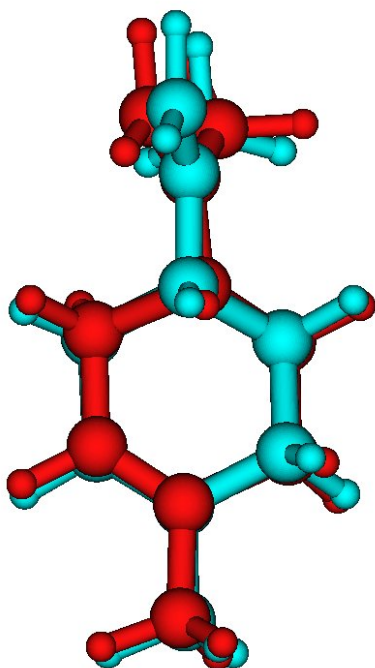
Cartesian coordinates

E(MP2/ZAPT)= -389.0641823394

6	-2.984952222	-0.999913944	-0.818957559
6	-2.128368719	-0.021796196	-0.105137918
6	-2.714215535	0.825208918	0.885505677
6	-0.695886318	0.026676447	-0.384841162
6	-0.097392789	-0.862674454	0.799474603
6	0.019579054	1.384843539	-0.374407211
6	1.358281034	-1.175369516	0.432261725
6	1.516605733	1.188599627	-0.376013525
6	2.136049950	0.034905407	-0.033047858
6	3.631609251	-0.129904684	-0.098217697
1	-3.293044723	-0.492283939	-1.760322988
1	-2.413970439	-1.890816005	-1.122199455
1	-3.896602180	-1.273361478	-0.268811073
1	-3.797304205	0.819027274	1.044706575
1	-2.102128121	1.490568367	1.499710943
1	-0.477222638	-0.517035881	-1.319909126
1	-0.149926013	-0.267797384	1.728070231
1	-0.673291895	-1.792251561	0.943059642
1	-0.284734479	1.952029204	-1.272157211
1	-0.284937864	1.992777151	0.498560887
1	1.839695426	-1.600198826	1.333203848
1	1.394378199	-1.968632988	-0.338482743
1	2.120732144	2.046869114	-0.692533902
1	4.120806131	0.773923344	-0.491722181
1	4.043632293	-0.344791870	0.903142288
1	3.898892926	-0.981771667	-0.748116808

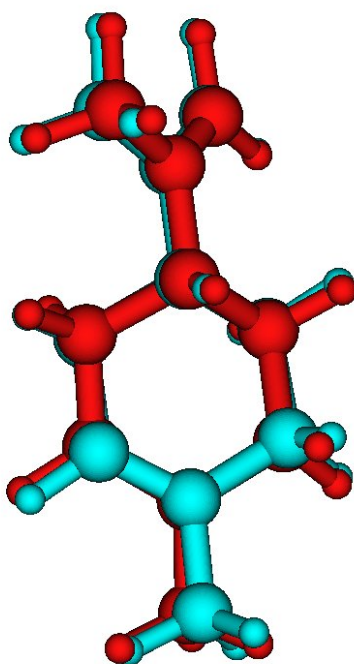
Comparison between neutral and ionic geometries (red = ion, blue = neutral) :

Down-I



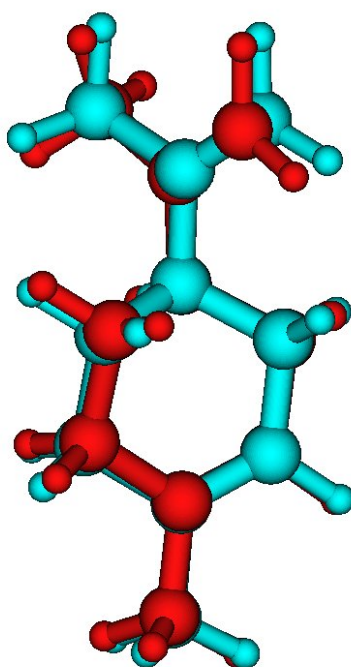
Weighted Root-Mean-Square distance = 0.30 Å

Down-II



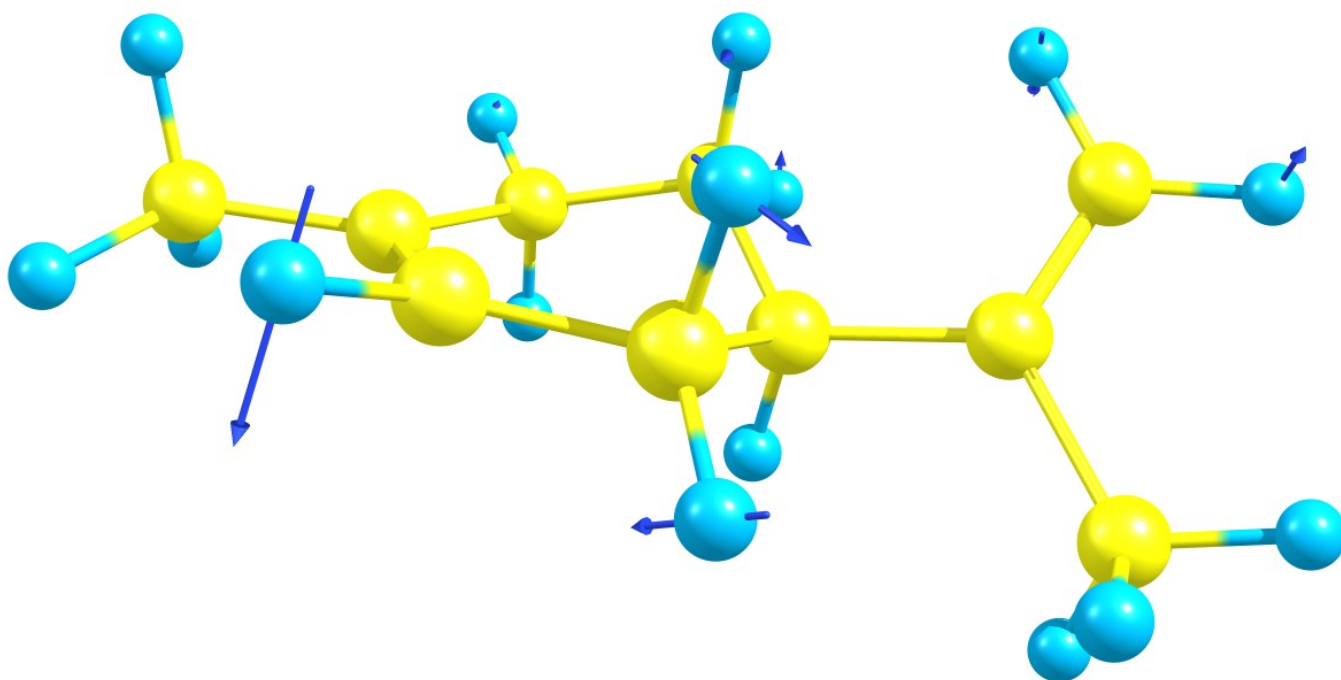
Weighted Root-Mean-Square distance = 0.15 Å

Down-III

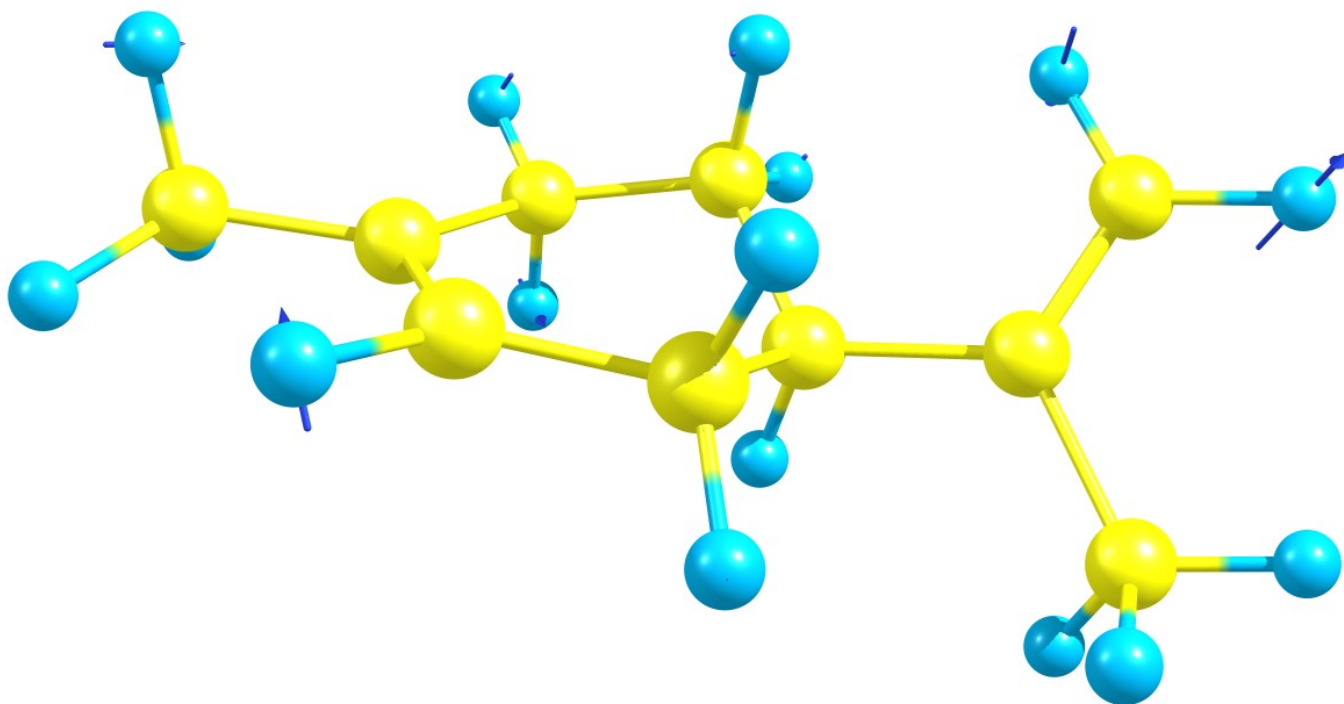


Weighted Root-Mean-Square distance = 0.36 Å

Down-II ν_{17} mode ($692\text{ cm}^{-1} = 86\text{ meV}$) :



Down-II ν_{18} mode ($717\text{ cm}^{-1} = 89\text{ meV}$) :



Down-II ν_{55} mode ($1589\text{ cm}^{-1} = 197\text{ meV}$) :

