Electronic Supplementary Material for PCCP

Spectroscopy and Dynamics of A 2B1 Allyl Radical

Luca Castiglioni, Andreas Bach and Peter Chen

SUPPORTING INFORMATION (ASCII)

A.) CCSD/cc-pVTZ optimized geometries and CCSD(T)/cc-pVXZ energies of all stationary points discussed in this work.

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A1. allyl radical (C2v)

6	.000000	.000000	.453087
6	.000000	1.236422	-.199983
6	.000000	-1.236422	-.199983
1	.000000	1.292722	-1.295402
1	.000000	.000000	1.552138
1	.000000	2.176963	.359971
1	.000000	-1.292722	-1.295402
1	.000000	-2.176963	.359971

Rotational constants (cm-1): 1.619, 0.314, 0.217

CCSD(T) energies / Hartree
cc-pVDZ: -116.91324984
cc-pVTZ: -117.03153584
cc-pVQZ: -117.06495454
CBS (est.): -117.07811400

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A2. 2-propenyl radical (Cs)

6	.000000	.431550	.000000
6	-1.198336	-.453558	.000000
6	1.322938	.292246	.000000
1	-.890376	-1.519907	.000000
1	-1.823253	-.274053	.892916
1	-1.823253	-.274053	-.892916
1	1.999855	1.155741	.000000
1	1.789413	-.709157	.000000

CCSD(T) energies / Hartree
cc-pVDZ: -116.88228932
cc-pVTZ: -116.99982427
cc-pVQZ: -117.03307264
CBS (est.): -117.04618810

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A3. cyclopropyl radical (Cs)

6	.029817	.902096	.000000
6	.029817	-.369614	.770597
6	.029817	-.369614	-.770597
1	-.686726	1.728456	.000000
1	-.884614	-.667188	1.301169
1	-.884614	-.667188	-1.301169
1	.959628	-.685641	1.261381
1	.959628	-.685641	-1.261381

CCSD(T) energies / Hartree
cc-pVDZ: -116.86721303
cc-pVTZ: -116.98596647
cc-pVQZ: -117.01931718
CBS (est.): -117.02690080

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A4. allene (D2d)

6	.000000	.000000	1.324407
6	.000000	.000000	.000000
6	.000000	.000000	-1.324407
1	.000000	.940059	1.888582
1	.000000	-.940059	1.888582
1	.940059	.000000	-1.888582
1	-.940059	.000000	-1.888582

CCSD(T) energies / Hartree
cc-pVDZ: -116.31664325
cc-pVTZ: -116.43288182
cc-pVQZ: -116.46584230
CBS (est.): -116.47888770

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A5. propine (C3v)

6	.000000	.000000	1.442312
6	.000000	.000000	.219068
6	.000000	.000000	-1.257982
1	.000000	.000000	2.519482
1	.000000	1.032697	-1.646624
1	.894342	-.516349	-1.646624
1	-.894342	-.516349	-1.646624

CCSD(T) energies / Hartree
cc-pVDZ: -116.31746385
cc-pVTZ: -116.43470447
cc-pVQZ: -116.46785976
CBS (est.): -116.48093310

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A6.   cyclopropene (C2v)
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  6         .689171    -.529137     .000000
  6        -.799772    -.213801     .000000
  6         .000000     .827856     .000000
  1        1.166492    -.895617     .923437
  1        1.166492    -.895617    -.923437
  1       -1.807690    -.626427     .000000
  1         .138313    1.908147     .000000

  CCSD(T) energies / Hartree
  cc-pVDZ:    -116.28090425
  cc-pVTZ:    -116.39728206
  cc-pVQZ:    -116.43046485
  CBS (est.): -116.44370000


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A7.   TS 1 (allyl -> allene + H) (Cs)
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  6        0.000000    0.056305    0.000000
  1        0.167286    1.969457    0.000000
  6       -1.324096    0.000108    0.000000
  6        1.303416   -0.261715    0.000000
  1       -1.949570    0.896642    0.000000
  1       -1.818706   -0.979504    0.000000
  1        1.862535   -0.327392    0.940515
  1        1.862535   -0.327392   -0.9405

  CCSD(T) energies / Hartree
  cc-pVDZ:    -116.80594811
  cc-pVTZ:    -116.92463326
  cc-pVQZ:    -116.95827402
  CBS (est.): -116.97158120


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A8.   TS 2 (allyl -> 2-propenyl) (C1)
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  6       -1.292335    0.146356    0.009413
  6        0.070060   -0.327066   -0.095371
  6        1.334536    0.114380   -0.000649
  1       -0.823230   -0.987078    0.585110
  1       -1.557523    1.022434    0.621142
  1       -2.036262   -0.246441   -0.692523
  1        1.576873    1.161723   -0.244930
  1        2.166576   -0.552656    0.250840

  CCSD(T) energies / Hartree
  cc-pVDZ:    -116.80353561
  cc-pVTZ:    -116.92372383
  cc-pVQZ:    -116.95759195
  CBS (est.): -116.97088030
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A9.   TS 3 (2-propenyl -> allene + H) (Cs)
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  6        0.000000    0.148337    0.000000
  6       -1.062158   -0.665021    0.000000
  6        1.117854    0.849184    0.000000
  1       -0.380704   -2.479781    0.000000
  1       -1.575750   -0.904345    0.937866
  1       -1.575750   -0.904345   -0.937866
  1        1.103319    1.945661    0.000000
  1        2.094708    0.347805    0.000000

  CCSD(T) energies / Hartree
  cc-pVDZ:    -116.80878104
  cc-pVTZ:    -116.92753249
  cc-pVQZ:    -116.96112485
  CBS (est.): -116.97437590


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A10.  TS 4 (2-propenyl -> propine + H) (Cs)
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  6        0.000000    0.205934    0.000000
  6        1.002284    0.926692    0.000000
  6       -1.040821   -0.839023    0.000000
  1        2.532283   -0.217369    0.000000
  1        1.635351    1.800771    0.000000
  1       -1.680324   -0.751869    0.894867
  1       -1.680324   -0.751869   -0.894867
  1       -0.575761   -1.841279    0.000000

  CCSD(T) energies / Hartree
  cc-pVDZ:    -116.80931712
  cc-pVTZ:    -116.92865334
  cc-pVQZ:    -116.96235276
  CBS (est.): -116.97561400


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A11.  TS 5 (allyl -> cyclopropyl) (C1)
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  6        0.078923    0.707383   -0.246773
  6        0.970402   -0.334311    0.037541
  6       -1.049056   -0.206742    0.064597
  1        0.179883    1.697879    0.210243
  1        1.777871   -0.266875    0.787864
  1        0.934312   -1.267596   -0.537761
  1       -1.422932   -0.930990   -0.668463
  1       -1.470749   -0.230401    1.075921

  CCSD(T) energies / Hartree
  cc-pVDZ:    -116.82729431
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cc-pVTZ: -116.94675083
cc-pVQZ: -116.98034966
CBS (est.): -116.99341146

A12. TS 6 (cyclopropyl -> cyclopropene + H) (C1)

6	0.855186	-0.270718	0.001220
6	-0.174401	0.837139	0.093907
6	-0.645622	-0.348601	-0.264358
1	1.563154	-0.269246	-0.843511
1	1.253117	-0.731468	0.918910
1	-0.348225	1.894619	0.287518
1	-1.436131	-0.913580	-0.755850
1	-1.242889	-1.287247	1.408321

CCSD(T) energies / Hartree
cc-pVDZ: -116.77504094
cc-pVTZ: -116.89376634
cc-pVQZ: -116.92751929
CBS (est.): -116.94092998

B.) HCTH147/TZ2P harmonic and anharmonic frequencies and zero point energies of all stationary points discussed in this work.

B1.   allyl radical (C2v)

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			1.841004	0.344158	0.289950
Ground State	14357.259	14216.010	1.824822	0.342020	0.287749
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	3228.040	3104.516	1.820927	0.341691	0.287465
2(1)	3130.504	3031.286	1.819125	0.341822	0.287471
3(1)	3116.125	3021.254	1.822124	0.341432	0.287283
4(1)	1497.166	1450.370	1.832854	0.342009	0.286887
5(1)	1255.318	1220.051	1.839652	0.341125	0.288468
6(1)	1024.205	990.742	1.837238	0.341708	0.287237
7(1)	422.402	427.378	1.796729	0.341012	0.287374
8(1)	782.040	788.739	1.799317	0.341607	0.288000
9(1)	539.354	536.306	1.817980	0.342078	0.287766
10(1)	997.210	975.707	1.810908	0.343337	0.287926
11(1)	804.693	805.734	1.810488	0.341126	0.287912
12(1)	520.630	531.176	1.857524	0.341924	0.288247
13(1)	3226.273	3102.844	1.820865	0.341709	0.287484
14(1)	3123.964	3026.419	1.818990	0.341855	0.287504
15(1)	1502.179	1437.759	1.820905	0.341888	0.287459
16(1)	1406.942	1374.974	1.826510	0.342744	0.287646
17(1)	1214.033	1193.427	1.811965	0.342379	0.285530
18(1)	923.440	911.801	1.850324	0.340631	0.287413

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 ZPEharm    = 14357.25875 cm-1  =  41.049 Kcal/mol  = 171.751 KJ/mol
 ZPEfund    = 13965.24180 cm-1  =  39.929 Kcal/mol  = 167.061 KJ/mol
 ZPEaver    = 14161.25028 cm-1  =  40.489 Kcal/mol  = 169.406 KJ/mol
 -1/4sumXii =    23.58486 cm-1  =   0.067 Kcal/mol  =   0.282 KJ/mol
 x0         =    31.17479 cm-1  =   0.089 Kcal/mol  =   0.373 KJ/mol
 ZPEtot     = 14216.00993 cm-1  =  40.646 Kcal/mol  = 170.061 KJ/mol
 ZPEtot/ZPEharm = 0.99016   ZPEfund/ZPEharm= 0.97270


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B2.   2-propenyl radical (Cs)
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 Vibrational Energies and Rotational Constants (cm-1)
 Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
 Equilibrium Geometry                     2.552185    0.287442    0.271379
 Ground State   14142.655    13905.997    2.558798    0.285048    0.269167
 Fundamental Bands (DE w.r.t. Ground State)
  1(1)           3130.805     2979.200    2.563291    0.284275    0.268559
  2(1)           3039.682     2882.204    2.553827    0.284832    0.269118
  3(1)           3018.478     2882.021    2.552003    0.284766    0.268859
  4(1)           2951.902     2815.517    2.554372    0.284956    0.269108
  5(1)           1719.658     1681.257    2.532867    0.284166    0.268118
  6(1)           1444.739     1391.200    2.732284    0.285387    0.270493
  7(1)           1396.879     1353.613    2.551507    0.285423    0.269059
  8(1)           1362.265     1322.648    2.529617    0.284108    0.267816
  9(1)           1081.078     1044.577    2.657329    0.284283    0.268190
 10(1)            918.129      899.049    2.570228    0.284088    0.268643
 11(1)            887.915      864.661    2.696950    0.285282    0.268354
 12(1)            306.108      284.686    2.625460    0.284799    0.268760
 13(1)           3067.291     2903.887    2.556326    0.284922    0.269076
 14(1)           1431.464     1392.935    2.429763    0.285920    0.269430
 15(1)           1025.950      988.251    2.492288    0.284962    0.269002
 16(1)            860.805      856.437    2.384103    0.284734    0.269388
 17(1)            460.689      457.481    2.581538    0.284718    0.269249
 18(1)            181.472      132.098    2.507836    0.284464    0.269363

 ZPEharm    = 14142.65522 cm-1  =  40.436 Kcal/mol  = 169.184 KJ/mol
 ZPEfund    = 13565.86038 cm-1  =  38.787 Kcal/mol  = 162.284 KJ/mol
 ZPEaver    = 13854.25780 cm-1  =  39.611 Kcal/mol  = 165.734 KJ/mol
 -1/4sumXii =    67.43361 cm-1  =   0.193 Kcal/mol  =   0.807 KJ/mol
 x0         =   -15.69464 cm-1  =  -0.045 Kcal/mol  =  -0.188 KJ/mol
 ZPEtot     = 13905.99677 cm-1  =  39.759 Kcal/mol  = 166.353 KJ/mol
 ZPEtot/ZPEharm = 0.98327   ZPEfund/ZPEharm= 0.95922


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B3.   cyclopropyl radical (Cs)
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 Vibrational Energies and Rotational Constants (cm-1)
 Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
 Equilibrium Geometry                     0.798537    0.694703    0.442777
 Ground State   14452.948    14231.995    0.794329    0.687603    0.437389
 Fundamental Bands (DE w.r.t. Ground State)
  1(1)           3205.813     3071.252    0.791899    0.686332    0.436832
  2(1)           3145.424     2993.039    0.793648    0.686864    0.436923
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3(1)	3065.870	2939.990	0.793302	0.686645	0.437082
4(1)	1457.843	1409.238	0.794439	0.686437	0.438366
5(1)	1254.607	1230.359	0.793483	0.687438	0.436397
6(1)	1073.534	1056.600	0.793985	0.725157	0.437818
7(1)	1000.368	958.528	0.794086	0.685609	0.435821
8(1)	849.520	821.047	0.796791	0.682357	0.427909
9(1)	754.901	730.862	0.795112	0.682908	0.413482
10(1)	524.160	452.360	0.795366	0.686001	0.435231
11(1)	3134.087	2981.561	0.793535	0.687050	0.436954
12(1)	3067.045	2940.886	0.793281	0.686597	0.437089
13(1)	1432.065	1391.372	0.795505	0.686755	0.438586
14(1)	1140.357	1108.449	0.800147	0.685024	0.441371
15(1)	1068.632	1032.641	0.789278	0.657863	0.432933
16(1)	1037.262	1005.551	0.793320	0.683664	0.435966
17(1)	927.804	903.224	0.790131	0.689340	0.442972
18(1)	766.605	756.026	0.792190	0.690623	0.460485

ZPEharm = 14452.94836 cm-1 = 41.323 Kcal/mol = 172.896 KJ/mol
ZPEfund = 13891.49345 cm-1 = 39.718 Kcal/mol = 166.179 KJ/mol
ZPEaver = 14172.22090 cm-1 = 40.520 Kcal/mol = 169.537 KJ/mol
-1/4sumXii = 47.57938 cm-1 = 0.136 Kcal/mol = 0.569 KJ/mol
x0 = 12.19495 cm-1 = 0.035 Kcal/mol = 0.146 KJ/mol
ZPEtot = 14231.99523 cm-1 = 40.691 Kcal/mol = 170.252 KJ/mol
ZPEtot/ZPEharm = 0.98471 ZPEfund/ZPEharm= 0.96115

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B4. allene (D2d)

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.000000	0.000000	0.000000
Ground State	11891.282	11783.869	-0.045303	-0.001008	-0.001008
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	3110.837	3006.809	-0.085769	-0.001275	-0.001275
2(1)	1452.083	1416.243	-0.016897	-0.001107	-0.001107
3(1)	1093.559	1081.292	-0.046806	-0.001412	-0.001412
4(1)	866.951	867.700	-0.113939	-0.001804	-0.001804
5(1)	3106.448	2998.064	-0.082146	-0.001281	-0.001281
6(1)	2005.423	1980.284	-0.048722	-0.002947	-0.002947
7(1)	1398.231	1366.265	0.007270	-0.000771	-0.000771
8(1)	3185.805	3064.912	-0.070316	-0.001297	-0.001335
9(1)	3185.805	3064.917	-0.070316	-0.001335	-0.001297
10(1)	992.289	981.369	0.171353	-0.001258	-0.000059
11(1)	992.289	981.364	0.171353	-0.000059	-0.001258
12(1)	838.895	840.469	-0.234812	-0.001366	-0.000750
13(1)	838.895	840.480	-0.234812	-0.000750	-0.001366
14(1)	357.528	365.961	-0.057798	0.000024	-0.000504
15(1)	357.528	365.961	-0.057798	-0.000504	0.000024

ZPEharm = 11891.28170 cm-1 = 33.999 Kcal/mol = 142.251 KJ/mol
ZPEfund = 11611.04454 cm-1 = 33.198 Kcal/mol = 138.899 KJ/mol
ZPEaver = 11751.16312 cm-1 = 33.598 Kcal/mol = 140.575 KJ/mol
-1/4sumXii = 21.81428 cm-1 = 0.062 Kcal/mol = 0.261 KJ/mol
x0 = 10.89176 cm-1 = 0.031 Kcal/mol = 0.130 KJ/mol
ZPEtot = 11783.86916 cm-1 = 33.692 Kcal/mol = 140.966 KJ/mol

ZPEtot/ZPEharm = 0.99097   ZPEfund/ZPEharm= 0.97643

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B5. propine (C3v)

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.000000	0.000000	0.000000
Ground State	11963.693	11858.027	-0.058959	-0.000737	-0.000735
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	3438.802	3328.680	-0.059099	-0.001405	-0.001403
2(1)	3008.244	2913.286	-0.112781	-0.000780	-0.000778
3(1)	2178.188	2141.441	-0.061566	-0.002151	-0.002149
4(1)	1379.256	1360.056	-0.029993	-0.002393	-0.002391
5(1)	935.832	925.804	-0.065272	-0.002144	-0.002142
6(1)	3081.491	2963.062	459.978236	-0.000754	-0.000777
7(1)	3081.490	2934.317	-460.164873	-0.000778	-0.000751
8(1)	1451.215	1401.591	**********	-0.000529	0.000907
9(1)	1451.214	1479.269	**********	0.000904	-0.000526
10(1)	1026.416	1032.873	**********	-0.000835	-0.000888
11(1)	1026.416	1016.393	**********	-0.000891	-0.000834
12(1)	607.277	613.892	**********	-0.000622	-0.000323
13(1)	607.277	607.705	**********	-0.000325	-0.000621
14(1)	327.137	342.609	**********	-0.000193	0.000369
15(1)	327.132	332.106	**********	0.000368	-0.000189

ZPEharm   = 11963.69276 cm-1 = 34.206 Kcal/mol = 143.118 KJ/mol
ZPEfund   = 11696.54239 cm-1 = 33.442 Kcal/mol = 139.922 KJ/mol
ZPEaver   = 11830.11757 cm-1 = 33.824 Kcal/mol = 141.520 KJ/mol
-1/4sumXii =   37.08225 cm-1 =   0.106 Kcal/mol =   0.444 KJ/mol
x0   =   -9.17299 cm-1 = -0.026 Kcal/mol = -0.110 KJ/mol
ZPEtot   = 11858.02684 cm-1 = 33.904 Kcal/mol = 141.854 KJ/mol
ZPEtot/ZPEharm = 0.99117   ZPEfund/ZPEharm= 0.97767

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B6. cyclopropene (C2v)

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			1.007453	0.734646	0.464191
Ground State	12119.867	11986.308	0.999337	0.729255	0.459958
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	3265.408	3159.313	0.996198	0.727800	0.458736
2(1)	3221.033	3122.196	0.996385	0.727849	0.458810
3(1)	3023.805	3047.436	0.997937	0.728629	0.459973
4(1)	1704.478	1674.849	0.996380	0.728620	0.459263
5(1)	1505.867	1467.880	0.999394	0.728489	0.461008
6(1)	1149.999	1089.178	1.001516	0.730909	0.459473
7(1)	1058.501	1029.814	0.981145	0.723010	0.457500
8(1)	1008.560	979.159	1.009077	0.737428	0.459162
9(1)	906.305	885.929	1.006706	0.733396	0.460744
10(1)	787.504	763.749	1.000696	0.727793	0.455994
11(1)	3093.135	2951.292	0.998610	0.729122	0.459947

12(1)	1102.225	1082.504	1.011899	0.730099	0.464612
13(1)	1006.674	977.718	0.994954	0.726327	0.454215
14(1)	823.476	822.609	0.988133	0.722387	0.460424
15(1)	582.765	587.349	0.994794	0.726184	0.461046

ZPEharm = 12119.86716 cm-1 = 34.652 Kcal/mol = 144.986 KJ/mol
ZPEfund = 11820.48728 cm-1 = 33.796 Kcal/mol = 141.404 KJ/mol
ZPEaver = 11970.17722 cm-1 = 34.224 Kcal/mol = 143.195 KJ/mol
-1/4sumXii = 50.14714 cm-1 = 0.143 Kcal/mol = 0.600 KJ/mol
x0 = -34.01606 cm-1 = -0.097 Kcal/mol = -0.407 KJ/mol
ZPEtot = 11986.30830 cm-1 = 34.271 Kcal/mol = 143.388 KJ/mol
ZPEtot/ZPEharm = 0.98898 ZPEfund/ZPEharm= 0.97530

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B7. TS 1 (allyl -> allene + H) (Cs)

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			2.030398	0.297417	0.274081
Ground State	11834.048	-nan	2.004501	0.296885	0.273154
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-679.831	-nan	2.010999	0.296877	0.273381
2(1)	3200.791	3104.342	2.000648	0.296596	0.272879
3(1)	3114.199	3012.243	1.995933	0.296658	0.272921
4(1)	3109.649	2995.758	1.996362	0.296642	0.272929
5(1)	1946.859	1896.003	1.997816	0.294974	0.271404
6(1)	1448.003	1408.536	2.010707	0.296761	0.273113
7(1)	1400.111	1362.574	2.013959	0.297136	0.273327
8(1)	1076.769	1064.257	2.008613	0.296385	0.272749
9(1)	989.054	979.717	2.015820	0.297723	0.272942
10(1)	826.832	768.192	1.976556	0.297028	0.272825
11(1)	452.416	447.668	1.998114	0.298576	0.275162
12(1)	414.571	414.720	2.094316	0.298178	0.271247
13(1)	3189.693	3051.864	1.998036	0.296609	0.272915
14(1)	996.915	985.492	2.066927	0.296634	0.273746
15(1)	853.120	855.194	1.968004	0.296512	0.273363
16(1)	833.280	814.437	1.997123	0.296025	0.272668
17(1)	371.485	374.077	1.895586	0.297040	0.274003
18(1)	124.179	50.235	1.983713	0.296508	0.273342

ZPEharm = 11834.04758 cm-1 = 33.835 Kcal/mol = 141.567 KJ/mol
ZPEfund = 11460.02431 cm-1 = 32.766 Kcal/mol = 137.027 KJ/mol
ZPEaver = 11647.03321 cm-1 = 33.300 Kcal/mol = 139.262 KJ/mol
-1/4sumXii = 42.31236 cm-1 = 0.121 Kcal/mol = 0.506 KJ/mol
x0 = 2.88371 cm-1 = 0.008 Kcal/mol = 0.034 KJ/mol
ZPEtot = -nan cm-1 = -nan Kcal/mol = -nan KJ/mol
ZPEtot/ZPEharm = -nan ZPEfund/ZPEharm= -nan

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B8. TS 2 (allyl -> 2-propenyl) (C1)

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)

Equilibrium Geometry			2.581521	0.298301	0.279463
Ground State	12245.326	-nan	2.586164	0.295564	0.277033
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-1820.338	-inf	2.588041	0.295654	0.277112
2(1)	3173.245	3077.321	2.581183	0.295419	0.276873
3(1)	3169.231	3073.143	2.589662	0.294925	0.276558
4(1)	3064.521	2932.156	2.580794	0.295200	0.276673
5(1)	3042.438	2904.419	2.577120	0.295465	0.276869
6(1)	2176.245	2107.426	2.570836	0.295367	0.276536
7(1)	1646.036	1628.256	2.549497	0.295141	0.276307
8(1)	1431.991	1387.569	2.601581	0.295446	0.276792
9(1)	1405.848	1368.003	2.597614	0.295861	0.277000
10(1)	1121.014	1083.956	2.573582	0.295850	0.277228
11(1)	1078.671	1050.431	2.622732	0.294409	0.275861
12(1)	1004.288	983.661	2.601670	0.294909	0.276539
13(1)	961.817	942.625	2.625370	0.295619	0.276846
14(1)	821.610	804.846	2.570954	0.294567	0.276488
15(1)	809.277	800.704	2.542591	0.295456	0.277367
16(1)	689.544	655.163	2.574190	0.294727	0.276662
17(1)	411.509	389.453	2.691436	0.294974	0.276883
18(1)	303.705	299.130	2.521376	0.295681	0.277135

ZPEharm	= 13368.46594	cm-1	= 38.222	Kcal/mol	= 159.922 Kj/mol
ZPEfund	= 11861.42435	cm-1	= 33.912	Kcal/mol	= 141.821 KJ/mol
ZPEaver	= 12244.88314	cm-1	= 35.010	Kcal/mol	= 146.413 KJ/mol
-1/4sumXii	= 73.11081	cm-1	= 0.209	Kcal/mol	= 0.875 KJ/mol
x0	= -30.74314	cm-1	= -0.088	Kcal/mol	= -0.368 KJ/mol
ZPEtot	= -nan	cm-1	= -nan	Kcal/mol	= -nan KJ/mol
ZPEtot/ZPEharm =	-nan	ZPEfund/ZPEharm=	-nan		

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B9. TS 3 (2-propenyl -> allene + H) (Cs)

Vibrational Energies and Rotational Constants (cm-1)					
Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			2.220816	0.273910	0.256679
Ground State	11892.852	-nan	2.195778	0.275296	0.256644
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-440.625	-nan	2.196031	0.275433	0.257128
2(1)	3176.364	3080.132	2.184475	0.275139	0.256392
3(1)	3115.691	3021.032	2.182836	0.275084	0.256484
4(1)	3100.940	2993.906	2.185841	0.275141	0.256388
5(1)	1980.607	1942.749	2.139006	0.274316	0.255031
6(1)	1446.812	1408.254	2.200391	0.275224	0.256537
7(1)	1395.959	1362.504	2.209416	0.275443	0.256805
8(1)	1082.064	1066.610	2.239586	0.275578	0.256221
9(1)	984.441	973.781	2.219322	0.275853	0.256459
10(1)	849.452	887.574	2.189232	0.275047	0.256411
11(1)	363.936	373.774	0.265592	0.231796	0.257103
12(1)	196.947	210.899	2.062240	0.277278	0.257192
13(1)	3191.432	3148.221	2.182755	0.275146	0.256430
14(1)	996.405	925.539	2.225493	0.275941	0.257440
15(1)	867.443	869.292	2.167070	0.274903	0.255984
16(1)	842.746	829.480	2.166810	0.274795	0.256856
17(1)	366.315	354.802	4.162293	0.319790	0.257517

```
 18(1)            268.773       67.159    2.295534    0.276198    0.257138

 ZPEharm    = 11892.85156 cm-1  =  34.003 Kcal/mol  = 142.270 KJ/mol
 ZPEfund    = 11544.21345 cm-1  =  33.006 Kcal/mol  = 138.031 KJ/mol
 ZPEaver    = 11718.53214 cm-1  =  33.505 Kcal/mol  = 142.204 KJ/mol
 -1/4sumXii =    13.45445 cm-1  =   0.038 Kcal/mol  =   0.161 KJ/mol
 x0         =    17.23218 cm-1  =   0.049 Kcal/mol  =   0.206 KJ/mol
 ZPEtot     =        -nan cm-1  =    -nan Kcal/mol  =    -nan KJ/mol
 ZPEtot/ZPEharm =    -nan   ZPEfund/ZPEharm=    -nan


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B10.  TS 4 (2-propenyl -> propine + H) (Cs)
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 Vibrational Energies and Rotational Constants (cm-1)
 Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
 Equilibrium Geometry                     2.261777    0.266349    0.249634
 Ground State   11858.908         -nan    2.221079    0.266443    0.250033
 Fundamental Bands (DE w.r.t. Ground State)
  1(1)           -472.363         -nan    2.223167    0.266629    0.250371
  2(1)           3433.554     3330.021    2.196727    0.266217    0.249536
  3(1)           3077.010     3080.142    2.210326    0.266333    0.250039
  4(1)           3007.154     2853.854    2.215263    0.266348    0.250004
  5(1)           2140.631     2104.985    2.186369    0.265516    0.248757
  6(1)           1450.373     1392.084   -1.163702    0.224570    0.251298
  7(1)           1378.261     1342.381    2.172071    0.265776    0.248752
  8(1)           1018.843      988.004    2.054773    0.263907    0.249952
  9(1)            935.758      925.990    2.230338    0.266367    0.248886
 10(1)            671.178    -1842.110    2.298143    0.269462    0.250603
 11(1)            352.894      301.940    2.657039    0.271135    0.250328
 12(1)            201.263     -327.437    2.263038    0.268496    0.250562
 13(1)           3081.077     2907.820    2.223880    0.266438    0.249989
 14(1)           1450.698     1412.651    5.659415    0.308990    0.250194
 15(1)           1028.712      995.078    2.385785    0.268948    0.249937
 16(1)            601.393      620.694    2.141157    0.264534    0.250350
 17(1)            334.146      334.805    1.845106    0.262319    0.250885
 18(1)             27.233     -381.093    2.099127    0.264181    0.250958

 ZPEharm    = 11858.90781 cm-1  =  33.906 Kcal/mol  = 141.864 KJ/mol
 ZPEfund    = 11454.60321 cm-1  =  32.750 Kcal/mol  = 136.961 KJ/mol
 ZPEaver    = 11656.75432 cm-1  =  33.328 Kcal/mol  = 139.379 KJ/mol
 -1/4sumXii =    57.88401 cm-1  =   0.165 Kcal/mol  =   0.692 KJ/mol
 x0         =   -25.85630 cm-1  =  -0.074 Kcal/mol  =  -0.309 KJ/mol
 ZPEtot     =        -nan cm-1  =    -nan Kcal/mol  =    -nan KJ/mol
 ZPEtot/ZPEharm =    -nan   ZPEfund/ZPEharm=    -nan


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B11.  TS 5 (allyl -> cyclopropyl) (C1)
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 Vibrational Energies and Rotational Constants (cm-1)
 Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
 Equilibrium Geometry                     1.044715    0.471748    0.368119
 Ground State   13368.466         -nan    1.033669    0.469202    0.365194
 Fundamental Bands (DE w.r.t. Ground State)
```

1(1)	-931.841	-inf	1.032497	0.468845	0.365154
2(1)	3206.012	3109.931	1.031808	0.468884	0.365029
3(1)	3176.137	3080.124	1.031061	0.468329	0.364665
4(1)	3152.494	3016.335	1.031369	0.469398	0.365021
5(1)	3103.842	2971.177	1.031458	0.468769	0.365066
6(1)	3032.673	2927.554	1.032002	0.469163	0.365071
7(1)	1493.617	1442.489	1.033280	0.468878	0.364903
8(1)	1421.659	1396.332	1.033329	0.469020	0.365497
9(1)	1326.517	1297.841	1.032657	0.468721	0.365169
10(1)	1256.300	1238.685	1.033398	0.469037	0.363883
11(1)	1098.462	1071.023	1.031494	0.469758	0.364450
12(1)	1030.880	994.359	1.031266	0.469490	0.365481
13(1)	907.492	879.376	1.052704	0.469922	0.364766
14(1)	895.944	875.216	1.012829	0.467449	0.365389
15(1)	747.279	714.539	1.031497	0.468062	0.364536
16(1)	638.368	597.294	1.036602	0.468766	0.364867
17(1)	617.059	608.832	1.032775	0.469555	0.364382
18(1)	564.040	550.822	1.031921	0.468508	0.364318

ZPEharm = 13368.46594 cm-1 = 38.222 Kcal/mol = 159.922 KJ/mol
ZPEfund = 12933.04112 cm-1 = 36.979 Kcal/mol = 154.645 KJ/mol
ZPEaver = 13150.75324 cm-1 = 37.401 Kcal/mol = 157.143 KJ/mol
-1/4sumXii = 68.28871 cm-1 = 0.195 Kcal/mol = 0.817 KJ/mol
x0 = -26.00637 cm-1 = -0.074 Kcal/mol = -0.311 KJ/mol
ZPEtot = -nan cm-1 = -nan Kcal/mol = -nan KJ/mol
ZPEtot/ZPEharm = -nan ZPEfund/ZPEharm= -nan

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B12. TS 6 (cyclopropyl -> cyclopropene + H) (C1)

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.730036	0.616669	0.426086
Ground State	12024.449	-nan	0.734175	0.605019	0.422382
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-533.586	-inf	0.735992	0.606100	0.422863
2(1)	3267.520	3168.102	0.731852	0.604328	0.421544
3(1)	3224.990	3080.231	0.731984	0.604376	0.421631
4(1)	3095.379	2947.318	0.733966	0.604590	0.422335
5(1)	3025.749	2951.894	0.733591	0.604412	0.422302
6(1)	1664.142	1633.419	0.731819	0.605064	0.421422
7(1)	1499.940	1455.545	0.734974	0.604271	0.422999
8(1)	1148.860	1106.966	0.734362	0.606326	0.422113
9(1)	1094.938	1069.041	0.745630	0.606254	0.425586
10(1)	1057.871	1031.749	0.722210	0.600223	0.420481
11(1)	1012.078	979.814	0.735514	0.606013	0.420581
12(1)	1002.110	971.439	0.733952	0.604961	0.419730
13(1)	902.872	880.020	0.737626	0.607474	0.423308
14(1)	813.370	615.691	0.730833	0.602292	0.421904
15(1)	784.482	735.189	0.733709	0.602892	0.419436
16(1)	601.929	12.217	0.732583	0.602688	0.423430
17(1)	236.833	265.617	0.740901	0.603637	0.425767
18(1)	149.420	178.264	0.741929	0.591137	0.418043

ZPEharm = 12024.44878 cm-1 = 34.380 Kcal/mol = 143.844 KJ/mol

```
 ZPEfund    = 11305.15832 cm-1  =  32.324 Kcal/mol  = 135.179 KJ/mol
 ZPEaver    = 11664.75223 cm-1  =  33.351 Kcal/mol  = 139.475 KJ/mol
 -1/4sumXii =    83.32950 cm-1  =   0.238 Kcal/mol  =   0.997 KJ/mol
 x0         =   -38.76695 cm-1  =  -0.111 Kcal/mol  =  -0.464 KJ/mol
 ZPEtot     =        -nan cm-1  =    -nan Kcal/mol  =    -nan KJ/mol
 ZPEtot/ZPEharm =    -nan   ZPEfund/ZPEharm=    -nan
```

C.) CASSCF(3,3)/6-311+G(3df,3pd) optimized geometries and MRCI/cc-pVXZ energies of selected points in the A 2B1 state

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C1. Ally A-state equilibrium (C2)

6	0.000000	0.000000	0.513175
6	0.000000	1.268989	-0.201252
6	0.000000	-1.268989	-0.201252
1	0.000000	0.000000	1.587233
1	0.464516	1.329960	-1.166598
1	-0.727013	2.022556	0.040967
1	-0.464516	-1.329960	-1.166598
1	0.727013	-2.022556	0.040967

Rotational constants (cm-1): 1.802, 0.346, 0.290

Energies / Hartree

CASSCF/6-311+G(3df,3pd): -116.4125602

MRCI cc-pVDZ: -116.7455417
cc-pVTZ: -116.8469879
cc-pVQZ: -116.8752536
CBS(est.): -116.8861711

C2. Allyl A/X conical intersection 1 (C2)

6	0.000000	0.000000	0.622739
6	0.000000	1.181953	-0.225158
6	0.000000	-1.181953	-0.225158
1	0.000000	0.000000	1.693407
1	0.783975	1.292737	-0.951707
1	-0.908202	1.729153	-0.412263
1	-0.783975	-1.292737	-0.951707
1	0.908202	-1.729153	-0.412263

Energies / Hartree

CASSCF/6-311+G(3df,3pd): -116.4108053

MRCI cc-pVDZ: -116.7475766
cc-pVTZ: -116.8488215
cc-pVQZ: -116.8770755
CBS(est.): -116.8880123

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C3.  Allyl A/X conical intersection 2 (Cs)
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    6       -0.033814    0.696634    0.000000
    6       -0.033814   -0.253291    1.089818
    6       -0.033814   -0.253291   -1.089818
    1       -0.864730   -0.915249    1.229171
    1        0.667470    1.508978    0.000000
    1        0.835316   -0.409396    1.700422
    1       -0.864730   -0.915249   -1.229171
    1        0.835316   -0.409396   -1.700422

  Energies / Hartree
    CASSCF/6-311+G(3df,3pd): -116.4186762

    MRCI            cc-pVDZ: -116.7543095
                    cc-pVTZ: -116.8569792
                    cc-pVQZ: -116.8857061
                  CBS(est.): -116.8968665


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C4.  Allyl ground state equilibrium (C2v)
--------------------------------------------------------------------------------

  Energies / Hartree
    CASSCF/cc-pVTZ: -116.52446947

    MRCI   cc-pVDZ: -116.85995664
           cc-pVTZ: -116.96074011
           cc-pVQZ: -116.98946263
         CBS(est.): -117.00091104
```