

Supplementary Materials for

**Gas-Phase Preparation of Silylacetylene (SiH3CCH) through a Counterintuitive Ethynyl Radical (C2H) Insertion**

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Supplementary Text

The quantum chemistry method employed in the AIMD simulation must accurately represent the potential energies of this reaction. The AIMD simulation involves millions of energy gradient calculations, hence finding a quantum chemistry method with of good accuracy/cost ratio is of utmost importance. In this study, the potential energy surface computed at the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3/cc-pV(T+d)Z+ZPE(B2PLYP-D3/cc-pV(T+d)Z) level of theory served as the benchmark to evaluate a series of affordable methods such as MP2 and DFT combined with different basis sets. The accuracy of the method (*A*) was determined by possessing a maximum overlap with the benchmark PES, e.g., smallest RMSD as computed with the following equation:

(**S1**)

(**S2**)

*K* is the number of stationary points including products and *K* = 8 in the present study. The index *i* indicates the *ith* structure. and are the mean relative energies of the candidate method and benchmark method after shifting the energies to the separated reactants to zero. *ΔE(A,ref)* is the optimum shift in energy between the PES profile by candidate method *EA* and benchmark method *Eref*.

Same convergence criteria such as maximum and RMSD in an energy gradient of < 1.5 × 10−5 and < 1.0 × 10−5 Hartree/Bohr respectively and maximum and RMSD in coordinates < 6.0 × 10-5 and < 4.0 × 10−5 Bohr respectively was applied to all candidate methods being surveyed. The RMSD values of 21 different quantum chemical methods are summarized in Table S1. The purpose of Table S1 is to assess the performance of these method on this specific system and should not be taken as their general performance. As shown, B3LYP has an overall better accuracy compared to MP2 and PBE0. Considering the wall time for the gradient calculation for B3LYP/def2-TZVP and B3LYP/def2-TZVPP being twice as long compared to B3LYP/cc-pVDZ and B3LYP/def2-SVP, these two methods are employed to test their stability in AIMD simulations. It turns out that they are less unstable (e.g., large energy jump, self-consistent field convergence failure, etc.) than B3LYP/cc-pVDZ trajectories, thus the latter was chosen to run AIMD simulations.

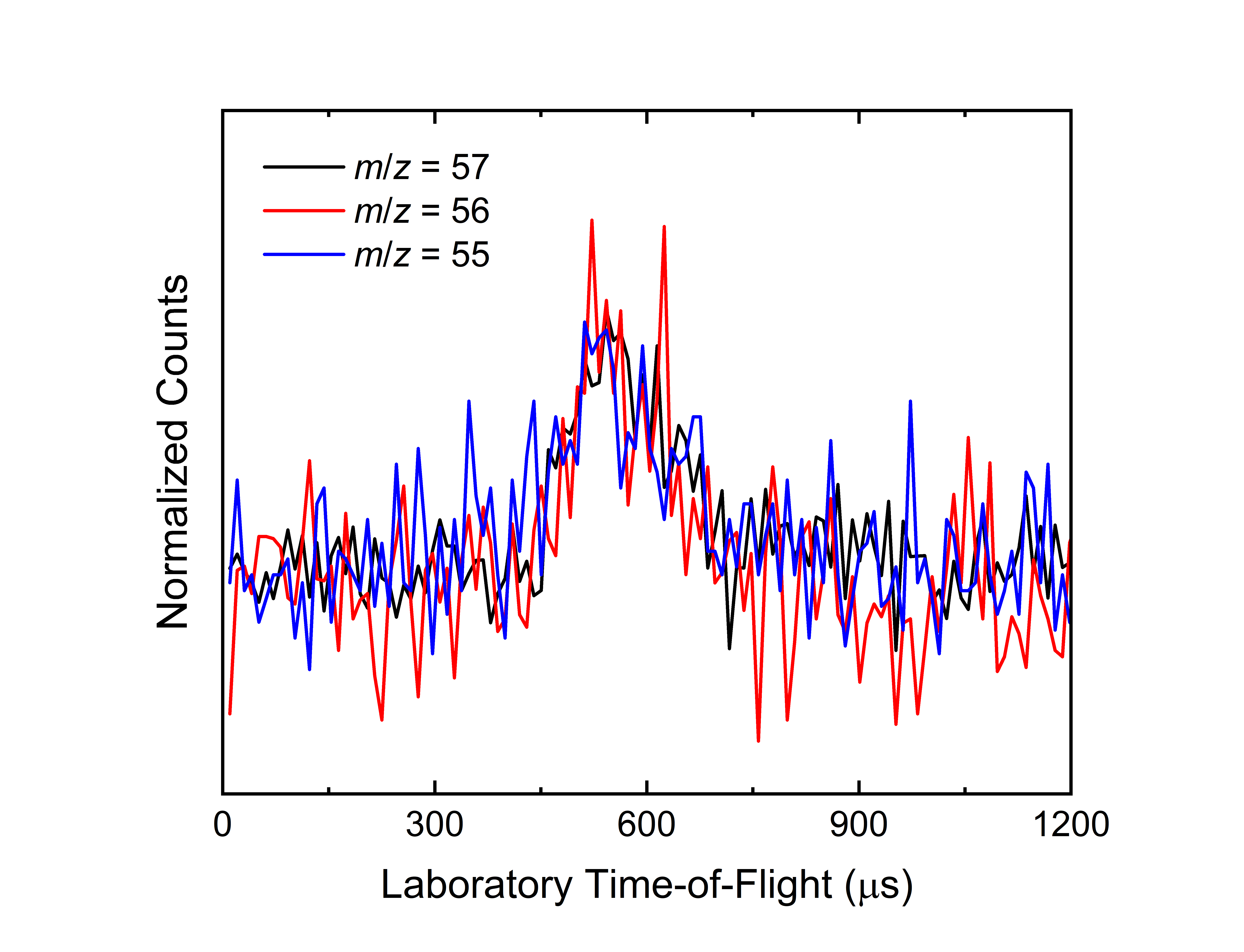
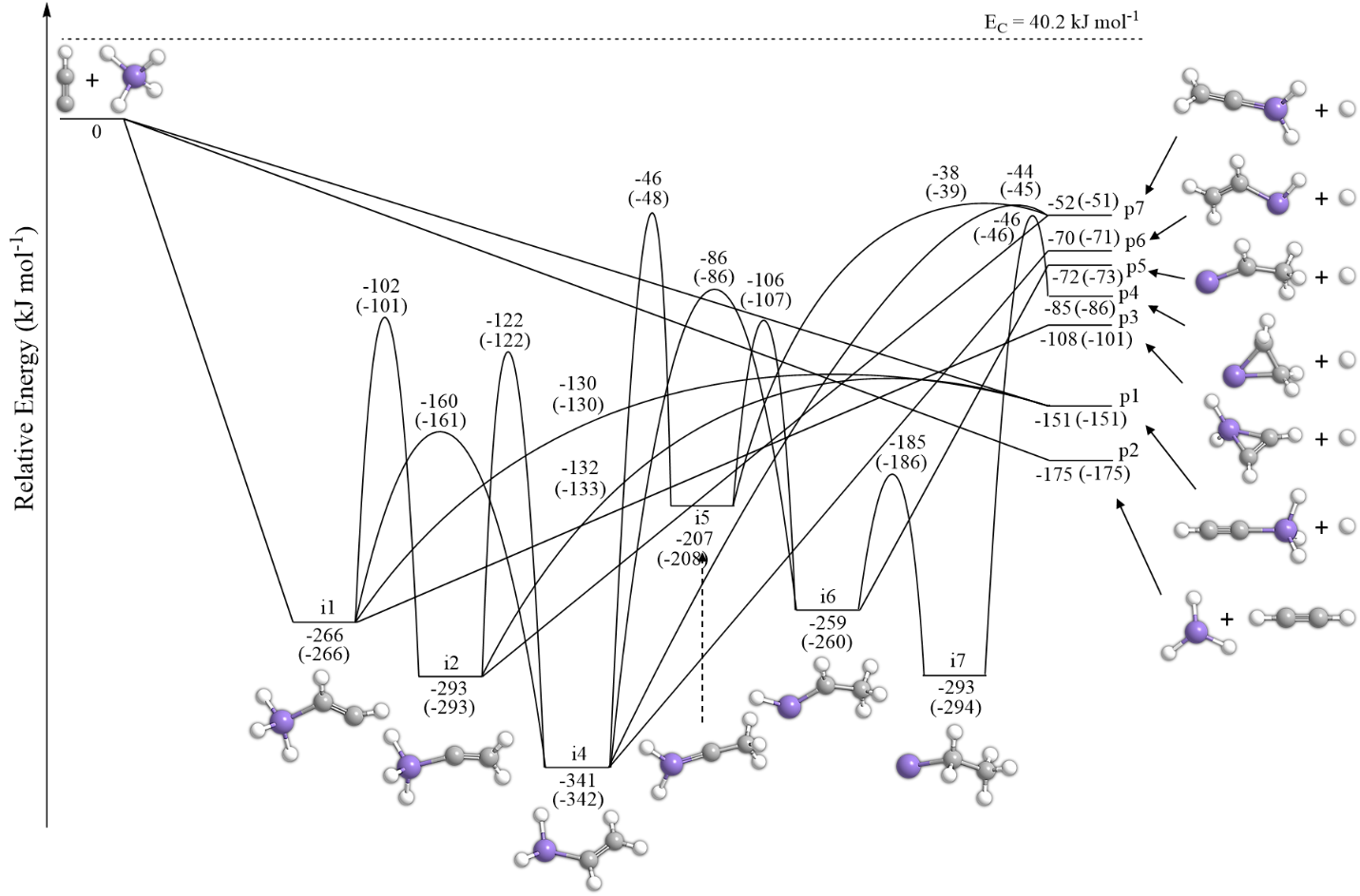


Fig. S1. Time-of-flight (TOF) overlay. TOF spectra for the reaction of D1-ethynyl radicals (C2D) with silane (SiH4) taken at *m*/*z* = 57 (black), 56 (red), and 55 (blue).

Fig. S2. Potential energy surface (PES) showing H loss products. Schematic PES for the reaction of ethynyl radicals (C2H) with silane (SiH4) at the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3/cc-pV(T+d)Z + ZPE(B2PLYP-D3/cc-pV(T+d)Z) level. Energies for the D1-ethynyl (C2D)–silane (SiH4) system are shown in parenthases. Carbon atoms are gray, silicon is purple, and hydrogen is white.

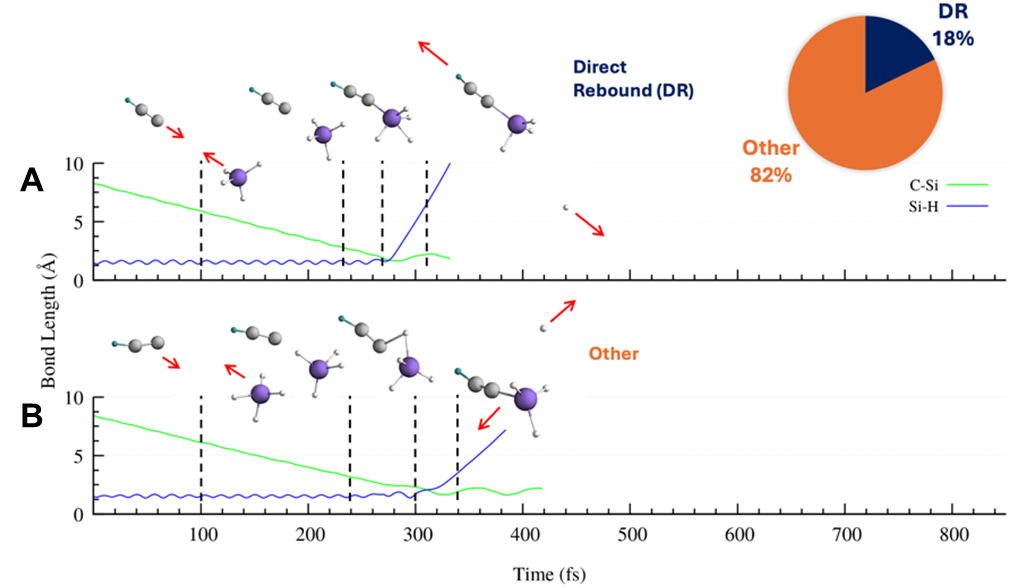


Fig. S3. Representative trajectories for the direct mechanisms. Key distances of the carbon–silicon (green line) and silicon–leaving-hydrogen-atom (blue line) versus time for the rebound (A) and other (B) direct reaction mechanisms with snapshots inserted from representative trajectories. The pie chart represents the percentage of reactive trajectories which follow rebound (dark blue area) and other (orange area) direct mechanisms.

Table S1. Deviation of the dynamics computational methods. RMSD in kJ mol−1 of each candidate method with respect to the benchmark method.

|  |  |  |  |
| --- | --- | --- | --- |
| Theory/Basis Set | MP2 | B3LYP | PBE0 |
| 6-31+G(d) ([*69*](#_ENREF_69)) | 40.26 | 10.08 | 14.38 |
| 6-31++G(d,p) ([*69*](#_ENREF_69)) | 32.52 | 10.21 | 14.86 |
| cc-pVDZ ([*57*](#_ENREF_57)) | 31.64 | **9.47** | 13.39 |
| def2-SVP ([*70*](#_ENREF_70)) | 31.73 | **9.71** | 15.82 |
| def2-SVPD ([*70*](#_ENREF_70)) | 32.81 | 10.05 | 15.86 |
| def2-TZVP ([*70*](#_ENREF_70)) | 30.40 | **7.33** | 12.48 |
| def2-TZVPP ([*70*](#_ENREF_70)) | 26.89 | **7.71** | 12.79 |

Data S1. Calculated parameters of all species. Optimized Cartesian coordinates (Å), and vibrational frequencies (cm-1) and T1 diagnostic of reactants, products, intermediates, and transition states involved in the ethynyl radical (C2H) plus silane (SiH4) reaction.

REACTANTS

C2H

C 0.00000000146191 0.00000000220594 -0.70844729709338

C -0.00000000292488 -0.00000000441126 0.49428100547783

H 0.00000000146297 0.00000000220532 1.55576329161555

Frequencies

590.11

590.11

2106.08

3482.03

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01672699

SiH4

Si -0.00001332228026 -0.00000000222891 0.00000331102526

H -0.00001030170425 -0.00000000793993 1.47600156518390

H 1.39157061199139 0.00000001364874 -0.49200940255825

H -0.69577299988246 -1.20516836239159 -0.49199472810344

H -0.69577298822443 1.20516835881168 -0.49199474544747

Frequencies

938.08

939.63

941.24

993.49

994.60

2263.75

2268.98

2269.06

2269.20

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01148048

PRODUCTS

p1

Si 1.06162311933641 -0.00007352059843 0.00006522838756

H 1.55027761511748 0.49525710315592 1.30012461081514

H 1.55095773841646 0.87793576554854 -1.07879500462537

H 1.55036174742045 -1.37362866672482 -0.22075924998399

C -0.76436869375482 0.00015830840292 -0.00032077571727

C -1.97599576749444 -0.00004185019798 0.00024293848432

H -3.03775853904155 -0.00017973958615 0.00065437263961

Frequencies

229.91

229.97

637.29

694.25

694.25

709.69

709.70

957.07

969.22

969.41

2104.00

2267.79

2269.03

2269.27

3471.99

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01346734

p3

Si -0.42158286715828 0.07488151716422 -0.67162197860765

H 0.44674751386367 0.15044588108155 2.02319064690855

H -1.15329612164573 1.22876870941426 -1.22269989439297

H -0.93283700088233 -1.19083395145836 -1.22587716713149

C 0.39277538345603 0.14633061621893 0.94517205877314

C 1.27487326317730 0.22833826515702 -0.05480609909307

H 2.34706482918934 0.32648896242239 -0.13118456645650

Frequencies

582.71

596.79

673.43

705.55

716.99

790.55

924.37

975.67

1010.87

1141.52

1518.66

2261.82

2266.05

3199.42

3222.47

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01282210

p4

Si -0.67902137078277 -0.29542878986675 -0.62862286502748

H 0.47447104841153 0.32063707402354 1.60657011329580

C 0.50446697328489 0.59651944458595 0.55887099134482

C 1.20566892245362 -0.33982403600966 -0.39756072748567

H 1.64444905162926 -1.24369076532077 0.00889828491811

H 1.82174469923042 0.09816357925630 -1.17429597644679

H 0.65105099203597 1.66163824449683 0.42183499010223

Frequencies

421.06

599.85

609.95

653.53

724.69

918.54

956.77

1048.95

1215.27

1423.55

1436.31

3110.14

3117.70

3174.36

3194.18

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01273538

p5

Si -1.20362659337936 -0.59351400124092 -0.12163875479135

H 0.17149104911034 0.82813847384918 0.91698664670142

C 0.36333781961967 0.00554146138493 0.20382710126987

C 1.81073124886914 -0.19848606805979 -0.13508339721924

H 2.39691234343567 -0.43532019755343 0.75440978364727

H 1.94325165690479 -1.01237817994327 -0.84513740034839

H 2.24610184908849 0.70002957463276 -0.57542789638529

Frequencies

109.70

187.04

541.47

687.32

900.95

1041.13

1158.30

1325.66

1415.38

1497.87

1511.02

2946.13

3035.52

3084.24

3118.70

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01468830

p6

Si 0.95841316139332 -0.53837122272724 -0.09673876910652

H 1.84330718246562 0.44352747608340 0.65458286456557

C -0.66968769095948 0.31343226267557 0.28750256570898

C -1.79201157812655 -0.23713195494337 -0.20722843365629

H -0.76859567426822 1.21777631042585 0.87843009881511

H -2.77860406643567 0.18044167333361 -0.04176750005266

H -1.74990332505422 -1.14143395178628 -0.80442506852714

Frequencies

123.87

289.93

502.20

670.31

822.51

1030.86

1035.46

1051.28

1298.88

1431.77

1613.35

2038.66

3120.77

3147.09

3205.28

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01363965

p7

Si 0.99436226358022 -0.56618251457043 0.15151783661986

H 1.87566997502431 0.58112148576267 0.38497843617565

C -0.65663615556965 -0.36133266646998 -0.12623182737186

C -1.93779338348966 -0.20057970114451 -0.34663757902363

H -2.66337876721283 -0.18802414008906 0.46112952395701

H -2.33586555268488 -0.07181640002204 -1.34865705546399

H 1.60549052422313 -1.89754124360763 0.17718231674793

Frequencies

174.84

240.87

405.26

663.63

663.96

766.75

943.89

963.08

1018.72

1445.95

1794.22

2305.92

2326.26

3099.66

3164.53

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01507913

INTERMEDIATES

i1

Si -1.04120847742225 -0.09595383504665 -0.43639675248801

H 0.45823474474887 0.66439977321315 1.51512983021557

H -1.72731472360011 1.19370577569384 -0.66812696861234

H -0.72344891610360 -0.73123433059603 -1.72844100748126

H -1.95374405592786 -0.96441994963803 0.33782751278226

C 0.53512662633929 0.19110892041377 0.53140841764773

C 1.70872858361279 -0.14720524044786 0.07363481864326

H 2.74362621835288 -0.11040211359219 0.37496514929279

Frequencies

203.48

262.83

524.59

623.82

683.91

728.79

867.39

868.99

951.30

967.02

980.56

1170.54

1655.21

2245.24

2246.25

2272.98

3025.90

3237.92

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01704178

i4

Si 1.00242759114693 -0.18744825743395 -0.21805744349478

H 1.96579044262332 0.08609699614580 0.87143926392091

C -0.70799890190654 0.38298476546374 0.18443113892889

C -1.81615416124095 -0.26952709181597 -0.18658361478132

H -0.82468655387063 1.32809662014097 0.70476565835903

H -2.80592277377591 0.11102821134536 0.02987955535026

H -1.77053763396141 -1.21299065078440 -0.71551880053594

H 1.01424434098519 -1.61449915306155 -0.61230844774705

Frequencies

249.98

287.90

489.88

628.70

684.34

721.58

935.36

987.24

1033.94

1053.79

1304.31

1449.70

1647.40

2217.87

2244.14

3138.91

3150.99

3223.43

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01762348

i2

Si -1.15909693235212 -0.07646277586191 -0.48544294948820

H -1.82479918910650 1.22980079869831 -0.31748516682781

H -1.26071095937194 -0.48304478597256 -1.90751425872853

H -1.84097662661076 -1.08646286767533 0.34689561772738

C 0.57440652018149 0.06459758191339 0.05017884908164

C 1.87558724017018 0.03505997702157 -0.02124115678785

H 2.51262347226160 0.27589455508357 0.82672031262350

H 2.39988721482805 -0.23356666320705 -0.93863287760013

Frequencies

129.10

218.82

319.75

627.93

656.35

705.78

942.18

948.14

956.99

968.44

969.76

1424.47

1758.24

2216.72

2259.77

2262.62

3057.82

3124.38

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01597262

i6

Si -1.72223683738152 -0.67899573062008 -0.13494303942036

H -2.99463009834926 -0.32828124244173 0.55570756896875

C -0.29112936137527 0.17517349035113 0.23008465042852

C 1.10557323813092 0.00387651734326 -0.28556323813828

H -0.45467791076750 0.99491571353230 0.92872863995645

H 1.80411271544763 -0.18754308383197 0.53164864012480

H 1.45375403611332 0.90406105585783 -0.79590667967749

H 1.18367521818168 -0.82531772019075 -0.98659554224240

Frequencies

185.20

258.16

292.44

532.23

667.68

844.30

999.17

1056.15

1158.25

1342.62

1422.30

1495.12

1514.04

2165.15

3030.81

3077.75

3100.64

3120.45

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01624596

i5

Si -1.09588099225871 -0.98453138587485 0.02530887439669

H -2.10675327573857 -0.31022925158377 0.85323407188340

C 0.49551592099904 -0.49888675596409 -0.02086601802513

C 1.90773361321269 -0.16652035171231 -0.14338138009520

H 2.41552148606527 -0.18906286717545 0.82353637845676

H 2.42319622084148 -0.88436558259386 -0.79102806470487

H 2.05688502231650 0.82341067671335 -0.57971861722830

H -1.61644891543771 -2.12137946180901 -0.75167701468334

Frequencies

121.23

242.24

258.13

504.96

614.48

705.77

967.58

1001.46

1041.62

1400.21

1471.89

1476.17

1483.76

2270.18

2283.41

3002.92

3058.51

3082.75

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01587254

i7

Si -1.18558862044069 -0.07461803414022 -0.33618833394666

H 0.35536409981864 0.24372909369418 1.44667531264417

C 0.48846978889156 0.47375877646368 0.37587609145401

C 1.76615372558846 -0.18980363382935 -0.15326309007966

H 2.64988802373708 0.13307997883455 0.39804771929897

H 1.70299478057328 -1.27467872333964 -0.08059887032451

H 1.92607778417892 0.05473789728650 -1.20272465241941

H 0.56935875765274 1.56488937503030 0.34591835337309

Frequencies

205.72

260.84

449.58

613.79

904.59

962.77

1019.34

1231.32

1254.14

1409.54

1423.19

1510.41

1519.74

2953.21

3036.49

3044.22

3110.04

3122.35

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01211346

TRANSITION STATES

TS1: i1 – i4

Si -1.06426958438164 -0.04341820443064 -0.32627455675262

H 0.63353462407756 0.72745624686887 1.71056075423981

H -1.80142544613904 1.14333171190468 -0.82801052902466

H -2.04397121275195 -1.03298816143266 0.18851528289338

C 0.40927999303197 0.29865254952733 0.74370966669119

C 1.28095611278432 -0.19398978879810 -0.12771458011438

H 2.35966511950820 -0.31611955321252 -0.16457460583947

H 0.22623039387059 -0.58292480042696 -1.19621043209327

Frequencies

1698.96 i

284.90

504.88

599.99

703.87

709.20

722.65

889.36

932.80

963.46

997.51

1165.81

1564.39

1755.85

2192.26

2213.28

3132.65

3199.78

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01954195

TS2: i1 – p1

Si -1.04423214459149 -0.11550705221300 -0.47915091134656

H -1.64193414451133 1.22858750916664 -0.53950638374157

H -1.04891664115412 -0.72534271054816 -1.82368971993403

H -1.79936035232725 -0.96437338334014 0.45788451123757

C 0.69351433186557 0.01130032253287 0.10514737516616

C 1.89890653792671 -0.11484000248837 0.23731406762565

H 2.94106392034477 -0.17028417373853 0.43455897963771

H 0.00095949244715 0.85045949062870 1.60744208135507

Frequencies

679.64 i

218.58

278.03

310.62

450.55

636.19

684.56

699.29

704.81

727.15

954.24

967.46

975.20

2070.43

2259.23

2278.83

2283.39

3467.26

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01873242

TS3: i1 – i2

Si -1.12508548086112 -0.11562021272207 -0.50549106721671

H -1.76444817733344 1.19663174275035 -0.71751085979867

H -0.92789753784043 -0.77641241782075 -1.81754174198865

H -1.99928219784775 -0.95786014002523 0.33238303203409

C 0.45670277219687 0.14815200033861 0.39586736011010

C 1.73626625574464 0.13466476692788 0.61141101743486

H 0.93124483382404 0.53857386039369 1.51232484932439

H 2.69249853211719 -0.16812959984250 0.18855841010059

Frequencies

1976.81 i

192.03

201.93

290.36

543.86

598.29

660.42

704.74

885.34

951.01

966.14

968.27

1779.71

2216.49

2265.00

2267.93

2409.39

3068.01

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01421002

TS4: i4 – i2

Si -1.39651939828009 -0.00782453693219 -0.43418462186376

H -2.18242342466352 1.16858888622297 -0.03234827582741

H -1.79255797752488 -0.50824475938113 -1.77925678619775

H -0.77252354059361 -0.60298804954816 0.90724512448439

C 0.29369599917324 0.12974877738601 0.08208029331818

C 1.57474204238366 -0.02474455200031 0.34903089900228

H 1.95481848696525 -0.23645443685076 1.34233987588870

H 2.32076881253995 0.08192067110357 -0.43490650880464

Frequencies

1629.55 i

171.94

315.15

504.36

611.29

642.04

679.46

897.33

904.91

975.21

999.85

1437.13

1689.78

1904.28

2152.07

2282.43

3088.35

3163.19

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01748318

TS5: i2 – p1

Si -1.37415486079575 -0.07513835293244 -0.20250112931413

H -1.78935695262346 1.15767069870577 0.49267843133603

H -1.81149432414046 -0.02378732310925 -1.60930946031476

H -1.96928876103319 -1.24789341553743 0.46327379121906

C 0.44567224528551 -0.22102647675417 -0.14434274823694

C 1.65699711110582 -0.27087923830737 -0.02073125086449

H 2.68988270174507 -0.51873742122930 -0.06077460120384

H 2.15174284045647 1.19979152916418 1.08170696737907

Frequencies

722.74 i

150.08

189.15

244.72

453.91

638.12

697.36

697.76

710.13

865.22

952.83

969.67

970.53

2085.37

2265.37

2271.66

2274.32

3449.96

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01756825

TS6: i4 – i6

Si -1.27659623572154 -0.46847356776671 -0.29855986313387

H -2.63383489663363 -0.94220755539350 0.14456606294371

C -0.21322194723963 0.61610204367238 0.51598862167002

C 1.02743175456696 0.12960006267608 -0.14055988290254

H -0.24195795312185 1.40726567852455 1.24792683533979

H 1.76323740533366 -0.39636888270463 0.46006089689484

H 1.43609623328110 0.63561820693266 -1.01015924701957

H 0.13884563953494 -0.98153698594083 -0.91926342379237

Frequencies

1545.94 i

333.28

492.73

565.37

582.33

866.43

894.73

937.63

1019.42

1068.53

1144.41

1466.98

1702.77

1826.27

2183.42

3085.86

3169.26

3229.49

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.02113635

TS7: i4 – i5

Si -1.38162752750326 -0.67717594933109 0.39741865259959

H -2.51346228534050 -0.07072469195009 1.13375799851159

C -0.06380253808361 0.51737333856021 0.04954380679690

C 1.25264607559996 0.31434524909181 -0.35207816766588

H 0.99194275147699 0.60630152435885 0.84981438301152

H 1.88285383408041 1.17101724434475 -0.58563533937647

H 1.69546188958536 -0.65618249634761 -0.58908809689194

H -1.86401219981535 -1.20495421872684 -0.90373223698531

Frequencies

1191.05 i

210.28

278.19

425.66

575.11

654.26

697.09

955.98

1023.20

1082.46

1268.72

1371.39

1523.17

2204.28

2225.48

2243.43

3018.93

3111.62

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.03544802

TS8: i4 – p7

Si 1.48267153734249 -0.30709319556549 -0.03767073492084

H 2.41840417200479 0.78274751717990 -0.32061656283038

C -0.18639651741804 -0.07004105881811 -0.18667132216921

C -1.44928867415075 0.02362816813891 -0.52364863223875

H -2.18393418967410 0.47117298361265 0.13557331176207

H -1.80690046462080 -0.34423262182231 -1.47955625987268

H 2.01147718695405 -1.45343873804235 0.70268959454905

H -0.28603305043764 0.89725794531680 1.70990060572074

Frequencies

593.52 i

217.05

257.25

327.26

363.65

515.00

662.03

700.96

777.79

946.40

972.21

1018.21

1435.74

1789.61

2314.13

2336.94

3117.77

3192.02

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01952866

TS9: i6 – i5

Si -1.76260195608639 -0.37367794024724 -0.58829472163641

H -1.46304106033434 0.45922899870854 0.67829399402802

H -2.32890367290726 -1.67692985595047 -0.10988532072111

C -0.07217095373388 -0.42919764984055 -0.10371065316091

C 1.14870537650600 0.36340262862536 0.01741445395698

H 1.63491295904534 0.19866563732334 0.98071212287297

H 1.84881593752951 0.02054447311213 -0.75010969712808

H 0.99428336998103 1.43796370826890 -0.12441917821146

Frequencies

927.03 i

201.39

221.32

383.85

645.92

665.20

859.59

977.02

1023.29

1247.62

1390.79

1450.37

1471.88

1972.77

2112.07

3001.62

3068.75

3089.16

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.03765285

TS10: i6 – i7

Si -2.01967782327599 -0.39453015279842 -0.66347662415851

H -1.75274550016134 -0.43532239129903 0.90147846641746

C -0.49600745267453 0.30298393150120 0.03045988173282

C 0.93163707673430 -0.09101705651509 -0.20904108307321

H 1.42339995739208 -0.39792291291963 0.71515799695656

H 1.02295261517703 -0.89414763151243 -0.93626829073369

H 1.48187343969385 0.78182940893809 -0.57498227700298

H -0.59143331288539 1.12812780460531 0.73667192986155

Frequencies

1079.99 i

179.29

279.26

591.19

688.54

926.59

1011.10

1061.93

1106.96

1311.26

1393.39

1483.10

1500.74

1804.49

3020.56

3084.99

3086.10

3135.78

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.03243384

TS11: i5 – p7

Si -1.68379844738846 -0.40741150231382 0.13428920206986

H -2.75195319607718 0.23705375312280 0.90336286966790

C -0.10922950124325 0.17317735882270 0.16194966558391

C 1.13922262215365 0.59091826330959 0.15094261139399

H 1.47571484782075 1.36853862072000 -0.52728745870491

H 1.85185487804780 0.28223109670580 0.90905851281679

H -2.05422706624411 -1.58338823573300 -0.65895112596144

H 2.13241486293081 -0.66111835463406 -1.07336427686611

Frequencies

594.16 i

198.72

222.51

338.60

376.99

468.70

665.86

768.01

804.86

951.58

996.97

1030.56

1450.26

1784.90

2304.18

2324.15

3105.01

3171.74

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.01919701

TS12: i7 – p4

Si -1.74240685772549 -0.45402425127277 -0.67881298555499

H -0.54863450809619 0.29155907044268 1.51307252889599

C -0.57684860334160 0.49394237808123 0.44804008869594

C 0.27549904688892 -0.36356649652645 -0.44462898555653

H 0.50115241641467 -1.39249729421439 -0.19178750452455

H 0.77070504656640 0.03069981207462 -1.31633258225697

H -0.49164383155085 1.55708450787428 0.24691579068293

H 1.81217729084416 -0.16319872645920 0.42353464961817

Frequencies

1078.66 i

295.46

454.95

494.13

569.61

664.73

755.07

875.05

926.66

1000.44

1059.61

1202.25

1421.08

1444.96

3105.81

3139.44

3173.20

3252.52

CCSD(T)-F12/cc-pVTZ-F12 - T1 diagnostic: 0.02428007

Optimized Cartesian coordinates (Å) and vibrational frequencies (cm-1) of reactants, products, intermediates, and transition states involved in the D1-ethynyl radical (C2D) plus silane (SiH4) reaction.

REACTANTS

CCD

C 0.00000000146191 0.00000000220594 -0.70844729709338

C -0.00000000292488 -0.00000000441126 0.49428100547783

D 0.00000000146297 0.00000000220532 1.55576329161555

Frequencies

452.599382

452.6048

1955.229304

2706.176905

INTERMEDIATES

i1

Si -1.04120847742225 -0.09595383504665 -0.43639675248801

H 0.45823474474887 0.66439977321315 1.51512983021557

H -1.72731472360011 1.19370577569384 -0.66812696861234

H -0.72344891610360 -0.73123433059603 -1.72844100748126

H -1.95374405592786 -0.96441994963803 0.33782751278226

C 0.53512662633929 0.19110892041377 0.53140841764773

C 1.70872858361279 -0.14720524044786 0.07363481864326

D 2.74362621835288 -0.11040211359219 0.37496514929279

Frequencies

201.627985

246.742646

457.087832

584.948019

626.747373

673.456819

795.808121

818.522218

951.161655

966.919138

980.510715

1154.005005

1612.861255

2245.232416

2246.242412

2272.97598

2414.021143

3026.859481

i4

Si 1.00242759114693 -0.18744825743395 -0.21805744349478

H 1.96579044262332 0.08609699614580 0.87143926392091

C -0.70799890190654 0.38298476546374 0.18443113892889

C -1.81615416124095 -0.26952709181597 -0.18658361478132

H -0.82468655387063 1.32809662014097 0.70476565835903

D -2.80592277377591 0.11102821134536 0.02987955535026

H -1.77053763396141 -1.21299065078440 -0.71551880053594

H 1.01424434098519 -1.61449915306155 -0.61230844774705

Frequencies

246.408122

282.178525

419.435426

622.612444

667.329226

685.921224

884.894255

914.423082

941.62481

1042.488541

1274.813878

1340.010429

1611.983586

2217.85273

2244.132002

2345.030148

3150.151383

3183.269421

i2

Si -1.15909693235212 -0.07646277586191 -0.48544294948820

H -1.82479918910650 1.22980079869831 -0.31748516682781

H -1.26071095937194 -0.48304478597256 -1.90751425872853

H -1.84097662661076 -1.08646286767533 0.34689561772738

C 0.57440652018149 0.06459758191339 0.05017884908164

C 1.87558724017018 0.03505997702157 -0.02124115678785

H 2.51262347226160 0.27589455508357 0.82672031262350

D 2.39988721482805 -0.23356666320705 -0.93863287760013

Frequencies

122.254545

205.574231

299.774997

623.019079

649.908735

705.752779

816.627936

858.532462

956.774213

965.840795

969.518935

1284.613196

1741.408768

2216.652813

2258.566549

2262.251562

2262.625014

3110.678868

i6

Si -1.72223683738152 -0.67899573062008 -0.13494303942036

H -2.99463009834926 -0.32828124244173 0.55570756896875

C -0.29112936137527 0.17517349035113 0.23008465042852

C 1.10557323813092 0.00387651734326 -0.28556323813828

H -0.45467791076750 0.99491571353230 0.92872863995645

D 1.80411271544763 -0.18754308383197 0.53164864012480

H 1.45375403611332 0.90406105585783 -0.79590667967749

H 1.18367521818168 -0.82531772019075 -0.98659554224240

Frequencies

166.411217

254.754031

283.66967

521.51122

664.819789

780.569495

931.271387

988.734342

1148.986075

1279.266368

1316.489216

1379.770547

1483.919883

2165.135962

2242.017054

3053.117281

3100.23041

3116.675954

i5

Si -1.09588099225871 -0.98453138587485 0.02530887439669

H -2.10675327573857 -0.31022925158377 0.85323407188340

C 0.49551592099904 -0.49888675596409 -0.02086601802513

C 1.90773361321269 -0.16652035171231 -0.14338138009520

H 2.41552148606527 -0.18906286717545 0.82353637845676

H 2.42319622084148 -0.88436558259386 -0.79102806470487

D 2.05688502231650 0.82341067671335 -0.57971861722830

H -1.61644891543771 -2.12137946180901 -0.75167701468334

Frequencies

119.612969

231.741632

261.306273

501.624495

614.336685

685.802023

870.802763

960.984454

980.506246

1284.701832

1308.163946

1449.138039

1479.916287

2242.580961

2270.204501

2283.425074

3015.800699

3066.994855

i7

Si -1.18558862044069 -0.07461803414022 -0.33618833394666

H 0.35536409981864 0.24372909369418 1.44667531264417

C 0.48846978889156 0.47375877646368 0.37587609145401

C 1.76615372558846 -0.18980363382935 -0.15326309007966

D 2.64988802373708 0.13307997883455 0.39804771929897

H 1.70299478057328 -1.27467872333964 -0.08059887032451

H 1.92607778417892 0.05473789728650 -1.20272465241941

H 0.56935875765274 1.56488937503030 0.34591835337309

Frequencies

181.024242

253.688714

448.666754

595.005224

819.912283

885.974462

1014.761161

1186.094273

1217.189463

1332.215249

1354.925103

1409.598006

1488.001139

2256.804088

2953.370871

3036.58643

3076.416995

3121.799931

PRODUCTS

p1

Si 1.06162311933641 -0.00007352059843 0.00006522838756

H 1.55027761511748 0.49525710315592 1.30012461081514

H 1.55095773841646 0.87793576554854 -1.07879500462537

H 1.55036174742045 -1.37362866672482 -0.22075924998399

C -0.76436869375482 0.00015830840292 -0.00032077571727

C -1.97599576749444 -0.00004185019798 0.00024293848432

D -3.03775853904155 -0.00017973958615 0.00065437263961

Frequencies

216.715670

216.773099

559.077619

559.083847

628.056195

694.328219

694.334544

957.073264

969.214880

969.410587

1970.463234

2267.786433

2269.024709

2269.228906

2685.076660

p3

Si -0.42158286715828 0.07488151716422 -0.67162197860765

H 0.44674751386367 0.15044588108155 2.02319064690855

H -1.15329612164573 1.22876870941426 -1.22269989439297

H -0.93283700088233 -1.19083395145836 -1.22587716713149

C 0.39277538345603 0.14633061621893 0.94517205877314

C 1.27487326317730 0.22833826515702 -0.05480609909307

D 2.34706482918934 0.32648896242239 -0.13118456645650

Frequencies

582.711615

596.794345

673.431045

705.551542

716.991016

790.550537

924.374545

975.670513

1010.872351

1141.519209

1518.663918

2261.818849

2266.046471

3199.424402

3222.472891

p4

Si -0.67902137078277 -0.29542878986675 -0.62862286502748

H 0.47447104841153 0.32063707402354 1.60657011329580

C 0.50446697328489 0.59651944458595 0.55887099134482

C 1.20566892245362 -0.33982403600966 -0.39756072748567

H 1.64444905162926 -1.24369076532077 0.00889828491811

H 1.82174469923042 0.09816357925630 -1.17429597644679

D 0.65105099203597 1.66163824449683 0.42183499010223

Frequencies

375.733739

573.846143

607.324915

620.026485

640.148117

849.665605

943.772856

1022.410489

1151.207182

1293.193092

1430.669004

2311.568179

3113.182989

3150.232705

3185.096195

p5

Si -1.20362659337936 -0.59351400124092 -0.12163875479135

H 0.17149104911034 0.82813847384918 0.91698664670142

C 0.36333781961967 0.00554146138493 0.20382710126987

C 1.81073124886914 -0.19848606805979 -0.13508339721924

H 2.39691234343567 -0.43532019755343 0.75440978364727

H 1.94325165690479 -1.01237817994327 -0.84513740034839

D 2.24610184908849 0.70002957463276 -0.57542789638529

Frequencies

108.271607

167.536489

528.777904

675.590941

816.610049

944.068614

1142.544531

1276.222072

1305.746067

1368.131491

1483.982870

2247.003106

2946.175361

3057.495977

3114.566224

p6

Si 0.95841316139332 -0.53837122272724 -0.09673876910652

H 1.84330718246562 0.44352747608340 0.65458286456557

C -0.66968769095948 0.31343226267557 0.28750256570898

C -1.79201157812655 -0.23713195494337 -0.20722843365629

H -0.76859567426822 1.21777631042585 0.87843009881511

D -2.77860406643567 0.18044167333361 -0.04176750005266

H -1.74990332505422 -1.14143395178628 -0.80442506852714

Frequencies

119.310354

280.407541

438.160942

643.345647

794.058741

913.940689

934.515225

1048.968502

1259.087374

1339.063809

1568.503902

2038.657219

2332.070690

3147.075451

3163.431237

p7

Si 0.99436226358022 -0.56618251457043 0.15151783661986

H 1.87566997502431 0.58112148576267 0.38497843617565

C -0.65663615556965 -0.36133266646998 -0.12623182737186

C -1.93779338348966 -0.20057970114451 -0.34663757902363

H -2.66337876721283 -0.18802414008906 0.46112952395701

H -2.33586555268488 -0.07181640002204 -1.34865705546399

D 1.60549052422313 -1.89754124360763 0.17718231674793

Frequencies

170.668988

229.516491

359.069539

560.787234

637.457279

760.252604

857.130563

963.070884

1017.517490

1445.810007

1666.875007

1794.353771

2315.499185

3099.660308

3164.528856

TRANSITION STATES

TS1: i1 – i4

Si -1.06426958438164 -0.04341820443064 -0.32627455675262

H 0.63353462407756 0.72745624686887 1.71056075423981

H -1.80142544613904 1.14333171190468 -0.82801052902466

H -2.04397121275195 -1.03298816143266 0.18851528289338

C 0.40927999303197 0.29865254952733 0.74370966669119

C 1.28095611278432 -0.19398978879810 -0.12771458011438

D 2.35966511950820 -0.31611955321252 -0.16457460583947

H 0.22623039387059 -0.58292480042696 -1.19621043209327

Frequencies

1698.274434 i

273.468562

479.553498

530.605376

637.822261

667.924371

706.641728

827.690127

850.449389

962.551072

982.859402

1138.373828

1528.695458

1754.788223

2192.224116

2213.260802

2332.365398

3196.708896

TS2: i1 – p1

Si -1.04423214459149 -0.11550705221300 -0.47915091134656

H -1.64193414451133 1.22858750916664 -0.53950638374157

H -1.04891664115412 -0.72534271054816 -1.82368971993403

H -1.79936035232725 -0.96437338334014 0.45788451123757

C 0.69351433186557 0.01130032253287 0.10514737516616

C 1.89890653792671 -0.11484000248837 0.23731406762565

D 2.94106392034477 -0.17028417373853 0.43455897963771

H 0.00095949244715 0.85045949062870 1.60744208135507

Frequencies

679.642474 i

212.426420

262.548007

302.209362

427.670966

551.141774

574.236651

649.765878

694.568847

704.497912

954.232281

967.454007

975.197955

1944.949839

2259.234093

2278.822429

2283.385648

2672.588913

TS3: i1 – i2

Si -1.12508548086112 -0.11562021272207 -0.50549106721671

H -1.76444817733344 1.19663174275035 -0.71751085979867

H -0.92789753784043 -0.77641241782075 -1.81754174198865

H -1.99928219784775 -0.95786014002523 0.33238303203409

C 0.45670277219687 0.14815200033861 0.39586736011010

C 1.73626625574464 0.13466476692788 0.61141101743486

H 0.93124483382404 0.53857386039369 1.51232484932439

D 2.69249853211719 -0.16812959984250 0.18855841010059

Frequencies

1969.593239 i

180.694776

191.198233

290.527163

448.521973

587.058313

660.124816

694.831116

703.238441

950.494227

966.025595

968.071603

1726.901088

2216.356260

2264.766644

2267.866194

2273.593011

2434.035124

TS4: i4 – i2

Si -1.39651939828009 -0.00782453693219 -0.43418462186376

H -2.18242342466352 1.16858888622297 -0.03234827582741

H -1.79255797752488 -0.50824475938113 -1.77925678619775

H -0.77252354059361 -0.60298804954816 0.90724512448439

C 0.29369599917324 0.12974877738601 0.08208029331818

C 1.57474204238366 -0.02474455200031 0.34903089900228

D 1.95481848696525 -0.23645443685076 1.34233987588870

H 2.32076881253995 0.08192067110357 -0.43490650880464

Frequencies

1627.918362 i

167.015175

298.058695

458.999553

604.961690

636.346451

660.147978

811.274321

862.462269

899.097323

973.819884

1293.899405

1671.501700

1904.130702

2151.991424

2282.418700

2314.976060

3109.554247

TS5: i2 – p1

Si -1.37415486079575 -0.07513835293244 -0.20250112931413

H -1.78935695262346 1.15767069870577 0.49267843133603

H -1.81149432414046 -0.02378732310925 -1.60930946031476

H -1.96928876103319 -1.24789341553743 0.46327379121906

C 0.44567224528551 -0.22102647675417 -0.14434274823694

C 1.65699711110582 -0.27087923830737 -0.02073125086449

D 2.68988270174507 -0.51873742122930 -0.06077460120384

H 2.15174284045647 1.19979152916418 1.08170696737907

Frequencies

708.430245 i

150.291982

183.100867

228.986992

451.274305

566.396666

624.255579

680.437254

698.963068

702.953532

952.810600

969.661724

970.521961

1959.533292

2265.325800

2271.658887

2274.319652

2660.833460

TS6: i4 – i6

Si -1.27659623572154 -0.46847356776671 -0.29855986313387

H -2.63383489663363 -0.94220755539350 0.14456606294371

C -0.21322194723963 0.61610204367238 0.51598862167002

C 1.02743175456696 0.12960006267608 -0.14055988290254

H -0.24195795312185 1.40726567852455 1.24792683533979

D 1.76323740533366 -0.39636888270463 0.46006089689484

H 1.43609623328110 0.63561820693266 -1.01015924701957

H 0.13884563953494 -0.98153698594083 -0.91926342379237

Frequencies

1545.548247 i

287.044415

490.727301

549.782280

572.217314

775.951695

861.929202

910.635507

947.074502

1061.615833

1138.634030

1321.351772

1683.929044

1800.075346

2156.092231

2311.937939

3124.743015

3229.445674

TS7: i4 – i5

Si -1.38162752750326 -0.67717594933109 0.39741865259959

H -2.51346228534050 -0.07072469195009 1.13375799851159

C -0.06380253808361 0.51737333856021 0.04954380679690

C 1.25264607559996 0.31434524909181 -0.35207816766588

H 0.99194275147699 0.60630152435885 0.84981438301152

D 1.88285383408041 1.17101724434475 -0.58563533937647

H 1.69546188958536 -0.65618249634761 -0.58908809689194

H -1.86401219981535 -1.20495421872684 -0.90373223698531

Frequencies

1170.531513 i

204.074245

276.018696

396.912039

543.867835

634.724922

684.282079

905.347383

964.659446

1003.063062

1165.431409

1311.478954

1409.056159

2204.271952

2225.429192

2240.935675

2272.073154

3037.229209

TS8: i4 – p7

Si 1.48267153734249 -0.30709319556549 -0.03767073492084

H 2.41840417200479 0.78274751717990 -0.32061656283038

C -0.18639651741804 -0.07004105881811 -0.18667132216921

C -1.44928867415075 0.02362816813891 -0.52364863223875

D -2.18393418967410 0.47117298361265 0.13557331176207

H -1.80690046462080 -0.34423262182231 -1.47955625987268

H 2.01147718695405 -1.45343873804235 0.70268959454905

H -0.28603305043764 0.89725794531680 1.70990060572074

Frequencies

590.649186 i

202.955203

255.512708

321.653628

355.934509

511.367283

600.545061

664.569883

745.273696

885.112595

897.829542

954.361408

1299.151495

1771.082810

2314.118649

2329.748825

2336.934357

3151.863025

TS9: i6 – i5

Si -1.76260195608639 -0.37367794024724 -0.58829472163641

H -1.46304106033434 0.45922899870854 0.67829399402802

H -2.32890367290726 -1.67692985595047 -0.10988532072111

C -0.07217095373388 -0.42919764984055 -0.10371065316091

C 1.14870537650600 0.36340262862536 0.01741445395698

D 1.63491295904534 0.19866563732334 0.98071212287297

H 1.84881593752951 0.02054447311213 -0.75010969712808

H 0.99428336998103 1.43796370826890 -0.12441917821146

Frequencies

926.591999 i

197.180888

200.063132

378.130099

624.630406

662.214594

844.885062

881.757151

957.238838

1215.115086

1274.102792

1321.436858

1431.490725

1972.717210

2112.065357

2250.324135

3016.209141

3071.054843

TS10: i6 – i7

Si -2.01967782327599 -0.39453015279842 -0.66347662415851

H -1.75274550016134 -0.43532239129903 0.90147846641746

C -0.49600745267453 0.30298393150120 0.03045988173282

C 0.93163707673430 -0.09101705651509 -0.20904108307321

D 1.42339995739208 -0.39792291291963 0.71515799695656

H 1.02295261517703 -0.89414763151243 -0.93626829073369

H 1.48187343969385 0.78182940893809 -0.57498227700298

H -0.59143331288539 1.12812780460531 0.73667192986155

Frequencies

1079.736356 i

158.063932

276.405548

568.387213

663.348362

883.727711

923.738129

1045.363650

1097.088508

1259.897107

1276.642228

1366.620198

1467.953177

1804.428619

2256.971164

3032.620235

3086.040195

3128.446923

TS11: i5 – p7

Si -1.68379844738846 -0.40741150231382 0.13428920206986

H -2.75195319607718 0.23705375312280 0.90336286966790

C -0.10922950124325 0.17317735882270 0.16194966558391

C 1.13922262215365 0.59091826330959 0.15094261139399

D 1.47571484782075 1.36853862072000 -0.52728745870491

H 1.85185487804780 0.28223109670580 0.90905851281679

H -2.05422706624411 -1.58338823573300 -0.65895112596144

H 2.13241486293081 -0.66111835463406 -1.07336427686611

Frequencies

592.750126 i

197.080025

213.057307

333.105879

372.813286

461.788456

647.586691

668.488393

774.704254

893.431793

933.441644

952.942423

1315.168498

1769.580478

2304.088924

2311.109925

2324.150274

3140.505622

TS12: i7 – p4

Si -1.74240685772549 -0.45402425127277 -0.67881298555499

H -0.54863450809619 0.29155907044268 1.51307252889599

C -0.57684860334160 0.49394237808123 0.44804008869594

C 0.27549904688892 -0.36356649652645 -0.44462898555653

D 0.50115241641467 -1.39249729421439 -0.19178750452455

H 0.77070504656640 0.03069981207462 -1.31633258225697

H -0.49164383155085 1.55708450787428 0.24691579068293

H 1.81217729084416 -0.16319872645920 0.42353464961817

Frequencies

1059.487535 i

284.492995

435.782918

490.616958

565.070044

644.685149

682.448387

735.691294

879.812668

998.428411

1038.115135

1148.396416

1309.092818

1427.592547

2319.516028

3105.876331

3173.166332

3232.631157

**Data S2. IRC trajectories for all transition states.**