Supporting Information: Heavy Atom Tunneling in Organic Reactions at Coupled Cluster Potential Accuracy with a Parallel Implementation of Anharmonic Constant Calculations and Semiclassical Transition State Theory

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1 Electronic Structure Calculations and Optimized Geometries

In our paper, we performed Single Point electronic structure Energy (SPE) calculations and geometry optimizations using the Gaussian16 software.\textsuperscript{1} The geometry optimizations are carried out requiring the lowest possible residual gradient in the optimization process. The following input keywords are set as default in our program for the geometry optimization step:

- SCF=(XQC,Tight) and Int=UltraFine (for DFT calculations)
- Opt=(VeryTight,CalcAll,MaxCycles=200) (add TS option for the transition state opt)

For the CCSD(T) optimization we started from the CCSD optimized geometry, for which we have analytic gradients available. Then we switched to numerical gradients for CCSD(T) calculations with the eigenvalue-following algorithm for the optimization process. A first
calculation is done using the standard setup, with a maximum step size of 0.1 Bohr. Once the Tight convergence is reached, new optimization parameters have been used for the VeryTight convergence criteria. The following overlay 1 options have been used for the R1 reactant molecule:

- IOp(1/8=4), maximum step size of 0.04 Bohr for the optimization
- IOp(1/19=8) Newton-Raphson and linear search
- IOp(1/13=9) BFGS Hessian update

and the same options with a 0.03 Bohr step size for the R1 TS molecule.

The optimized geometries are listed below in Cartesian coordinates for the MP2, DFT and CCSD calculations as well as the Z-matrix for the CCSD(T). All the coordinates are given in Ångström. The R1, R2, R3 notation refers to the one defined in the article in figure 4.

Table 1: R1 optimized geometries at B3LYP/6-31G* and MP2/aug-cc-pVDZ level of theory

|        | R, MP2                                      |        | R, DFT/B3LYP                                             |        | TS, DFT/B3LYP                                             |
|--------|--------------------------------------------|--------|----------------------------------------------------------|--------|----------------------------------------------------------|
|        | (a)                                        | (b)    | (c)                                                      | (d)    |                                                          |
| H      | 0.000000                                   | H      | 0.000000                                                 | H      | 1.087931                                                 |
| C      | -0.000000                                  | C      | 1.063482                                                 | C      | -1.878131                                                |
| C      | -0.000000                                  | C      | -1.064062                                                | C      | 1.330943                                                 |
| C      | -0.000000                                  | C      | 0.690129                                                 | C      | 0.844037                                                 |
| H      | 0.898056                                   | H      | -1.878131                                                | H      | -0.835014                                                |
| H      | 0.898056                                   | H      | 1.330943                                                 | H      | 1.352296                                                 |
| H      | 0.898056                                   | H      | 1.330943                                                 | H      | 1.352296                                                 |
| H      | 0.898056                                   | H      | 1.330943                                                 | H      | 1.352296                                                 |
| H      | 0.898056                                   | H      | 1.330943                                                 | H      | 1.352296                                                 |
| C      | -0.000000                                  |        |                                                          | C      |                                                          |
| C      | -0.000000                                  |        |                                                          | C      |                                                          |
| C      | -0.000000                                  |        |                                                          | C      |                                                          |
| C      | -0.000000                                  |        |                                                          | C      |                                                          |
| H      | 0.898056                                   |        |                                                          | H      |                                                          |
| H      | 0.898056                                   |        |                                                          | H      |                                                          |
| H      | 0.898056                                   |        |                                                          | H      |                                                          |
| H      | 0.898056                                   |        |                                                          | H      |                                                          |
| H      | 0.898056                                   |        |                                                          | H      |                                                          |

Table 1: R1 optimized geometries at B3LYP/6-31G* and MP2/aug-cc-pVDZ level of theory
Table 2: R1 optimized geometries at CCSD(T)/aug-cc-pVDZ level of theory

(a) R, CCSD(T)

| H | C | B1 | B2 | A2 | C | B3 | A3 | D3 | 0 | C | B4 | A4 | D4 | 0 | C | B5 | A5 | D5 | 0 |
|---|---|----|----|----|---|----|----|----|---|---|----|----|----|---|---|----|----|----|---|
| H | 1 | B1 |    |    | C | 2 | B2 | 1 | A2 |   | C | 2 | B3 | 1 | A3 | 3 | D3 | 0 |
| H | 2 | B3 | 1 | A3 | 3 | D3 | 0 | C | 2 | B4 | 2 | A4 | 1 | D4 | 0 | C | 2 | B5 | 2 | A5 | 1 | D5 | 0 |
| H | 5 | B6 | 3 | A6 | 1 | D6 | 0 | H | 5 | B7 | 1 | A7 | 3 | D7 | 0 | H | 2 | B8 | 2 | A8 | 1 | D8 | 0 |
| H | 4 | B9 | 2 | A9 | 1 | D9 | 0 | H | 4 | B9 | 2 | A9 | 1 | D9 | 0 |

Variables:

| B1 | 2.2636 | B2 | 1.097 | A2 | 25.9704 | B3 | 1.5359 | A3 | 114.7223 | D3 | -0.0092 | B4 | 1.5359 | A4 | 132.4663 | D4 | 80.0901 | B5 | 1.1053 | A5 | 115.5891 | D5 | 295.3521 | B6 | 1.1053 | A6 | 115.589 |
|---|--------|----|-------|----|---------|----|--------|----|---------|----|--------|----|--------|----|---------|----|---------|----|--------|----|---------|----|---------|----|---------|----|---------|
| D6 | 64.6487 | B7 | 1.097 | A7 | 112.8104 | D7 | 180.0904 | B8 | 1.1053 | A8 | 115.5891 | D8 | 115.3521 | B9 | 1.1053 | A9 | 115.589 |
| D9 | 244.6487 |

(b) TS, CCSD(T)

| H | C | B1 | B2 | A2 | C | B3 | A3 | D3 | 0 | C | B4 | A4 | D4 | 0 | C | B5 | A5 | D5 | 0 |
|---|---|----|----|----|---|----|----|----|---|---|----|----|----|---|---|----|----|----|---|
| H | 1 | B1 |    |    | C | 2 | B2 | 1 | A2 |   | C | 2 | B3 | 1 | A3 | 3 | D3 | 0 |
| H | 2 | B3 | 1 | A3 | 3 | D3 | 0 | C | 2 | B4 | 2 | A4 | 1 | D4 | 0 | C | 2 | B5 | 2 | A5 | 1 | D5 | 0 |
| H | 5 | B6 | 3 | A6 | 1 | D6 | 0 | H | 5 | B7 | 1 | A7 | 3 | D7 | 0 | H | 2 | B8 | 2 | A8 | 1 | D8 | 0 |
| H | 4 | B9 | 2 | A9 | 1 | D9 | 0 | H | 4 | B9 | 2 | A9 | 1 | D9 | 0 |

Variables:

| B1 | 2.163 | B2 | 1.104 | A2 | 132.4179 | B3 | 1.4050 | A3 | 122.7685 | D3 | -97.9636 | B4 | 1.3928 | A4 | 104.1597 | D4 | 144.3749 | B5 | 1.104 | A5 | 132.4154 | D5 | 106.7401 | B6 | 1.098 | A6 | 129.5336 |
|---|--------|----|-------|----|---------|----|--------|----|---------|----|--------|----|--------|----|---------|----|---------|----|--------|----|---------|----|---------|----|---------|----|---------|
| D6 | 154.4381 | B7 | 1.0944 | A7 | 114.6331 | D7 | 106.9788 | B8 | 1.0944 | A8 | 85.1134 | D8 | -3.5028 | B9 | 1.098 | A9 | 126.1322 |
| D9 | 179.9994 |

(c) P, CCSD(T)

| H | C | B1 | B2 | A2 | C | B3 | A3 | D3 | 0 | C | B4 | A4 | D4 | 0 | C | B5 | A5 | D5 | 0 |
|---|---|----|----|----|---|----|----|----|---|---|----|----|----|---|---|----|----|----|---|
| H | 1 | B1 |    |    | C | 2 | B2 | 1 | A2 |   | C | 2 | B3 | 1 | A3 | 3 | D3 | 0 |
| H | 3 | B4 | 2 | A4 | 1 | D4 | 0 | C | 3 | B5 | 2 | A5 | 1 | D5 | 0 |
| H | 6 | B6 | 3 | A6 | 2 | D6 | 0 | H | 1 | B7 | 2 | A7 | 3 | D7 | 0 |
| H | 1 | B8 | 2 | A8 | 3 | D8 | 0 | H | 6 | B9 | 3 | A9 | 2 | D9 | 0 |

Variables:

| B1 | 1.3609 | B2 | 1.4734 | A2 | 123.5227 | B3 | 1.1001 | A3 | 119.6435 | D3 | 180.0507 | B4 | 1.1001 | A4 | 116.8342 | D4 | 0.0002 | B5 | 1.3609 | A5 | 123.5222 | D5 | 180.0030 | B6 | 1.0977 | A6 | 121.0953 |
|---|--------|----|-------|----|---------|----|--------|----|---------|----|--------|----|--------|----|---------|----|---------|----|--------|----|---------|----|---------|----|---------|----|---------|
| D6 | -0.0003 | B7 | 1.0957 | A7 | 121.4771 | D7 | 179.9994 | B8 | 1.0977 | A8 | 121.0954 | D8 | 359.9993 | B9 | 1.0957 | A9 | 121.4771 | D9 | -31.1543 |
Table 3: (Part 1) R2 optimized geometries at B3LYP/6-31G*, MP2/aug-cc-pVDZ and CCSD/jun-cc-pVDZ level of theory

(a) R, MP2

| C   | -1.144539 | 1.580279 | 0.599986 |
| C   | -0.014074 | 1.580910 | 0.202089 |
| C   | 1.132553  | 1.669393 | 0.590952 |
| C   | 1.105216  | -0.678990| 0.256434 |
| C   | -0.065110 | -1.581610| 0.200895 |
| H   | 0.104563  | 2.347844 | -0.921662|
| H   | 2.121210  | 1.146338 | 0.062437 |
| H   | 2.066366  | -1.163418| 0.471945 |
| H   | -0.127343 | -2.348760| 0.983367 |
| H   | -1.825039 | -2.291984| 0.267400 |
| H   | -0.958198 | -0.846767| 1.135930 |
| H   | -1.288151 | 1.134839 | 1.404652 |

(b) R, DFT/B3LYP

| C   | 1.65971   | -1.09333 | -0.41294 |
| C   | 1.62945   | 0.05969  | 0.267400 |
| C   | 0.66188   | 1.15916  | 0.13335  |
| C   | -0.66188  | 1.15916  | -0.13335 |
| C   | -1.62945  | 0.05969  | -0.26740 |
| C   | -1.65971  | -1.09333 | 0.41294  |
| H   | 2.45336   | 0.27023  | 0.95152  |
| H   | 1.11156   | 2.14467  | 0.26383  |
| H   | -1.11156  | 2.14467  | -0.26383 |
| H   | -2.45336  | 0.27023  | -0.95152 |
| H   | -2.46114  | -1.81113 | 0.26383  |
| H   | -0.8939   | -1.3569  | 1.13593  |
| H   | 0.8939    | -1.3569  | -1.13593 |
| H   | 2.46114   | -1.81113 | -0.26383 |
| H   | 0.8939    | -1.3569  | -1.13593 |

(c) R, CCSD/jun-cc-pVDZ

| C   | -1.138302 | 1.627065 | 0.628833 |
| C   | -0.023081 | 1.592411 | -0.132320|
| C   | 1.126319  | 0.668228 | 0.071648 |
| C   | -0.101938 | -0.677789| 0.242771 |
| C   | -0.071052 | -1.593053| 0.186014 |
| H   | 0.095883  | 2.336243 | -0.934377|
| H   | 2.114224  | 1.152275 | 0.085986 |
| H   | 2.064731  | -1.169327| 0.447428 |
| H   | -0.138537 | -2.337083| 0.993850 |
| H   | -0.138537 | -2.337083| -0.790324|
| H   | -0.094623 | -0.918581| -1.645326|
| H   | -1.931411 | 2.358577 | 0.434331 |
| H   | -1.287684 | 0.926156 | 1.458790 |

(d) TS, MP2

| C   | -1.212831 | 1.136147 | -0.110743|
| C   | -0.116110 | 1.481498 | 0.203290 |
| C   | 1.251613  | 0.708474 | -0.125272|
| C   | 1.251613  | -0.708474| -0.125272|
| C   | -0.116110 | -1.481498| 0.203290 |
| H   | 0.287860  | 2.316791 | 0.896076 |
| H   | 2.235936  | 1.184919 | -0.044816|
| H   | 2.235936  | -1.184919| -0.044816|
| H   | -2.020621 | -1.628122| 0.446537 |
| H   | -1.450297 | -0.920735| -1.147908|
| H   | -2.020621 | 1.628122 | 0.446537 |
| H   | -1.450297 | 0.920735 | -1.147908|

(e) TS, DFT/B3LYP

| C   | -1.203685 | 1.140779 | -0.106145|
| C   | 0.119802  | 1.482612 | 0.188744 |
| C   | 1.242310  | 0.702978 | -0.101682|
| C   | 1.242310  | -0.702978| -0.101682|
| C   | 0.119802  | -1.482612| 0.188744 |
| C   | -1.203685 | 1.140779 | -0.106145|
| H   | 0.296293  | 2.340220 | 0.841809 |
| H   | 2.220032  | 1.175092 | -0.016766|
| H   | 2.220032  | -1.175092| -0.016766|
| H   | 0.296293  | -2.340220| 0.841809 |
| H   | -1.999232 | -1.641166| 0.447018 |
| H   | -1.467751 | -0.936630| -1.131315|
| H   | -1.999232 | 1.641166 | 0.447018 |

(f) TS, CCSD/jun-cc-pVDZ

| C   | -1.211632 | 1.124331 | -0.107417|
| C   | 0.118882  | 1.484638 | 0.197519 |
| C   | 1.252491  | 0.708684 | -0.116752|
| C   | 1.252491  | -0.708684| -0.116752 |
| C   | 0.118882  | -1.484638| 0.197519 |
| C   | -1.211632 | -1.124331| -0.107417|
| H   | 0.291166  | 2.342573 | 0.865193 |
| H   | 2.237920  | 1.185894 | -0.028450|
| H   | 2.237920  | -1.185894| -0.028450 |
| H   | 0.291166  | -2.342573| 0.865193 |
| H   | -2.019247 | -1.618255| 0.454315 |
| H   | -1.461810 | -0.925646| -1.147245|
| H   | -2.019247 | 1.618255 | 0.454315 |
| H   | -1.461810 | 0.925646 | -1.147245|
Table 4: (Part2) R2 optimized geometries at B3LYP/6-31G*, MP2/aug-cc-pVDZ and CCSD/jun-cc-pVDZ level of theory

|      | (a) P, MP2          | (b) P, DFT/B3LYP      | (c) P, CCSD/jun-cc-pVDZ |
|------|---------------------|-----------------------|-------------------------|
| C    | 1.426702 0.088132 -0.093129 | C 1.425046 0.064445 -0.113679 | C 1.430623 0.078158 -0.103671 |
| H    | 2.510264 0.246382 -0.093261 | H 2.506220 0.185099 -0.115735 | H 2.518668 0.220737 -0.103296 |
| C    | 0.722838 0.134715 -1.258504 | C 0.726173 0.104203 -1.260201 | C 0.731163 0.119921 -1.264847 |
| H    | 1.228474 0.351742 -2.204801 | H 1.227139 0.272675 -2.210923 | H 1.236753 0.318142 -2.217625 |
| C    | -0.722831 -0.134716 -1.258508 | C -0.726166 -0.104204 -1.260205 | C -0.731156 -0.119922 -1.264851 |
| H    | -1.228461 -0.351744 -2.204808 | H -1.227126 -0.272676 -2.210931 | H -1.236740 -0.318143 -2.217632 |
| C    | -1.426702 -0.088133 -0.093137 | C -1.425046 -0.064446 -0.113687 | C -1.430623 -0.078158 -0.103680 |
| H    | -2.510263 -0.246383 -0.093275 | H -2.506220 -0.185100 -0.115750 | H -2.518667 -0.220738 -0.103311 |
| C    | -0.716645 0.275583 1.193979  | C -0.731549 0.239765 1.195321   | C -0.724201 0.260273 1.198691    |
| H    | -0.685023 1.381124 1.281898  | H -0.762431 1.330411 1.361316   | H -0.721606 1.365381 1.321730    |
| H    | -1.271664 -0.103120 2.066951  | H -1.272151 -0.208877 2.037036  | H -1.276600 -0.152333 2.062151  |
| C    | 0.716637 -0.275583 1.193983  | C 0.731541 -0.239765 1.195325   | C 0.724193 -0.260273 1.198696    |
| H    | 0.685015 -1.381124 1.281902  | H 0.762423 -1.330411 1.361321   | H 0.721598 -1.365381 1.321735    |
| H    | 1.271651 0.103121 2.066959   | H 1.272139 0.208877 2.037043    | H 1.276587 0.152333 2.062158     |
Table 5: R3 optimized geometries at B3LYP/6-31G* and MP2/aug-cc-pVDZ level of theory

(a) R and P, MP2

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | -0.25452 | 1.50213 | -0.08789 |
| C    | 0.25452  | -1.50213 | -0.08789 |
| C    | 0.25452  | 0.7308  | 1.10044 |
| C    | -0.53006 | -2.06965 | -1.02957 |
| C    | 0.53006  | 2.06965  | -1.02957 |
| C    | -0.25452 | -0.7308 | 1.10044 |
| H    | -0.07904 | 1.21977 | 2.03351 |
| H    | -0.10155 | -2.6105 | -1.87694 |
| H    | 1.359    | 0.73899 | 1.10346 |
| H    | -1.62099 | -2.00237 | -0.97052 |
| H    | 1.62099  | 2.00237  | -0.97052 |
| H    | -1.359   | -0.73899 | 1.10346 |
| H    | 0.10155  | 2.6105   | -1.87694 |
| H    | -0.07904 | -1.21977 | 2.03351 |
| H    | -1.34542 | 1.58492  | -0.18742 |
| H    | 1.34542  | -1.58492 | -0.18742 |

(b) R and P, DFT/B3LYP

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | -0.25184 | 1.54322 | -0.10493 |
| C    | 0.25184  | -1.54322 | -0.10493 |
| C    | 0.25184  | 0.73198 | 1.05765 |
| C    | -0.513   | -2.20013 | -0.97705 |
| C    | 0.513    | 2.20013  | -0.97705 |
| C    | -0.25184 | -0.73198 | 1.05765 |
| H    | -0.07625 | 1.2006  | 1.99765 |
| H    | -0.0865  | -2.77542 | -1.79452 |
| H    | 1.34985  | 0.74498 | 1.0695  |
| H    | -1.59913 | -2.18861 | -0.90696 |
| H    | 1.59913  | 2.18861  | -0.90696 |
| H    | -1.34985 | -0.74498 | 1.0695  |
| H    | 0.0865   | 2.77542  | -1.79452 |
| H    | 0.07625  | -1.2006 | 1.99765 |
| H    | -1.33705 | 1.58054  | -0.21967 |
| H    | 1.33705  | -1.58054 | -0.21967 |

(c) R and P, CCSD/jun-cc-pVDZ

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | -0.239559 | 1.532230 | -0.104424 |
| C    | 0.239559  | -1.532230 | -0.104424 |
| C    | 0.260201  | 0.728091 | 1.074583 |
| C    | -0.549475 | -2.159706 | -1.000217 |
| C    | 0.549475  | 2.159706  | -1.000217 |
| C    | -0.260201 | -0.728091 | 1.074583 |
| H    | -0.067580 | 1.216240 | 2.014202 |
| H    | -0.125671 | -2.730822 | -1.834575 |
| H    | 1.367817  | 0.729851 | 1.082336 |
| H    | -1.644122 | -2.118272 | -0.924977 |
| H    | 1.644122  | 2.118272  | -0.924977 |
| H    | -1.367817 | -0.729851 | 1.082336 |
| H    | 0.067580  | -1.216240 | 2.014202 |
| H    | -1.332957 | 1.593605  | -0.221844 |
| H    | 1.332957  | -1.593605 | -0.221844 |

(d) TS, MP2

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 1.412634  | 0.000454 | -0.270789 |
| C    | -1.412634 | -0.000454 | 0.270789 |
| C    | 0.876961  | -1.223498 | 0.249260 |
| C    | -0.876961 | 1.223498  | -0.249260 |
| C    | 0.876177  | 1.224058  | 0.249269 |
| C    | -0.876177 | -1.224058 | -0.249269 |

(e) TS, DFT/B3LYP

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 1.419737 | 0.000460 | -0.260245 |
| C    | -1.419737 | -0.000460 | 0.260245 |
| C    | 0.913744  | -1.224745 | 0.254008 |
| C    | -0.913744 | 1.224745  | -0.254008 |
| C    | 0.912959  | 1.225328  | 0.254018 |
| C    | -0.912959 | -1.225328 | -0.254018 |

(f) TS, CCSD/jun-cc-pVDZ

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 1.419737 | 0.000460 | -0.260245 |
| C    | -1.419737 | -0.000460 | 0.260245 |
| C    | 0.913744  | -1.224745 | 0.254008 |
| C    | -0.913744 | 1.224745  | -0.254008 |
| C    | 0.912959  | 1.225328  | 0.254018 |
| C    | -0.912959 | -1.225328 | -0.254018 |

7
2 Scalability Tests

The here reported tests with the Gaussian16 software have been run using the following machines:

CINECA GALILEO NeXtScale cluster CentOS 7.4: 1022 compute nodes with $2 \times 18$ core Intel Xeon E5-2697 v4 (Broadwell) at 2.30 GHz 128 GB RAM.\textsuperscript{2}

Figure 1: Speedup and Efficiency plots for the anharmonic constants calculation using Gaussian16. Calculations are done on the 10 atoms \textbf{cyclobutene} molecule using the MP2 post-HF method with the jun-cc-pVDZ and the DFT/B3LYP with the 6-31G* Basis Set (BS).
Figure 2: Speedup and Efficiency plots for the anharmonic constants calculation using Gaussian16. Calculations are done on the 14 atoms cis-1,3,5-hexatriene molecule using the MP2 post-HF method with the jun-cc-pVDZ and the DFT/B3LYP with the 6-31G\(^*\) Basis Set (BS).

### 3 Accuracy Tests

We report here the results from the direct comparison of our anharmonic constants with the ones obtained using Gaussian16. The definitions of the difference \(\Delta \chi\) and the percentage difference \(\%_{\text{diff}}\) are given in the article in eq. 30.
Figure 3: Comparison between anharmonic constants calculated with Gaussian16 and our program for the cyclobutene molecule. The horizontal and vertical axes indicate the normal mode indexes for the $\chi_{k,k'}$ and the colour gradient indicates the magnitude of the difference between the results. Anharmonic constants are calculated using the DFT/B3LYP functional with the 6-31G* Basis Set (BS) and the MP2 post-HF method with the aug-cc-pVDZ BS.
Figure 4: Comparison between anharmonic constants calculated with Gaussian16 and our program for the cyclobutene opening reaction transition state. The horizontal and vertical axes indicate the normal mode indexes for the $\chi_{k,k'}$ and the colour gradient indicates the magnitude of the difference between the results. Anharmonic constants are calculated using the DFT/B3LYP functional with the 6-31G* Basis Set (BS) and the MP2 post-HF method with the aug-cc-pVDZ BS.
Figure 5: Comparison between anharmonic constants calculated with the Gaussian16 software and our program for the TS molecule of the hexatriene ring closing electrocyclic reaction. The horizontal and vertical axes indicate the normal mode indexes for the $\chi_{k,k'}$ and the colour gradient indicates the magnitude of the difference between the results. Anharmonic constants are calculated using the DFT/B3LYP functional with the 6-31G* Basis Set (BS) and the MP2 post-HF method with the aug-cc-pVDZ BS.
Figure 6: Comparison between anharmonic constants calculated with Gaussian and our program for the $C_2$ hexatriene molecule. The horizontal and vertical axes indicate the normal mode indexes for the $\chi_{k,k'}$ and the colour gradient indicates the magnitude of the difference between the results. Anharmonic constants are calculated using the DFT/B3LYP functional with the 6-31G* Basis Set (BS) and the MP2 post-HF method with the aug-cc-pVDZ BS.
Figure 7: Comparison between anharmonic constants calculated with Gaussian16 and our program for the 1,5-hexadiene molecule. The horizontal and vertical axes indicate the normal mode indexes for the $\chi_{k,k'}$ and the colour gradient indicates the magnitude of the difference between the results. Anharmonic constants are calculated using the DFT/B3LYP functional with the 6-31G* Basis Set (BS) and the MP2 post-HF method with the aug-cc-pVDZ BS.
Figure 8: Comparison between anharmonic constants calculated with Gaussian16 and our program for the TS molecule of the 1,5-hexadiene Cope rearrangement. The horizontal and vertical axes indicate the normal mode indexes for the $\chi_{k,k'}$ and the colour gradient indicates the magnitude of the difference between the results. Anharmonic constants are calculated using the DFT/B3LYP functional with the 6-31G* Basis Set (BS) and the MP2 post-HF method with the aug-cc-pVDZ BS.
The impact on the SCTST reaction rate constants of small variations between the anharmonic constants calculated with our program and the Gaussian software is shown in the following results for the three reactions studied in our paper.

Figure 9: SCTST Reaction Rate Constants at different temperatures for the R1 reaction. The anharmonic constants matrix was calculated using our program and the Gaussian16 software starting from the same geometry and ab initio calculation options. DFT calculations have been carried out using the B3LYP functional with the 6-31G* basis set while in the MP2 calculations we used the aug-cc-pVDZ one.
Figure 10: SCTST Reaction Rate Constants at different temperatures for the R2 reaction. The anharmonic constants matrix was calculated using our program and the Gaussian16 software starting from the same geometry and ab initio calculation options. DFT calculations have been carried out using the B3LYP functional with the 6-31G* basis set, while in the MP2 calculations we used the aug-cc-pVDZ one.
Figure 11: SCTST Reaction Rate Constants at different temperatures for the R3 reaction. The anharmonic constants matrix was calculated using our program and the Gaussian16 software starting from the same geometry and ab initio calculation options. DFT calculations have been carried out using the B3LYP functional with the 6-31G* basis set, while in the MP2 calculations we used the aug-cc-pVDZ basis set.
4 Energetic of the Reactions

The barriers here reported are the classical barriers corrected for the harmonic Zero Point Energy (ZPE): 

\[ E_{\text{harm}ZPE}^R = \frac{1}{2} \sum_{k=1}^{N} \omega_k, \quad E_{\text{harm}ZPE}^T = \frac{1}{2} \sum_{k=1}^{N-1} \omega_k \]

and corrected for the anharmonic ZPE:

\[ E_{\text{anharm}ZPE}^R = \frac{1}{2} \sum_{k=1}^{N} \omega_k + \frac{1}{4} \sum_{k,k'=1}^{N} \chi_{k,k'} + G_0^R \]

\[ E_{\text{anharm}ZPE}^T = \frac{1}{2} \sum_{k=1}^{N-1} \omega_k + \frac{1}{4} \sum_{k,k'=1}^{N-1} \chi_{k,k'} + G_0^{TS} \]

where \( N \) is the number of vibrational degrees of freedom, \( \omega_k \) are the harmonic vibrational frequencies, \( G_0^R \) and \( G_0^{TS} \) are the constant terms coming from the VPT2 perturbation expansion and \( R \) and \( TS \) refer to the formula for the reactant and the transition state.

Table 6: Harmonic and anharmonic ZPE corrected forward (\( E_f \)) and backward (\( E_b \)) reaction barriers and TS reactive mode harmonic frequencies (\( \tilde{\omega} \)) for the R1 reaction.

| Method/BS          | \( E_f(\text{ZPE}_{\text{harm}}; \text{ZPE}_{\text{anh}}) \) /[kJmol\(^{-1}\)] | \( E_b \) /[kJmol\(^{-1}\)] | \( \tilde{\omega} \) /[cm\(^{-1}\)] |
|--------------------|---------------------------------|-----------------|-----------------|
| B3LYP/6-31G*       | 141.769; 141.592                 | 195.143         | 742.429         |
| MP2/aug-cc-pVDZ    | 130.561; 130.248                 | 175.961         | 713.852         |
| CCSD(T)/aug-cc-pVDZ| 132.407; 131.551                 | 185.975         | 730.328         |

Table 7: Harmonic and anharmonic ZPE corrected forward (\( E_f \)) and backward (\( E_b \)) reaction barriers and TS reactive mode harmonic frequencies (\( \tilde{\omega} \)) for the R2 reaction.

| Method/BS          | \( E_f(\text{ZPE}_{\text{harm}}; \text{ZPE}_{\text{anh}}) \) /[kJmol\(^{-1}\)] | \( E_b \) /[kJmol\(^{-1}\)] | \( \tilde{\omega} \) /[cm\(^{-1}\)] |
|--------------------|---------------------------------|-----------------|-----------------|
| B3LYP/6-31G*       | 86.692; 86.585                   | 179.028         | 571.875         |
| MP2/aug-cc-pVDZ    | 67.549; 68.182                   | 170.841         | 443.303         |
| CCSD/jun-cc-pVDZ   | 116.063; 116.087                 | 208.533         | 746.523         |
| CCSD/aug-cc-pVDZ   | 110.570                         |                 | 737.491         |

Table 8: Harmonic and anharmonic ZPE corrected forward (\( E_f \)) and backward (\( E_b \)) reaction barriers and TS reactive mode harmonic frequencies (\( \tilde{\omega} \)) for the R3 reaction.

| Method/BS          | \( E_f(\text{ZPE}_{\text{harm}}; \text{ZPE}_{\text{anh}}) \) /[kJmol\(^{-1}\)] | \( E_b \) /[kJmol\(^{-1}\)] | \( \tilde{\omega} \) /[cm\(^{-1}\)] |
|--------------------|---------------------------------|-----------------|-----------------|
| B3LYP/6-31G*       | 141.682; 141.451                 | 140.031         | 569.246         |
| MP2/aug-cc-pVDZ    | 102.317; 109.111                 | 100.840         | 110.546         |
| CCSD/jun-cc-pVDZ   | 174.181; 173.940                 | 172.511         | 696.535         |
5 Hindered Rotations Treatment

For the hindered rotational modes (HRM) treatment, involved in the low frequency modes of the R2 and R3 reactants, we used the Pitzer and Gewin (PG) coefficients for the correction of the harmonic oscillator partition function.

The overall correction values for the total harmonic partition functions associated with the HRM are listed in Tables (9) and (10).
Table 9: Overall PG correction coefficients for the HRM in the R2 reaction at the MP2/aug-cc-pVDZ, B3LYP/6-31G* and CCSD/jun-cc-pVDZ level of theory.

(a) MP2 PG coefficients.

| $\omega_1$/[cm$^{-1}$] | 100.213 |
|------------------------|---------|
| $\omega_2$/[cm$^{-1}$] | 103.936 |
| Multiplicity           | 1.000   |

| T/[K] | Overall PG coefficient |
|-------|------------------------|
| 100   | 1.018                  |
| 120   | 1.022                  |
| 130   | 1.024                  |
| 150   | 1.028                  |
| 200   | 1.039                  |
| 250   | 1.052                  |
| 300   | 1.065                  |
| 350   | 1.080                  |
| 400   | 1.095                  |
| 450   | 1.110                  |
| 500   | 1.125                  |

(b) DFT PG coefficients.

| $\omega_1$/[cm$^{-1}$] | 55.059 |
|------------------------|--------|
| $\omega_2$/[cm$^{-1}$] | 93.797 |
| Multiplicity           | 1.000  |

| T/[K] | Overall PG coefficient |
|-------|------------------------|
| 100   | 1.024                  |
| 120   | 1.029                  |
| 130   | 1.032                  |
| 150   | 1.038                  |
| 200   | 1.054                  |
| 250   | 1.071                  |
| 300   | 1.090                  |
| 350   | 1.110                  |
| 400   | 1.130                  |
| 450   | 1.148                  |
| 500   | 1.165                  |

(c) CCSD PG coefficients.

| $\omega_1$/[cm$^{-1}$] | 93.754 |
|------------------------|--------|
| $\omega_2$/[cm$^{-1}$] | 97.654 |
| Multiplicity           | 1.000  |

| T/[K] | Overall PG coefficient |
|-------|------------------------|
| 100   | 1.022                  |
| 120   | 1.027                  |
| 130   | 1.029                  |
| 150   | 1.034                  |
| 200   | 1.048                  |
| 250   | 1.064                  |
| 300   | 1.081                  |
| 350   | 1.098                  |
| 400   | 1.116                  |
| 450   | 1.134                  |
| 500   | 1.151                  |
Table 10: Overall PG correction coefficients for the HRM in the R3 reaction at the MP2/aug-cc-pVDZ, B3LYP/6-31G* and CCSD/jun-cc-pVDZ level of theory.

(a) MP2 PG coefficients.  

| $\omega_1$/[cm$^{-1}$] | 51.106 | $\omega_1$/[cm$^{-1}$] | 65.675 |
|------------------------|--------|------------------------|--------|
| $\omega_2$/[cm$^{-1}$] | 90.513 | $\omega_2$/[cm$^{-1}$] | 101.710 |
| $\omega_3$/[cm$^{-1}$] | 105.307 | $\omega_3$/[cm$^{-1}$] | 108.148 |
| Multiplicity           | 2.000  | Multiplicity           | 2.000  |

T/[K] | Overall PG coefficient | T/[K] | Overall PG coefficient
---|------------------------|---|------------------------|
100   | 2.211                  | 100.000 | 2.150                  |
120   | 2.268                  | 120.000 | 2.188                  |
130   | 2.298                  | 130.000 | 2.208                  |
150   | 2.359                  | 150.000 | 2.251                  |
200   | 2.511                  | 200.000 | 2.372                  |
250   | 2.647                  | 250.000 | 2.501                  |
300   | 2.758                  | 300.000 | 2.629                  |
350   | 2.845                  | 350.000 | 2.748                  |
400   | 2.908                  | 400.000 | 2.851                  |
450   | 2.952                  | 450.000 | 2.939                  |
500   | 2.977                  | 500.000 | 3.009                  |

(b) DFT PG coefficients.  

| $\omega_1$/[cm$^{-1}$] | 65.675 |
|------------------------|--------|
| $\omega_2$/[cm$^{-1}$] | 101.710 |
| $\omega_3$/[cm$^{-1}$] | 108.148 |
| Multiplicity           | 2.000  |

T/[K] | Overall PG coefficient
---|------------------------|
100   | 2.211                  |
120   | 2.268                  |
130   | 2.298                  |
150   | 2.359                  |
200   | 2.511                  |
250   | 2.647                  |
300   | 2.758                  |
350   | 2.845                  |
400   | 2.908                  |
450   | 2.952                  |
500   | 2.977                  |

(c) CCSD PG coefficients.  

| $\omega_1$/[cm$^{-1}$] | 65.916 |
|------------------------|--------|
| $\omega_2$/[cm$^{-1}$] | 99.219 |
| $\omega_3$/[cm$^{-1}$] | 114.051 |
| Multiplicity           | 2.000  |

T/[K] | Overall PG coefficient
---|------------------------|
100.000 | 2.144                  |
120.000 | 2.179                  |
130.000 | 2.199                  |
150.000 | 2.239                  |
200.000 | 2.354                  |
250.000 | 2.478                  |
300.000 | 2.601                  |
350.000 | 2.715                  |
400.000 | 2.816                  |
450.000 | 2.901                  |
500.000 | 2.971                  |
6 Kinetic Rate Constants

For the computation of the reactants and the TS Density of State (DOS) with the Paraden-sum and Parsctst program\(^3\)\(^-\)\(^5\) we used the following parameters:

- Number of Walkers: 1
- Window Overlap: 70 %
- Flatness: 95 %
- Windows Balance: constant
- Energy Grain / [cm\(^{-1}\)]: 5
- Upper Energy Limit: 30000
- Number of Elements in the Double Array: 2500

The absolute values of the rate constants for the three reactions at different temperatures and ab initio levels of theory are here shown in the reported tables\(^1\).

Table 11: TST and SCTST reaction rate constants at the MP2/aug-cc-pVDZ, CCSD(T)/aug-cc-pVDZ and B3LYP/6-31G* level of theory for the R1 reaction.

| T/[K] | \(k_{\text{TST}}^{\text{DFT}}(T)/[\text{s}^{-1}]\) | \(k_{\text{SCTST}}^{\text{DFT}}(T)/[\text{s}^{-1}]\) | \(k_{\text{TST}}^{\text{MP2}}(T)/[\text{s}^{-1}]\) | \(k_{\text{SCTST}}^{\text{MP2}}(T)/[\text{s}^{-1}]\) |
|-------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 100   | 2.11675E-062                    | 2.13928E-044                    | 1.49633E-056                    | 6.29877E-042                    |
| 120   | 5.53349E-050                    | 1.45661E-041                    | 4.11002E-045                    | 1.524785E-038                   |
| 130   | 3.32983E-045                    | 1.19574E-039                    | 1.03871E-040                    | 1.94188E-036                    |
| 150   | 1.49548E-037                    | 3.65046E-035                    | 1.16246E-033                    | 9.65712E-032                    |
| 200   | 4.26616E-025                    | 2.28611E-024                    | 3.44999E-022                    | 1.71203E-021                    |
| 250   | 1.32929E-017                    | 3.43512E-017                    | 2.75416E-015                    | 7.23676E-015                    |
| 300   | 1.36253E-012                    | 2.57491E-012                    | 1.13615E-010                    | 2.24878E-010                    |
| 350   | 5.30245E-009                    | 8.48404E-009                    | 2.30435E-007                    | 3.91287E-007                    |
| 400   | 2.66162E-006                    | 3.81852E-006                    | 7.08679E-005                    | 1.09741E-004                    |
| 450   | 3.40065E-004                    | 4.55119E-004                    | 6.17995E-003                    | 9.02378E-003                    |
| 500   | 1.66349E-002                    | 2.12066E-002                    | 0.22255                         | 0.31260                        |

| T/[K] | \(k_{\text{TST}}^{\text{CCSD(T)}}(T)/[\text{s}^{-1}]\) | \(k_{\text{SCTST}}^{\text{CCSD(T)}}(T)/[\text{s}^{-1}]\) |
|-------|-------------------------------------------------|-------------------------------------------------|
| 100   | 2.11675E-062                                    | 1.49633E-056                                    |
| 120   | 5.53349E-050                                    | 4.11002E-045                                    |
| 130   | 3.32983E-045                                    | 1.03871E-040                                    |
| 150   | 1.49548E-037                                    | 1.16246E-033                                    |
| 200   | 4.26616E-025                                    | 3.44999E-022                                    |
| 250   | 1.32929E-017                                    | 2.75416E-015                                    |
| 300   | 1.36253E-012                                    | 1.13615E-010                                    |
| 350   | 5.30245E-009                                    | 2.30435E-007                                    |
| 400   | 2.66162E-006                                    | 7.08679E-005                                    |
| 450   | 3.40065E-004                                    | 6.17995E-003                                    |
| 500   | 1.66349E-002                                    | 0.22255                                         |

\(^{1}\)Values here reported refer to kinetic rate constants calculated using the anharmonic couplings obtained with our program.
Table 12: TST and SCTST reaction rate constants at the MP2/aug-cc-pVDZ, B3LYP/6-31G* and CCSD/jun-cc-pVDZ level of theory for the R2 reaction.

| T/K  | $k_{DFT}^{TST}(T)$/$s^{-1}$ | $k_{DFT}^{SCTST}(T)$/$s^{-1}$ | $k_{MP2}^{TST}(T)$/$s^{-1}$ | $k_{MP2}^{SCTST}(T)$/$s^{-1}$ |
|------|--------------------------|---------------------------|------------------------|-----------------------------|
| 100  | 4.03881E-034             | 1.13132E-029              | 9.48905E-024           | 5.13281E-018                |
| 120  | 1.40522E-026             | 8.74949E-025              | 7.74599E-018           | 4.17104E-017                |
| 130  | 1.10653E-023             | 2.06538E-022              | 1.44387E-015           | 2.33636E-015                |
| 150  | 4.68877E-019             | 2.78935E-018              | 6.11954E-012           | 5.42185E-012                |
| 200  | 1.45733E-011             | 3.29232E-011              | 4.55622E-006           | 3.86076E-006                |
| 250  | 3.99407E-007             | 6.85389E-007              | 1.49388E-002           | 6.09145E-003                |
| 300  | 5.14018E-002             | 6.09214E-002              | 136.78973              | 45.89433                    |
| 350  | 1.93873                 | 2.13278                  | 2345.40624             | 739.52197                   |
| 400  | 32.41599                | 33.78148                 | 21240.54872            | 6212.91933                  |
| 450  | 307.11192               | 307.00269                | 123225.99859           | 34104.14281                 |
| 500  | 3.23214E-049            | 1.33064E-040             |                       |                             |

| T/K  | $k_{CCSD}^{TST}(T)$/$s^{-1}$ | $k_{CCSD}^{SCTST}(T)$/$s^{-1}$ |
|------|-----------------------------|--------------------------------|
| 100  | 3.23214E-049               | 1.33064E-040                   |
| 120  | 4.29893E-039               | 9.79458E-035                   |
| 130  | 3.33972E-035               | 3.96741E-032                   |
| 150  | 5.51741E-029               | 2.15141E-027                   |
| 200  | 6.62577E-019               | 1.98934E-018                   |
| 250  | 7.01376E-013               | 1.02646E-012                   |
| 300  | 7.05351E-009               | 7.32893E-009                   |
| 350  | 4.99767E-006               | 4.23927E-006                   |
| 400  | 6.77155E-004               | 5.00719E-004                   |
| 450  | 3.05601E-002               | 2.04616E-002                   |
| 500  | 0.64053                   | 0.39729                       |
Table 13: TST and SCTST reaction rate constants at the MP2/aug-cc-pVDZ, B3LYP/6-31G* and CCSD/jun-cc-pVDZ level of theory for the R3 reaction.

| T/K  | $k_{\text{DFT}}^\text{TST}(T)$/[s$^{-1}$] | $k_{\text{DFT}}^\text{SCTST}(T)$/[s$^{-1}$] | $k_{\text{MP2}}^\text{TST}(T)$/[s$^{-1}$] | $k_{\text{MP2}}^\text{SCTST}(T)$/[s$^{-1}$] |
|------|---------------------------------|---------------------------------|-----------------|-----------------|
| 100  | 5.14108E-063                    | 4.40637E-058                    | 1.38839E-042    | 3.61820E-046    |
| 120  | 1.02706E-050                    | 7.23459E-049                    | 9.4086E-034     | 1.00828E-036    |
| 130  | 5.46408E-046                    | 1.09358E-044                    | 2.49353E-030    | 4.25883E-033    |
| 150  | 1.95583E-038                    | 1.26557E-037                    | 6.71034E-025    | 2.63201E-027    |
| 200  | 3.46576E-026                    | 8.9942E-026                     | 4.1694E-016     | 6.2555E-018     |
| 250  | 7.38090E-019                    | 1.37385E-018                    | 7.48352E-011    | 2.48835E-012    |
| 300  | 5.53659E-014                    | 8.84309E-014                    | 2.33016E-007    | 1.30769E-008    |
| 350  | 1.66324E-010                    | 2.44717E-010                    | 7.22687E-005    | 5.86116E-006    |
| 400  | 6.73489E-008                    | 9.46018E-008                    | 5.33657E-003    | 5.86098E-004    |
| 450  | 7.18979E-006                    | 9.83407E-006                    | 0.15179         | 1.98863E-002    |
| 500  | 3.02751E-004                    | 4.07996E-004                    | 2.21997         | 0.34226         |

| T/K  | $k_{\text{CCSD}}^\text{TST}(T)$/[s$^{-1}$] | $k_{\text{CCSD}}^\text{SCTST}(T)$/[s$^{-1}$] |
|------|---------------------------------|---------------------------------|
| 100  | 5.38555E-080                    | 1.49492E-045                    |
| 120  | 7.28489E-065                    | 2.14694E-045                    |
| 130  | 4.75194E-059                    | 2.80869E-045                    |
| 150  | 9.39617E-050                    | 8.32189E-045                    |
| 200  | 1.12907E-034                    | 5.72588E-034                    |
| 250  | 1.20154E-025                    | 3.20860E-025                    |
| 300  | 1.22244E-019                    | 2.50631E-019                    |
| 350  | 2.36388E-015                    | 4.23288E-015                    |
| 400  | 3.86298E-012                    | 6.41795E-012                    |
| 450  | 1.22057E-009                    | 1.94476E-009                    |
| 500  | 1.22293E-007                    | 1.90647E-007                    |
The values of the % difference between the SCTST and the TST rate constants are reported in the following tables.

The definition of the % difference can be found in the article in eq. 33.

Table 14: % difference at the MP2/aug-cc-pVDZ, CCSD(T)/aug-cc-pVDZ, B3LYP/6-31G* and CCSD/jun-cc-pVDZ level of theory for the R1, R2 and R3 reactions.

(a) R1 % difference.

| T/[K] | % Diff DFT | % Diff MP2 | % Diff CCSD(T) |
|-------|------------|------------|----------------|
| 100   | 100.000    | 100.000    | 100.000        |
| 120   | 99.999     | 99.999     | 99.999         |
| 130   | 99.999     | 99.999     | 99.999         |
| 150   | 99.590     | 98.796     | 97.728         |
| 200   | 81.339     | 79.848     | 77.397         |
| 250   | 61.303     | 61.889     | 72.601         |
| 300   | 47.084     | 49.477     | 61.267         |
| 350   | 37.237     | 41.108     | 53.076         |
| 400   | 30.297     | 35.422     | 47.217         |
| 450   | 25.279     | 31.515     | 43.028         |
| 500   | 21.558     | 28.807     | 40.037         |

(b) R2 % difference.

| T/[K] | % Diff DFT | % Diff MP2 | % Diff CCSD |
|-------|------------|------------|-------------|
| 100   | 99.996     | 99.999     | 99.999      |
| 120   | 98.393     | 99.999     | 99.999      |
| 130   | 94.642     | 98.200     | 99.916      |
| 150   | 83.190     | 99.916     | 97.435      |
| 200   | 55.735     | 99.998     | 66.694      |
| 250   | 37.012     | 97.435     | 31.670      |
| 300   | 24.453     | 97.351     | -137.357    |
| 350   | 15.626     | 97.973     | -198.054    |
| 400   | 9.098      | 92.215     | -221.059    |
| 450   | 4.042      | 94.935     | -241.877    |
| 500   | 0.036      | 96.122     | -261.323    |

(c) R3 % difference.

| T/[K] | % Diff DFT | % Diff MP2 | % Diff CCSD |
|-------|------------|------------|-------------|
| 100   | 99.998     | -3836.2300 | 100.000     |
| 120   | 98.580     | -9849.313  | 100.000     |
| 130   | 95.003     | -5849.588  | 99.999      |
| 150   | 84.546     | -2539.567  | 99.998      |
| 200   | 61.056     | -6564.150  | 80.281      |
| 250   | 46.276     | -2907.423  | 62.552      |
| 300   | 37.391     | -1681.889  | 51.225      |
| 350   | 32.034     | -1132.799  | 44.155      |
| 400   | 28.808     | -839.375   | 39.809      |
| 450   | 26.889     | -663.272   | 37.238      |
| 500   | 25.796     | -548.612   | 35.854      |

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