

## SUPPORTING INFORMATION

### Newtonian Kinetic Isotope Effects. Observation, Prediction, and Origin of Heavy-Atom Dynamic Isotope Effects

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## A. Experimental Procedures.

**Dicyclopentadiene. Kinetic Dimer.** Fresh samples of neat cyclopentadiene were prepared in 10 g to 40 g lots by the cracking of commercial dicyclopentadiene in a fractional distillation apparatus (*SI*), then allowed to dimerize to approximately 55% conversion by standing at 25 °C for 36 h. The resulting dimer was purified by two sequential vacuum distillations, without heating, to afford 4 g to 10 g samples of *endo*-dicyclopentadiene as a colorless solid, mp 32 °C. The samples of *endo*-dicyclopentadiene were stored at -10 °C until analysis. A total of seven samples were prepared in this way.

**Equilibration of Dicyclopentadiene.** In a typical procedure, 2.00 g of freshly purified dicyclopentadiene was placed in a pressure tube and heated for 6 h at 140 °C. The resulting dicyclopentadiene was then repurified by vacuum distillation. An alternative equilibration period of only 2 h at 140 °C resulted in an isotopic composition that was indistinguishable by NMR analysis, suggesting that the 6 h equilibration period is sufficient.

By closely analogous procedures, six other samples of equilibrated dimer were prepared from independent dimerization reactions.

**NMR Measurements.** All NMR samples were prepared using a constant 500 mg of dicyclopentadiene in 5 mm NMR tubes filled to a constant height of 5 cm with CDCl<sub>3</sub> or acetone-d<sub>6</sub>. The <sup>13</sup>C spectra were recorded at 125.81 MHz using inverse gated decoupling, 100 s delays between calibrated  $\pi/2$  pulses, and a 6 s acquisition time to collect 200 084 points. Integrations were numerically determined using a constant integration region for each peak. A zero-order

baseline correction was generally applied, but no first-order correction was applied. Six spectra were recorded for each sample of equilibrated dimer and kinetic dimer.

The complete results from the NMR measurements and the details of the calculation of the  $^{13}\text{C}$  ratios and KIEs are given in the last section.

## **B. General Computational Procedures.**

Standard calculations of minima or transition structures employed Gaussian03 (S2). Default procedures in Gaussian03 were employed unless otherwise noted. Full structures and energetics are provided in a section below.

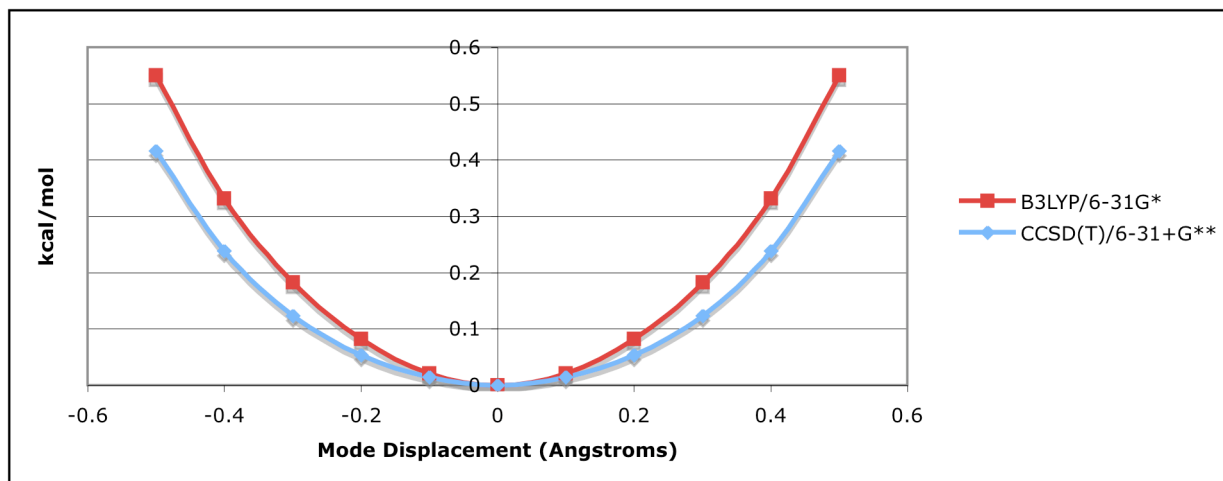
The program suite PROGDYN used for direct dynamics is listed at the end of the Supporting Information as a series of component programs as either Unix shell scripts or awk or c programs. Gaussian03 was used to calculate the forces at each point in the trajectories. The latest version of this program can be obtained by emailing Daniel Singleton at [singleton@mail.chem.tamu.edu](mailto:singleton@mail.chem.tamu.edu). Some minor variations in PROGDYN were used to accomplish the special calculational experiments in which trajectories were initialized with  $^{12}\text{C}$  but propagated with  $^{140}\text{C}$  or initialized with  $^{140}\text{C}$  but propagated with  $^{12}\text{C}$ , keeping the momentum of the atoms constant in each case. As will be discussed, another modification was used to equalize the sampling of trajectories with positive and negative signs for the velocities of the lowest-energy real vibrational mode (“mode #2”, see Figure S2). The program modifications used to accomplish these studies are given at the end of the PROGDYN listings.

Steepest-descent paths in mass-weighted coordinates were carried out in either of two ways: using the IRC option in Gaussian03 or using standard options available in PROGDYN. The latter uses a Euler algorithm with an adaptive step size and automatically decreasing step sizes when instability is detected. The standard Gaussian03 algorithm is tremendously faster while the PROGDYN algorithm succeeds in some cases where the more sophisticated Gaussian03 algorithm fails.

### C. Calculations Supporting $C_2$ Symmetry in the Dimerization Transition Structure.

Because the thesis of the work described hinges on the  $C_2$  symmetry of the transition structure **1** for the dimerization of cyclopentadiene, the calculational support for  $C_2$  symmetry, originally described by Caramella and coworkers (see ref 2 of main text), was evaluated in detail. A series of transition structures located in B3LYP/6-31G\*, B3LYP/6-31+G\*\*, MP2/6-31G\*, MP2/6-311+G\*\*, MP4(sdq)/6-31+G\*\*, MPW1K/6-31+G\*\*, MPWB1K/6-31+G\*\*, B3PW91/6-31+G\*\*, MPW1B95/6-31+G\*\*, MPW3LYP/6-31+G\*\*, PBE1KCIS/6-31+G\*\*, BB1K/6-31+G\*\*, O3LYP/6-31+G\*\*, BP86/6-31+G\*\*, and PW91/6-31+G\*\* calculations in each case exhibited  $C_2$  symmetry. All of these structures have exactly one imaginary frequency. The frequency of the lowest-energy desymmetrizing real normal mode (mode #2 in Figure S2), a measure of the calculational preference for  $C_2$  symmetry, ranged from 54 to 114  $\text{cm}^{-1}$ . The position of the transition structure varied in standard ways (e.g., relatively early in MP2/6-31G\* calculations that underestimate the barrier, relatively late in B3LYP/6-31+G\*\* calculations that underestimate the reaction exothermicity) but otherwise no substantial difference was observable in the series of structures.

To examine the symmetry of **1** using a higher-level calculational method, a series of geometries constituting a “transition state ridge” was defined by the displacement (in Cartesian coordinates) of the atoms in the B3LYP/6-31G\* transition structure along the lowest-energy desymmetrizing transverse vibrational normal mode (mode #2 in Figure S2, 73.6  $\text{cm}^{-1}$  for B3LYP/6-31G\*). Single point energies for the structures along the ridge were then determined in CCSD(T)/6-31+G\*\* calculations. The resulting energies are plotted in the graph below and compared to the B3LYP/6-31G\* energies for the same structures. The key observations are that the CCSD(T)/6-31+G\*\* energy is at a minimum at the central,  $C_2$ -symmetric structure and that the rise in the CCSD(T)/6-31+G\*\* energy is roughly harmonic. These observations weigh against an asymmetric transition structure. The CCSD(T)/6-31+G\*\* frequency for mode #2 would be estimated as approximately 60  $\text{cm}^{-1}$ .



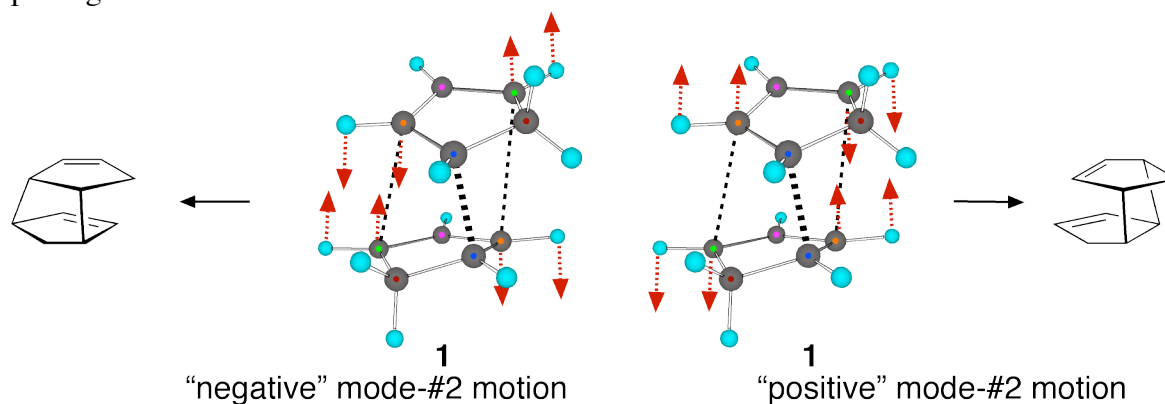
**Figure S1.** Plot of the potential energy versus displacement along the lowest-energy desymmetrizing transverse vibrational normal mode for transition structure **1**.

#### D. Initialization of Trajectories.

The trajectories employed for Table 1 of the main text are quasiclassical, i.e., the initial energies of the normal modes are quantized within the harmonic oscillator approximation and include zero-point energy. Additional trajectories mentioned in the main text and delineated below were fully classical, i.e., without zero-point energy. For trajectories started from **1**, the desired energy in each of the normal modes was mapped from a random number generator to a Boltzmann distribution. The phase of each of the normal modes was mapped from a Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (erring unavoidably by ignoring mode displacements outside of the classical limit). The sign of the initial velocity of each real normal mode was determined by a random-number generator, except that the initialization was adjusted to equalize the sampling of trajectories with positive and negative signs for the velocities of the lowest-energy real vibrational mode, as discussed in the next section. After an energy / force calculation on the initial geometry, the total initial energy was calculated and the trajectory was discarded if the total energy did not agree within 1.0 kcal/mol with the desired energy. (This is a variation of the conventional practice of scaling energies (S3).)

### E. Statistical Issues in the Sampling of Trajectories, and the Calculation of Confidence Ranges

The sign of the initial velocity for mode #2 (the lowest-energy real vibrational mode) in the cycloaddition transition structure **1** has a strong impact on the outcome of individual trajectories. In 85.2% of the trajectories, the product outcome corresponds to that favored by the sign of the initial velocity of this mode (Figure S2). This correlation provided us with an opportunity to improve our sampling of trajectories and decrease the uncertainty associated with the KIEs. The ideas used here seem most easily understood with the aid of an extended analogy – pre-election polling.



**Figure S2.** Motion associated with the lowest-energy real vibrational mode (“mode #2”) and the usual effect of the sign of this motion on trajectory outcomes. “Positive” and “negative” are assigned arbitrarily.

Suppose that a pollster wants to predict the outcome of an election between a Democratic candidate and a Republican candidate in a county where there are 50,000 registered Republicans and 50,000 registered Democrats. We will assume that most Republicans vote for the Republican candidate and most Democrats vote for the Democratic candidate. If a pollster polls 400 people, a normal number, by random chance alone about 34% of the time the sample will contain at least 20 more of one party than the other. This excess can throw off the ratio of voters for one candidate versus the other by 10%. To correct for this as well as possible systematic errors in contacting one party versus the other, pollsters weight their results versus a “true” ratio of voters from the parties. They could also achieve the same effect by contacting more of the

underrepresented party. To continue the analogy, if the polling finds that every one of 200 Democratic voters is voting for the Democratic candidate while 10 out of 200 of the Republican voters are voting for the Democratic candidate, the poll can confidently place the Democratic candidate ahead, despite the fact that the 95% confidence range on a 210 to 190 ratio, knowing nothing else, is from 0.91 to 1.35. The low number of crossover voters, all going one way, decreases the margin of error. If the number of crossover voters were larger, for example 80 going one way and 90 going the other, the poll could no longer be statistically certain that one candidate was favored over the other.

These standard statistical ideas led to two actions here. The first was that the initialization was adjusted to equalize the sampling of trajectories with positive and negative signs for the velocities of mode #2. This adjustment reflects the known equal likelihood of positive versus negative signs in reality. The second action is that the 95% confidence ranges on the KIEs are calculated in a way that reflects the additional knowledge of the low proportion of “crossover trajectories.”

For each set of trajectories with a particular isotope in a particular position, we divide the trajectories into four categories: negative-x', negative-x, positive-x', and positive-x. “Negative” and “positive” refer to the sign of mode #2. These signs are arbitrary, arising from the arbitrary signs given to the Cartesian normal modes in the frequency calculations used as input in starting trajectories, but the signs are consistent within any single set of trajectories. (For example, the quasiclassical trajectories performed with a  $^{44}\text{C}$  in the *c* position all used the same assignment of signs, while the quasiclassical trajectories performed with a  $^{28}\text{C}$  in the *c* position all used a sign assignment that was reversed from that used for  $^{44}\text{C}$ .) The terms *x* and *x'* refer to whether the product of the trajectory has the labeled carbon in the *a*, *b*, *c*, *d*, or *e* position or the *a'*, *b'*, *c'*, *d'*, or *e'* position.

For simplicity in the formulas below, negative-x', negative-x, positive-x', and positive-x will be replaced by J, K, L, and M, respectively. The “Nominal KIE” was calculated by eq 1. When  $J+K = L+M$ , this equation reduces to  $(J+L)/(K+M)$  or total *x'*/total *x*, but eq 1 is more general.

$$\text{KIE} = \frac{\frac{J}{J+K} + \frac{L}{L+M}}{\frac{K}{J+K} + \frac{M}{L+M}} \quad (1)$$

The uncertainty in J or K at two standard deviations (95% confidence) is given by eq 2.

$$\Delta J = \Delta K = 2*(J*K/(J+K))^{1/2} \quad (2)$$

Similarly:

$$\Delta L = \Delta M = 2*(L*M/(L+M))^{1/2} \quad (3)$$

The errors in J versus K are not independent, and the errors in L versus M are not independent. The uncertainty in the KIE caused by each of these uncertainties was calculated numerically – that is, for example, by filling in  $J + \Delta J$  and  $K - \Delta J$  into eq 1 or filling in  $J - \Delta J$  and  $K + \Delta J$  into eq 1. The errors in J and K versus L and M are independent and can be combined in a standard way as in eq 4.

$$\frac{\Delta \text{KIE}}{\text{KIE}} = \left( \left( \frac{\Delta \text{KIE}}{\text{KIE}} \right)_{JK}^2 + \left( \frac{\Delta \text{KIE}}{\text{KIE}} \right)_{LM}^2 \right)^{1/2} \quad (4)$$

## F. Results from All Trajectories.

Table S1 summarizes the results of the trajectory studies. The column labels may be understood with reference to the previous section. It should be noted that the KIEs listed in the main text have been ‘centered’ within the confidence range. This leads to some minor apparent discrepancies between the table below and the table in the main text. For example, the nominal KIE for the first line rounds to 1.78 with a 95% confidence range from 1.52 to 2.09, but the center of the confidence limit rounds to 1.80 and the main text list the 95% confidence range as just  $1.80 \pm 0.28$  for simplicity.

It may be noted that a total of 14,884 trajectories are listed in the table, arising from approximately one million force calculations. Each force calculation required approximately 2 processor-minutes on an AMD Opteron 270 cpu, totaling approximately 4-processor years.



**Table S1.**

| Position /<br>mass   | Total<br>runs | Negative<br>x' | Negative<br>x | Positive<br>x' | Positive<br>x | Nominal<br>KIE | Total<br>x' | Total<br>x | 95%<br>confidence<br>limits |      |
|--|---------------|----------------|---------------|----------------|---------------|----------------|-------------|------------|-----------------------------|------|
| <u>Quasiclassical</u>                                      |               |                |               |                |               |                |             |            |                             |      |
| a/a' 140   | 420           | 73             | 137           | 196            | 14            | 1.78           | 269         | 151        | 2.09                        | 1.52 |
| a/a' 76  | 402           | 62             | 139           | 183            | 18            | 1.56           | 245         | 157        | 1.83                        | 1.33 |
| a/a' 44  | 448           | 54             | 170           | 202            | 22            | 1.33           | 256         | 192        | 1.54                        | 1.15 |
| a/a' 28  | 456           | 44             | 184           | 207            | 21            | 1.22           | 251         | 205        | 1.39                        | 1.07 |
| a/a' 20  | 568           | 49             | 235           | 247            | 37            | 1.09           | 296         | 272        | 1.23                        | 0.96 |
| b/b' 140   | 486           | 40             | 203           | 209            | 34            | 1.05           | 249         | 237        | 1.19                        | 0.92 |
| b/b' 76  | 450           | 30             | 195           | 193            | 32            | 0.98           | 223         | 227        | 1.12                        | 0.86 |
| c/c' 140   | 320           | 105            | 55            | 10             | 150           | 0.56           | 115         | 205        | 0.67                        | 0.46 |
| c/c' 76  | 278           | 106            | 33            | 6              | 133           | 0.67           | 112         | 166        | 0.79                        | 0.57 |
| c/c' 44  | 558           | 227            | 52            | 16             | 263           | 0.77           | 243         | 315        | 0.86                        | 0.69 |
| c/c' 28  | 540           | 24             | 246           | 230            | 40            | 0.89           | 254         | 286        | 0.99                        | 0.79 |
| c/c' 20  | 544           | 26             | 246           | 236            | 36            | 0.93           | 262         | 282        | 1.03                        | 0.83 |
| d/d' 140   | 540           | 199            | 71            | 27             | 243           | 0.72           | 226         | 314        | 0.82                        | 0.63 |
| d/d' 76  | 500           | 200            | 50            | 16             | 234           | 0.76           | 216         | 284        | 0.86                        | 0.67 |
| d/d' 44  | 308           | 124            | 30            | 16             | 138           | 0.83           | 140         | 168        | 0.98                        | 0.70 |
| d/d' 28  | 1684          | 682            | 160           | 95             | 747           | 0.86           | 777         | 907        | 0.92                        | 0.80 |
| d/d' 20  | 1314          | 548            | 109           | 79             | 578           | 0.91           | 627         | 687        | 0.99                        | 0.84 |
| e/e' 140   | 486           | 22             | 221           | 212            | 31            | 0.93           | 234         | 252        | 1.04                        | 0.83 |
| e/e' 76  | 652           | 50             | 276           | 284            | 42            | 1.05           | 334         | 318        | 1.17                        | 0.94 |
| <u>Classical</u>   |               |                |               |                |               |                |             |            |                             |      |
| a/a' 140   | 224           | 34             | 78            | 106            | 6             | 1.67           | 140         | 84         | 2.05                        | 1.35 |
| a/a' 76  | 226           | 26             | 87            | 108            | 5             | 1.46           | 134         | 92         | 1.75                        | 1.21 |
| b/b' 140   | 172           | 7              | 79            | 76             | 10            | 0.93           | 83          | 89         | 1.11                        | 0.77 |
| b/b' 76  | 340           | 22             | 148           | 147            | 23            | 0.99           | 169         | 171        | 1.14                        | 0.85 |
| c/c' 140   | 448           | 157            | 67            | 14             | 210           | 0.62           | 171         | 277        | 0.71                        | 0.53 |
| c/c' 76  | 244           | 97             | 25            | 3              | 119           | 0.69           | 100         | 144        | 0.81                        | 0.59 |
| d/d' 140   | 200           | 61             | 39            | 6              | 94            | 0.50           | 67          | 133        | 0.64                        | 0.39 |
| d/d' 76  | 256           | 100            | 28            | 7              | 121           | 0.72           | 107         | 149        | 0.85                        | 0.60 |
| e/e' 140   | 262           | 19             | 112           | 113            | 18            | 1.02           | 132         | 130        | 1.20                        | 0.85 |
| e/e' 76  | 234           | 11             | 106           | 105            | 12            | 0.98           | 116         | 118        | 1.14                        | 0.84 |
| C-140 Initialization, C12 propagation at constant momentum |               |                |               |                |               |                |             |            |                             |      |
| a/a'   | 210           | 8              | 97            | 93             | 12            | 0.93           | 101         | 109        | 1.09                        | 0.78 |
| c/c'   | 224           | 96             | 16            | 12             | 100           | 0.93           | 108         | 116        | 1.11                        | 0.78 |
| d/d'   | 250           | 118            | 7             | 10             | 115           | 1.05           | 128         | 122        | 1.19                        | 0.92 |
| C-12 Initialization, C140 propagation at constant momentum |               |                |               |                |               |                |             |            |                             |      |
| a/a'   | 188           | 38             | 56            | 83             | 11            | 1.81           | 121         | 67         | 2.35                        | 1.38 |
| c/c'   | 246           | 12             | 111           | 94             | 29            | 0.76           | 106         | 140        | 0.91                        | 0.62 |
| d/d'   | 206           | 15             | 88            | 74             | 29            | 0.76           | 89          | 117        | 0.95                        | 0.60 |

### G. Extrapolation of Trajectory Results to $^{13}\text{C}$

The process for extrapolation of the trajectory results to  $^{13}\text{C}$  starts with the assumption that the additional isotope effect per additional mass unit decreases as the mass grows. For example, the effect of going from  $^{13}\text{C}$  to  $^{14}\text{C}$  would be larger than the effect of going from  $^{140}\text{C}$  to  $^{141}\text{C}$ . We further assumed that this decrease with mass is nonlinear with a decreasing slope, that is, that a plot of the additional isotope effect per additional mass versus mass would have a greater slope at low masses (e.g.,  $^{13}\text{C}$  to  $^{14}\text{C}$ ) than at high masses (e.g.  $^{140}\text{C}$  to  $^{141}\text{C}$ ). These simple assumptions exclude some extrapolation processes that would lead to physically unreasonable isotope effects at both high masses and at  $^{13}\text{C}$ .

Table S2 and the associated graph show the data used in the extrapolation, the extrapolated results, and the complete linear regression analysis and statistics. The Nominal KIEs come from the Table in the previous section. The “additional mass” is defined as the mass beyond 12 amu. The “isotope effect per mass” is defined as the geometric average (eq 5).

$$\text{isotope effect per mass} = (\text{Nominal KIE})^{1/(\text{additional mass})} \quad (5)$$

The extrapolation was then carried out by assuming a linear relationship between the log of the additional mass (the base is arbitrary but set conveniently here as 2) versus the isotope effect per mass. While the unavoidable scatter in the underlying data leads to unimpressive  $R^2$ 's (0.80, 0.86, 0.97 for  $a$ ,  $c$ , and  $d$ , respectively), there is no sign of a systematic departure from linearity. [Linearity of the functional form used here would have to break down at sufficiently higher masses.] The extrapolation process used the Regression tool in Microsoft Excel 2004 for Mac, Version 11.3.3. The reported standard deviations and confidence limits are based on that analysis and the uncertainties are based on the fit of the points to the regression line.

**Table S2.**

| label    | Nominal KIE | mass | additional mass | log <sub>2</sub> | isotope effect per mass |
|----------|-------------|------|-----------------|------------------|-------------------------|
| <i>a</i> | 1.781       | 140  | 128             | 7                | 1.005                   |
|          | 1.561       | 76   | 64              | 6                | 1.007                   |
|          | 1.333       | 44   | 32              | 5                | 1.009                   |
|          | 1.224       | 28   | 16              | 4                | 1.013                   |
|          | 1.088       | 20   | 8               | 3                | 1.011                   |
|          |             | 16   | 4               | 2                |                         |
|          |             | 14   | 2               | 1                |                         |
|          |             | 13   | 1               | 0                |                         |
|          |             |      |                 |                  |                         |
| <i>c</i> | 0.561       | 140  | 128             | 7                | 0.995                   |
|          | 0.675       | 76   | 64              | 6                | 0.994                   |
|          | 0.771       | 44   | 32              | 5                | 0.992                   |
|          | 0.888       | 28   | 16              | 4                | 0.993                   |
|          | 0.929       | 20   | 8               | 3                | 0.991                   |
|          |             | 16   | 4               | 2                |                         |
|          |             | 14   | 2               | 1                |                         |
|          |             | 13   | 1               | 0                |                         |
|          |             |      |                 |                  |                         |
| <i>d</i> | 0.720       | 140  | 128             | 7                | 0.997                   |
|          | 0.761       | 76   | 64              | 6                | 0.996                   |
|          | 0.833       | 44   | 32              | 5                | 0.994                   |
|          | 0.857       | 28   | 16              | 4                | 0.990                   |
|          | 0.913       | 20   | 8               | 3                | 0.989                   |
|          |             | 16   | 4               | 2                |                         |
|          |             | 14   | 2               | 1                |                         |
|          |             | 13   | 1               | 0                |                         |
|          |             |      |                 |                  |                         |

**Complete Regression statistics.**

| <i>Label a</i>    |        |
|-------------------|--------|
| Multiple R        | 0.8929 |
| R Square          | 0.7972 |
| Adjusted R Square | 0.7296 |
| Standard Error    | 0.0017 |
| Observations      | 5      |

| ANOVA      |           |             |             |             |                  |
|------------|-----------|-------------|-------------|-------------|------------------|
|            | <i>df</i> | <i>SS</i>   | <i>MS</i>   | <i>F</i>    | <i>Signif. F</i> |
| Regression | 1         | 3.22714E-05 | 3.22714E-05 | 11.79277833 | 0.041415024      |
| Residual   | 3         | 8.20961E-06 | 2.73654E-06 |             |                  |
| Total      | 4         | 4.0481E-05  |             |             |                  |

|              | <i>Coefficients</i> | <i>Standard Error</i> | <i>t Stat</i> | <i>P-value</i> | <i>Lower 95%</i> | <i>Upper 95%</i> | <i>Lower 68.0%</i> | <i>Upper 68.0%</i> |
|--------------|---------------------|-----------------------|---------------|----------------|------------------|------------------|--------------------|--------------------|
| Intercept    | 1.0178              | 0.0027                | 374.4         | 0.0000         | 1.0091           | 1.0264           | 1.0145             | 1.0210             |
| X Variable 1 | -0.0018             | 0.0005                | -3.4341       | 0.0414         | -0.0035          | -0.0001          | -0.0024            | -0.0012            |

*Label c*

|                   |        |
|-------------------|--------|
| Multiple R        | 0.9288 |
| R Square          | 0.8626 |
| Adjusted R Square | 0.8168 |
| Standard Error    | 0.0008 |
| Observations      | 5      |

ANOVA

|            | <i>df</i> | <i>SS</i>   | <i>MS</i>   | <i>F</i>    | <i>Signif. F</i> |
|------------|-----------|-------------|-------------|-------------|------------------|
| Regression | 1         | 1.11377E-05 | 1.11377E-05 | 18.83334438 | 0.022579894      |
| Residual   | 3         | 1.77414E-06 | 5.9138E-07  |             |                  |
| Total      | 4         | 1.29118E-05 |             |             |                  |

|              | <i>Coefficients</i> | <i>Standard Error</i> | <i>t Stat</i> | <i>P-value</i> | <i>Lower 95%</i> | <i>Upper 95%</i> | <i>Lower 68.0%</i> | <i>Upper 68.0%</i> |
|--------------|---------------------|-----------------------|---------------|----------------|------------------|------------------|--------------------|--------------------|
| Intercept    | 0.9877              | 0.0013                | 781.6         | 0.0000         | 0.9837           | 0.9917           | 0.9862             | 0.9892             |
| X Variable 1 | 0.00106             | 0.00024               | 4.33974       | 0.02258        | 0.00028          | 0.00183          | 0.00077            | 0.00134            |

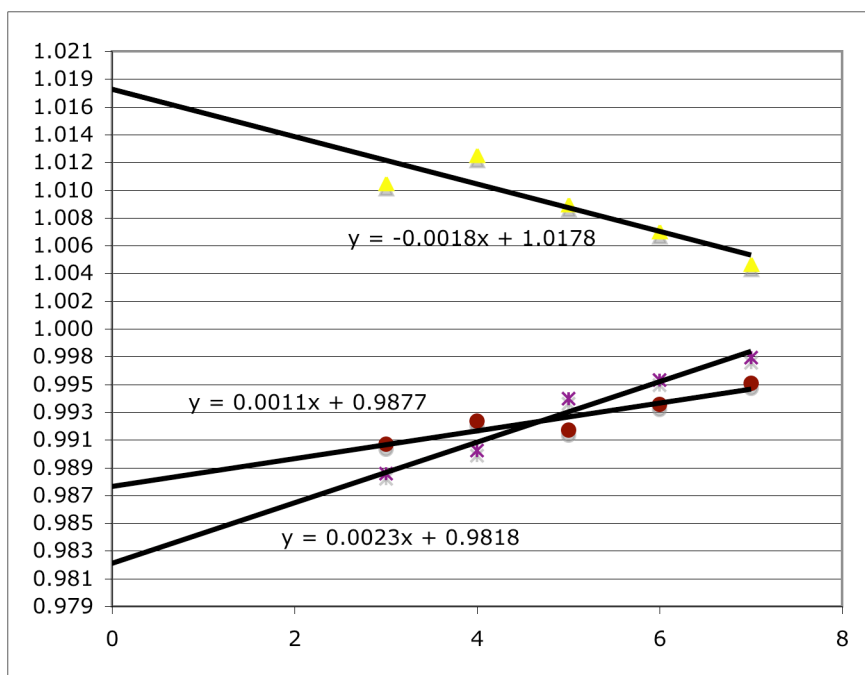
Label d

|                   |        |
|-------------------|--------|
| Multiple R        | 0.9846 |
| R Square          | 0.9694 |
| Adjusted R Square | 0.9592 |
| Standard Error    | 0.0007 |
| Observations      | 5      |

ANOVA

|            | <i>df</i> | <i>SS</i>   | <i>MS</i>   | <i>F</i>    | <i>Signif. F</i> |
|------------|-----------|-------------|-------------|-------------|------------------|
| Regression | 1         | 5.262E-05   | 5.262E-05   | 94.95549434 | 0.002295968      |
| Residual   | 3         | 1.6626E-06  | 5.54203E-07 |             |                  |
| Total      | 4         | 5.42872E-05 |             |             |                  |

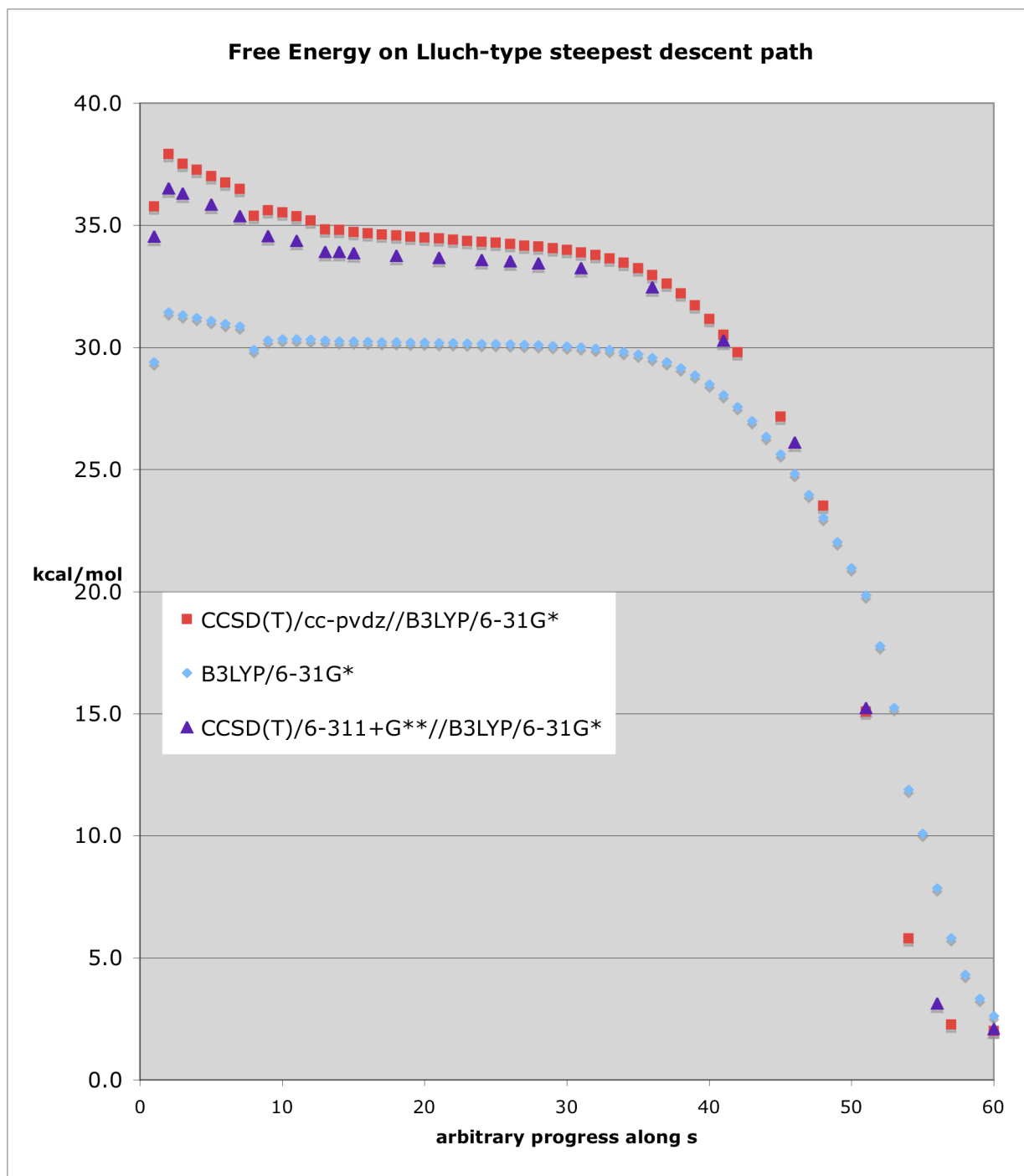
|              | <i>Coefficients</i> | <i>Standard Error</i> | <i>t Stat</i> | <i>P-value</i> | <i>Lower 95%</i> | <i>Upper 95%</i> | <i>Lower 68.0%</i> | <i>Upper 68.0%</i> |
|--------------|---------------------|-----------------------|---------------|----------------|------------------|------------------|--------------------|--------------------|
| Intercept    | 0.9818              | 0.0012                | 802.6         | 0.0000         | 0.9779           | 0.9857           | 0.9804             | 0.9833             |
| X Variable 1 | 0.00229             | 0.00024               | 9.74451       | 0.00230        | 0.00154          | 0.00304          | 0.00201            | 0.00257            |



## H. Exploration of the Variational Transition State Theory Approach

Following the procedure of Lluch (ref 6 of the main text), the valley-ridge inflection point (VRI) was first located on the B3LYP/6-31G\* surface. This was achieved by following the steepest-descent path in mass weighted coordinates from the cycloaddition transition structure until an orthogonal desymmetrizing mode (the morphed mode #2) had approximately zero curvature. This initial path was obtained with  $^{12}\text{C} / ^1\text{H}$  in all positions. The VRI geometry obtained is given in a later section. For the VRI, new frequency calculations were carried out with isotopic substitution, and the remainder of the discussion will refer to the most-carefully explored case where a  $^{13}\text{C}$  was placed in carbon *a*. From the VRI, a 0.05 Å step was taken along the zero-curvature mode in each direction to obtain two new points that were used as the starting points for new steepest-descent paths in mass weighted coordinates (including the  $^{13}\text{C}$  in carbon *a*). The complete paths obtained, consisting of approximately 600 structures each, are available on request. Frequency calculations were carried out at 10-point intervals along these paths. For one of these paths, a plot of the free energies calculated by Gaussian03, based on frequencies in Cartesian coordinates, is given below. Two discontinuities are obvious – one at the beginning as the path passes from an area containing one imaginary frequency and one very small real frequency ( $5\text{ cm}^{-1}$ ) to an area where Gaussian03 calculates two imaginary frequencies (at least in a Cartesian coordinate system) and another a few points in as the path passes back into an area with only one imaginary frequency. Such discontinuities with changes in the number of imaginary frequencies are not real bottlenecks, and the remainder of the free-energy path is monotonically downhill. Calculation of the intramolecular isotope effects at the first “bottleneck” gives intramolecular KIEs of 1.001, 1.000, 1.000, 0.999, and 1.000 for carbons *a*, *b*, *c*, *d*, and *e*, respectively. Calculation of the intramolecular isotope effects at the second “bottleneck” gives intramolecular KIEs of 1.004, 1.000, 0.999, 0.997, and 1.000 for carbons *a*, *b*, *c*, *d*, and *e*, respectively. The KIE at carbon *c* remains at 0.999 until point 49 on the graph, well into an area where the free-energy is falling rapidly.

The absence of a dynamical bottleneck on the B3LYP/6-31G\* surface may of course be incorrect for the real energy surface, and one could readily envision that a more accurate energy surface might exhibit a dynamical bottleneck. From general ideas we considered this to be unlikely; B3LYP tends to underestimate the strength of sigma bonds versus pi bonds so the real energy surface corresponding to the L1uch path, in which sigma bonds are being formed from pi bonds, should have a greater slope than seen in the B3LYP/6-31G\* calculations. A greater slope would naturally be less likely to contain a dynamical bottleneck.



**Figure S3.** Plot of the harmonic free-energy estimate for points along the Lluch-type steepest descent path, including B3LYP/6-31G\* (blue diamonds), CCSD(T)/cc-pvdz//B3LYP/6-31G\* (red squares), and CCSD(T)/6-311+G\*\*//B3LYP/6-31G\* (purple triangles). The latter two include the B3LYP/6-31G\* harmonic thermal correction to the Gibbs free energy with the CCSD(T) potential energy. The zero of free energy was set as the product structure.

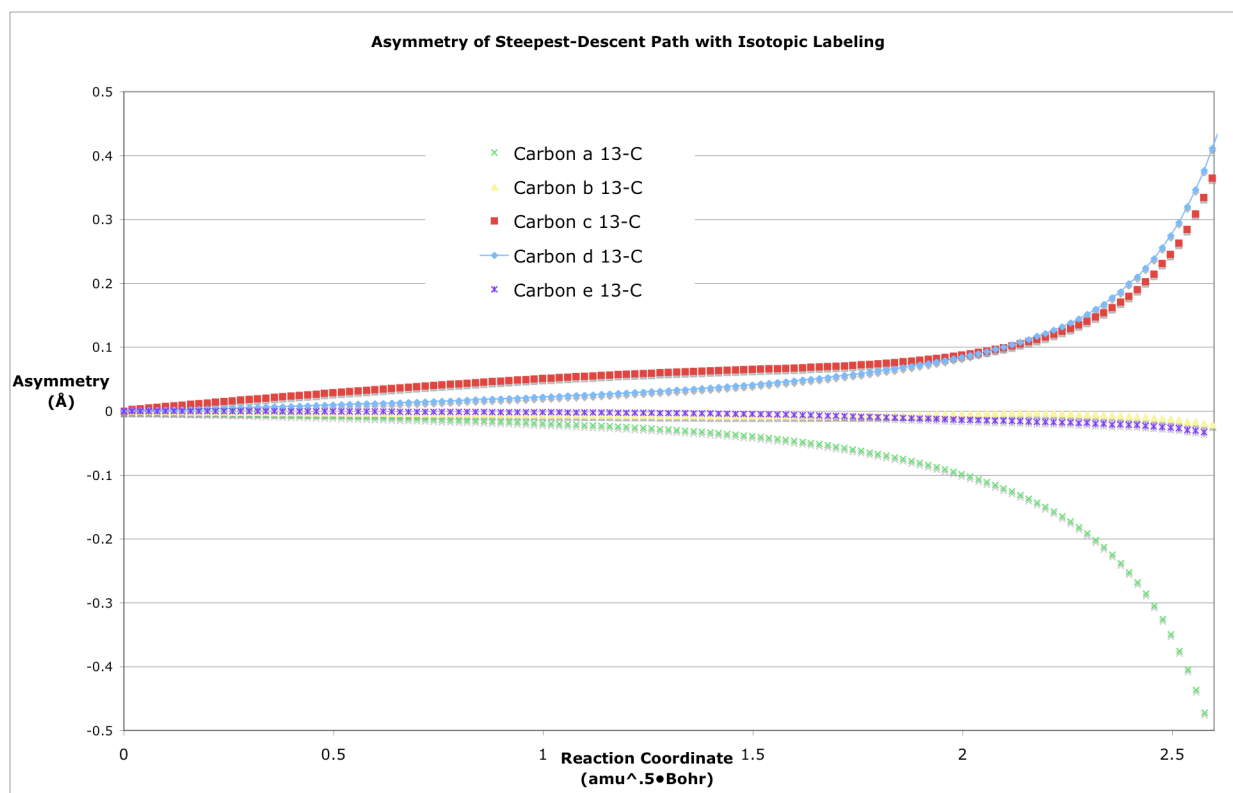
To address this issue more specifically, limited sets of CCSD(T)/cc-pvdz and CCSD(T)/6-311+G\*\* single point calculations were carried out for points along the B3LYP/6-31G\* path discussed above. The CCSD(T)/cc-pvdz//B3LYP/6-31G\* and CCSD(T)/6-311+G\*\*//B3LYP/6-31G\* free energies for these points were then calculated by combining the CCSD(T) potential energy with the B3LYP/6-31G\* harmonic thermal correction to the Gibbs free energy. The results are plotted in Figure S3. As would be expected from the general considerations above, the CCSD(T) free-energy plots have a generally greater downward slope, going against the possibility of a dynamical bottleneck.

### **I. Isotopic Desymmetrization of Steepest-Descent Paths in Mass-Weighted Coordinates.**

The graph below shows the asymmetry of the steepest-descent paths in mass-weighted coordinates for paths started from the cycloaddition transition structure with structures containing  $^{13}\text{C}$  in each of the possible positions. The asymmetry of the structures along the path was measured by the total distance in Angstroms of atoms from their  $C_2$ -rotated counterpart. The sign of the asymmetry was set such that a positive sign indicates that the path is leading toward the product with the  $^{13}\text{C}$  in the unprimed positions a, b, c, d, or e in the product, while a negative sign indicates that the path is leading toward the product with the  $^{13}\text{C}$  in the primed positions a', b', c', d', or e' in the product.

Notably, a  $^{13}\text{C}$  in the a, c, and d positions results in steepest-descent paths that lead to the major product. A  $^{13}\text{C}$  in positions b and e results in minimal desymmetrization of the paths.

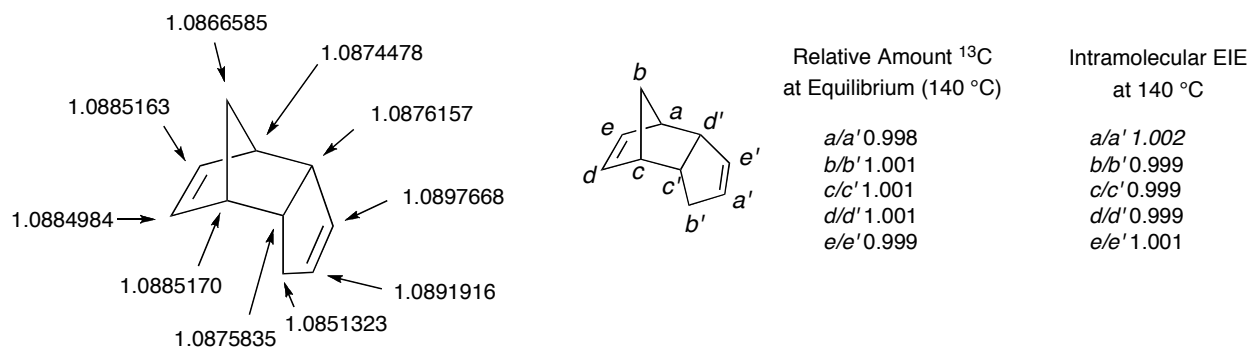




## J. Calculated Equilibrium Isotope Effects

The equilibrium isotope effects were calculated based on the B3LYP/6-311+G\*\* product structure by the method of Bigeleisen and Mayer (*S4*), employing a locally modified version of the program QUIVER (*S5*) (the changes do not affect the basic algorithm but make the program easier to use and make it easier to verify its results). Frequencies were scaled by 0.9614. The exact choice of scaling factor makes little difference in the isotope effects.

The figure below at left shows the reduced isotopic partition functions (see *S4*) obtained from QUIVER. These numbers are a measure of the preference for  $^{13}\text{C}$  in a position if the atoms were in equilibrium with free atoms in space. Equilibrium isotope effects are determined from their ratio. While the particular values of the reduced isotopic partition functions vary significantly for differing theoretical levels, their ratio does not. For example, the corresponding EIEs at B3LYP/6-31G\* differ by at most 0.00021.



These small factors were used to correct the isotope effects obtained by integration of kinetic dimer versus equilibrated dimer in order to allow for the equilibrium difference in <sup>13</sup>C composition in the paired carbons of the equilibrated dimer.

### K. Boltzmann-Weighted Integration of the Transition State Hypersurface

The process used to integrate the transition state hypersurface does not determine the absolute integration (a 60-dimension problem, not counting the energy in each mode), but rather it is purely aimed at determining the relative areas of the hypersurface that are closer to one product versus the other. The idea employed is that one can easily make a Boltzmann-weighted random choice of points on the hypersurface, and decide whether the chosen point is closer to one product versus the other. When this process is repeated a great number of times, the ratio of points obtained closer to one product versus the other should reflect the relative areas of the hypersurface closer to each product.

For this process, the B3LYP/6-31G\* transition structure was treated within the harmonic oscillator approximation quasiclassically, that is, giving each mode its zero-point energy and quantizing the energy levels. The choice of energy in each of the normal modes was mapped from a random number generator to a Boltzmann distribution. A random phase was then chosen for each mode. The resulting geometry was then reoriented to a standard orientation for the determination of its distance from the two products. The total distance from the two products was assigned as the square-root of the sum of the squares of the individual atomic distances. The results are summarized in the Table below.

| Label | Mass | Total Runs | x     | x'    | Ratio and uncertainty |
|-------|------|------------|-------|-------|-----------------------|
| a     | 140  | 38811      | 19316 | 19495 | 1.009 ± 0.020         |
| c     | 140  | 21440      | 21447 | 21440 | 1.000 ± 0.019         |
| d     | 140  | 22604      | 22233 | 22604 | 1.017 ± 0.019         |

The program used for this process was a modification of PROGDYN, modified to simply set up a normal dynamic trajectory run but not propagate the trajectories. Standard orientations were obtained using Gaussian03, but no energy or force calculation was necessary. The simple program employed is available on request.

It may be noted that there was no reason to expect that the asymmetry of the transition state hypersurface upon isotopic substitution would favor one product over the other and account for the isotope effects. However, due to the complexity of the system, we could not make a compelling qualitative argument against this possibility. This necessitated consideration of the quantitative evidence of the outcome of the trajectory studies initialized with  $^{12}\text{C}$  but propagated with  $^{140}\text{C}$  and initialized with  $^{140}\text{C}$  but propagated with  $^{12}\text{C}$ , along with the results in this section, which add up to a reasonably compelling argument.

## References

- 
- S1. Moffett, R. B. *Org. Synth., Coll. Vol. IV* **1963**, 238.
- S2. Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.

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Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

- S3. Chapman, S.; Bunker, D. L. *J. Chem. Phys.* **1975**, *62*, 2890-2899.
- S4. Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261-267. Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225-233. Bigeleisen, J. *J. Chem. Phys.* **1949**, *17*, 675-678.
- S5. Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989-8994.

## L. Calculated Structures and Energies.

### Cyclopentadiene dimerization transition structures.

#### B3LYP/6-31G\*

E(RB+HF-LYP) = -388.171140904

Zero-point correction= 0.188584 (Hartree/Particle)  
 Thermal correction to Energy= 0.196662  
 Thermal correction to Enthalpy= 0.197606  
 Thermal correction to Gibbs Free Energy= 0.156427  
 Sum of elec / zero-point Energies= -387.982557  
 Sum of elec / thermal Energies= -387.974479  
 Sum of elec / thermal Enthalpies= -387.973535  
 Sum of elec / thermal Free Energies= -388.014714

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 123.407                 |                      | 33.208              |
| 86.667 |                         |                      |                     |

C,0,0.7573024846,0.1147215462,1.3621111122  
 C,0,0.8054943168,-1.0519497396,0.5566187913  
 C,0,1.8873379538,-0.8018051406,-0.4902098446  
 C,0,1.94349082,0.7023975797,-0.5031367954  
 C,0,1.4007509182,1.1734882269,0.6626673743  
 H,0,1.7059048606,-1.269833136,-1.4626756286  
 H,0,2.8436569153,-1.2022731125,-0.1117582938  
 C,0,-0.8054943168,-1.0519497396,-0.5566187913  
 C,0,-1.8873379538,-0.8018051406,-0.4902098446  
 C,0,-1.94349082,0.7023975797,0.5031367954  
 C,0,-1.4007509182,1.1734882269,-0.6626673743  
 C,0,-0.7573024846,0.1147215462,-1.3621111122  
 H,0,-1.7059048606,-1.269833136,1.4626756286  
 H,0,-2.8436569153,-1.2022731125,0.1117582938  
 H,0,2.4831998625,1.2856413069,-1.2408809237  
 H,0,1.4015053565,2.2112139115,0.9822492281  
 H,0,0.2997558048,0.1943878256,2.3401476732  
 H,0,0.7072142253,-2.0399892682,1.0023839162  
 H,0,-0.7072142253,-2.0399892682,-1.0023839162  
 H,0,-0.2997558048,0.1943878256,-2.3401476732  
 H,0,-1.4015053565,2.2112139115,-0.9822492281  
 H,0,-2.4831998625,1.2856413069,1.2408809237

#### B3LYP/6-311+G\*\*

E(RB+HF-LYP) = -388.276987559

Zero-point correction= 0.187089 (Hartree/Particle)  
 Thermal correction to Energy= 0.195167  
 Thermal correction to Enthalpy= 0.196111  
 Thermal correction to Gibbs Free Energy= 0.155051  
 Sum of elec / zero-point Energies= -388.089898  
 Sum of elec / thermal Energies= -388.081821  
 Sum of elec / thermal Enthalpies= -388.080877  
 Sum of elec / thermal Free Energies= -388.121936

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 122.469                 |                      | 33.429              |
| 86.418 |                         |                      |                     |

C,0,0.7583319435,0.1211543073,1.3542759778

C,0,0.7916504736,-1.0468552441,0.5413671038  
 C,0,1.8861967625,-0.8044663482,-0.4943540506  
 C,0,1.9614276821,0.6971131168,-0.5003469032  
 C,0,1.4140494248,1.1714453473,0.6614523277  
 H,0,1.7100011418,-1.2652971877,-1.4681123615  
 H,0,2.8314142122,-1.2141445598,-0.1054916495  
 C,0,-0.7916504736,-1.0468552441,-0.5413671038  
 C,0,-1.8861967625,-0.8044663482,0.4943540506  
 C,0,-1.9614276821,0.6971131168,0.5003469032  
 C,0,-1.4140494248,1.1714453473,-0.6614523277  
 C,0,-0.7583319435,0.1211543073,-1.3542759778  
 H,0,-1.7100011418,-1.2652971877,1.4681123615  
 H,0,-2.8314142122,-1.2141445598,0.1054916495  
 H,0,2.5008880426,1.2780728533,-1.2362656264  
 H,0,1.4257469675,2.2058798848,0.9818101005  
 H,0,0.3025041798,0.2024801582,2.3300927296  
 H,0,0.6978659209,-2.029382328,0.9942532466  
 H,0,-0.6978659209,-2.029382328,-0.9942532466  
 H,0,-0.3025041798,0.2024801582,-2.3300927296  
 H,0,-1.4257469675,2.2058798848,-0.9818101005  
 H,0,-2.5008880426,1.2780728533,1.2362656264

#### MP2/6-31G\*

Zero-point correction= 0.190627 (Hartree/Particle)  
 Thermal correction to Energy= 0.198647  
 Thermal correction to Enthalpy= 0.199591  
 Thermal correction to Gibbs Free Energy= 0.158123  
 Sum of elec / zero-point Energies= -386.651171  
 Sum of elec / thermal Energies= -386.643151  
 Sum of elec / thermal Enthalpies= -386.642207  
 Sum of elec / thermal Free Energies= -386.683675

|        | E (Thermal)<br>KCAL/MOL | CV<br>CAL/MOL-KELVIN | S<br>CAL/MOL-KELVIN |
|--------|-------------------------|----------------------|---------------------|
| TOTAL  | 124.653                 |                      | 33.124              |
| 87.277 |                         |                      |                     |

C,0,-0.516972584,-0.5165597217,1.3731506565  
 C,0,-1.2546041524,-0.7761407426,0.2119210821  
 C,0,-0.5929657182,-1.9433399333,-0.4869497453  
 C,0,0.7834100811,-1.9134490407,0.1094572049  
 C,0,0.7406605281,-1.1899889537,1.270549916  
 H,0,-0.6250901948,-1.9076758044,-1.5797415227  
 H,0,-1.1012553599,-2.8694207509,-0.1713861281  
 C,0,-0.6590575213,0.7156387439,-1.12963148  
 C,0,-0.8503089513,1.8973692856,-0.2047128888  
 C,0,0.4758190694,1.9527358973,0.4947942627  
 C,0,1.3910548716,1.2576599773,-0.2486764584  
 C,0,0.7199214766,0.5236222924,-1.2763970112  
 H,0,-1.7199037334,1.8327438066,0.4556827736  
 H,0,-0.9697435196,2.8038173775,-0.8208656669  
 H,0,1.6115868749,-2.5273010518,-0.2313561088  
 H,0,1.5629333876,-1.0713808884,1.9708442072  
 H,0,-0.8403027028,0.0854353468,2.2158253033  
 H,0,-2.329289202,-0.6149173614,0.1524144413  
 H,0,-1.3687534342,0.4978217293,-1.9254728495  
 H,0,1.2054182689,-0.0727396507,-2.0417116093  
 H,0,2.4565509877,1.1990144626,-0.0440024456  
 H,0,0.6961060296,2.5993159588,1.3387363745

#### MP2/6-311+G\*\*

TSMP211PS  
 E(RHF) = -385.612407795

Zero-point correction= 0.187740 (Hartree/Particle)

Thermal correction to Energy= 0.195891  
 Thermal correction to Enthalpy= 0.196835  
 Thermal correction to Gibbs Free Energy= 0.155847  
 Sum of elec / zero-point Energies= -386.892664  
 Sum of elec / thermal Energies= -386.884513  
 Sum of elec / thermal Enthalpies= -386.883569  
 Sum of elec / thermal Free Energies= -386.924558

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 122.924                 |                      | 33.894              |
| 86.268 |                         |                      |                     |

C,0,0.7408394559,0.1148923128,1.3694001946  
 C,0,0.8568216811,-1.0644986058,0.6186967447  
 C,0,1.8790923791,-0.8088208117,-0.4698307755  
 C,0,1.9054973968,0.6934838435,-0.5230967593  
 C,0,1.3467963538,1.1856075199,0.6307134545  
 H,0,1.6736142779,-1.302765197,-1.4234523273  
 H,0,2.8568451339,-1.1663244979,-0.1055838688  
 C,0,-0.8568216811,-1.0644986058,-0.6186967447  
 C,0,-1.8790923791,-0.8088208117,0.4698307755  
 C,0,-1.9054973968,0.6934838435,0.5230967593  
 C,0,-1.3467963538,1.1856075199,-0.6307134545  
 C,0,-0.7408394559,0.1148923128,-1.3694001946  
 H,0,-1.6736142779,-1.302765197,1.4234523273  
 H,0,-2.8568451339,-1.1663244979,0.1055838688  
 H,0,2.4267449881,1.2737492302,-1.277843545  
 H,0,1.3067525912,2.2330014295,0.9147382174  
 H,0,0.266168678,0.2108295425,2.3399391385  
 H,0,0.7086128779,-2.0531547665,1.0468969058  
 H,0,-0.7086128779,-2.0531547665,-1.0468969058  
 H,0,-0.266168678,0.2108295425,-2.3399391385  
 H,0,-1.3067525912,2.2330014295,-0.9147382174  
 H,0,-2.4267449881,1.2737492302,1.277843545

### MPW1K/6-31+G\*\*

E(RmPW+HF-PW91) = -388.103603241

Zero-point correction= 0.193766 (Hartree/Particle)  
 Thermal correction to Energy= 0.201597  
 Thermal correction to Enthalpy= 0.202542  
 Thermal correction to Gibbs Free Energy= 0.161267  
 Sum of elec / zero-point Energies= -387.909837  
 Sum of elec / thermal Energies= -387.902006  
 Sum of elec / thermal Enthalpies= -387.901062  
 Sum of elec / thermal Free Energies= -387.942336

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 126.504                 |                      | 32.099              |
| 86.870 |                         |                      |                     |

C,0,-0.5050523981,-0.5246763888,1.358960443  
 C,0,-1.220017294,-0.7481479651,0.1763223987  
 C,0,-0.5877433054,-1.9393617898,-0.4982481449  
 C,0,0.7676207091,-1.9462145145,0.1250538968  
 C,0,0.7265665885,-1.2236755872,1.2745919036  
 H,0,-0.5987201715,-1.9146936847,-1.5851878827  
 H,0,-1.1286322415,-2.8404757246,-0.1861615719  
 C,0,-0.6644594531,0.687546285,-1.0795360941  
 C,0,-0.8569395527,1.8928330531,-0.1940730921  
 C,0,0.475337623,1.9861293409,0.4706784607  
 C,0,1.3827619944,1.2916154044,-0.263794748  
 C,0,0.7151863663,0.5315936637,-1.2584107307  
 H,0,-1.7090197179,1.8402923472,0.479250969  
 H,0,-0.9991396028,2.772022573,-0.833424271

H,0,1.5877891158,-2.5599146312,-0.2108234572  
 H,0,1.531706532,-1.1353110885,1.9871267743  
 H,0,-0.8274596162,0.0749547131,2.1933171069  
 H,0,-2.2879165102,-0.5875905663,0.1197192157  
 H,0,-1.3676844428,0.469977013,-1.8717016979  
 H,0,1.1948264562,-0.0629177101,-2.0174611804  
 H,0,2.4455912727,1.263393732,-0.0811427619  
 H,0,0.6943176143,2.6331893361,1.3046321287

### MPWB1K/6-31+G\*\*

E(RmPW+HF-B95) = -387.993570959

Zero-point correction= 0.193216 (Hartree/Particle)  
 Thermal correction to Energy= 0.201058  
 Thermal correction to Enthalpy= 0.202002  
 Thermal correction to Gibbs Free Energy= 0.160719  
 Sum of elec / zero-point Energies= -387.800355  
 Sum of elec / thermal Energies= -387.792513  
 Sum of elec / thermal Enthalpies= -387.791569  
 Sum of elec / thermal Free Energies= -387.832852

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 126.166                 |                      | 32.266              |
| 86.888 |                         |                      |                     |

C,0,-0.504416308,-0.5108420689,1.3524639341  
 C,0,-1.2178501052,-0.7382833784,0.1712172384  
 C,0,-0.5849416895,-1.9270177149,-0.4996812485  
 C,0,0.7690385698,-1.9260069278,0.1195457315  
 C,0,0.725865447,-1.2056342438,1.2685729552  
 H,0,-0.5969864693,-1.9000161926,-1.586065819  
 H,0,-1.1211752456,-2.8294577092,-0.1872422385  
 C,0,-0.6665409594,0.6776033219,-1.0742679431  
 C,0,-0.8555949932,1.8806609772,-0.1907047649  
 C,0,0.4730920879,1.9660823661,0.4756298265  
 C,0,1.3786353729,1.2734142791,-0.2600669912  
 C,0,0.7112673539,0.5174639404,-1.2533180327  
 H,0,-1.7077490484,1.8258333525,0.4815555662  
 H,0,-0.9947414945,2.7613314897,-0.826801557  
 H,0,1.5910762017,-2.5353854394,-0.2171878551  
 H,0,1.5317349902,-1.112448171,1.9786769244  
 H,0,-0.8284300602,0.0908559871,2.1839339372  
 H,0,-2.2854935071,-0.5804607843,0.1159192352  
 H,0,-1.368721111,0.4627934043,-1.867128237  
 H,0,1.1877470596,-0.0793183424,-2.011727441  
 H,0,2.4402814376,1.2403600667,-0.0752092366  
 H,0,0.6928224374,2.6090395981,1.3115736807

### RB3PW91/6-31+G(d,p)

E(RB+HF-PW91) = -388.061494029

Zero-point correction= 0.188224 (Hartree/Particle)  
 Thermal correction to Energy= 0.196319  
 Thermal correction to Enthalpy= 0.197263  
 Thermal correction to Gibbs Free Energy= 0.155567  
 Sum of elec / zero-point Energies= -387.873270  
 Sum of elec / thermal Energies= -387.865175  
 Sum of elec / thermal Enthalpies= -387.864231  
 Sum of elec / thermal Free Energies= -387.905927

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 123.192                 |                      | 33.457              |
| 87.756 |                         |                      |                     |

C,0,-0.5083671066,-0.5464808109,1.3717939362  
 C,0,-1.2225418033,-0.7594277536,0.1744097217  
 C,0,-0.5880382248,-1.9609327202,-0.5016170335  
 C,0,0.7679143792,-1.9872127734,0.1381660345  
 C,0,0.7254905251,-1.2543682,1.2931904767  
 H,0,-0.5879511943,-1.9353563684,-1.5952251833  
 H,0,-1.1473267661,-2.8627305254,-0.1989430844  
 C,0,-0.6680662517,0.6984853827,-1.0803455657  
 C,0,-0.8607573435,1.9143306672,-0.1927580078  
 C,0,0.4837714405,2.02777389177,0.4614612351  
 C,0,1.3950755296,1.3226669797,-0.2769733209  
 C,0,0.7220139544,0.5531740878,-1.2692623383  
 H,0,-1.7109933752,1.861434777,0.4934900804  
 H,0,-1.0219499097,2.7928362132,-0.8407536553  
 H,0,1.5894157605,-2.6115090762,-0.1951564078  
 H,0,1.5300782853,-1.1736551035,2.0170165611  
 H,0,-0.830306819,0.0622024815,2.2079078229  
 H,0,-2.2974281102,-0.6021156152,0.117696747  
 H,0,-1.3758857912,0.483768725,-1.8779885545  
 H,0,1.203762844,-0.0503814262,-2.0287775355  
 H,0,2.4659559488,1.302351102,-0.1020349402  
 H,0,0.7050539945,2.6857488498,1.2943906764

### MPW1B95V6-31+G(d,p)

CpTsmpw1b95

E(RmPW+HF-B95) = -388.002804566

Zero-point correction= 0.190102 (Hartree/Particle)  
 Thermal correction to Energy= 0.198104  
 Thermal correction to Enthalpy= 0.199048  
 Thermal correction to Gibbs Free Energy= 0.157392  
 Sum of elec / zero-point Energies= -387.812702  
 Sum of elec / thermal Energies= -387.804700  
 Sum of elec / thermal Enthalpies= -387.803756  
 Sum of elec / thermal Free Energies= -387.845413

| E (Thermal) | CV             | S        |
|-------------|----------------|----------|
| KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol- |
| Kelvin      |                |          |
| Total       | 124.312        | 33.011   |
| 87.673      |                |          |

C,0,-0.5047717788,-0.5205529215,1.3586138507  
 C,0,-1.2204710959,-0.7449477222,0.1720371816  
 C,0,-0.5864570045,-1.9382128315,-0.5009942153  
 C,0,0.7693093757,-1.9463871007,0.1242540598  
 C,0,0.7278072356,-1.2185030159,1.2752004924  
 H,0,-0.5945234692,-1.910392962,-1.5911979519  
 H,0,-1.1311112898,-2.8418270798,-0.1924416189  
 C,0,-0.6678907318,0.6841421349,-1.0769912619  
 C,0,-0.8581503903,1.891725532,-0.191342673  
 C,0,0.4758604762,1.9865566877,0.4723803634  
 C,0,1.3843366292,1.2865282033,-0.2630321863  
 C,0,0.7153257399,0.5272966662,-1.2576951895  
 H,0,-1.7107515547,1.8361954643,0.4864270632  
 H,0,-1.0056436426,2.7730307295,-0.8315908337  
 H,0,1.5920003268,-2.5610646097,-0.212643218  
 H,0,1.535471561,-1.127343134,1.9890757209  
 H,0,-0.8268952433,0.0870652253,2.1911699505  
 H,0,-2.2917960787,-0.5872295923,0.1167091971  
 H,0,-1.3724013113,0.4692443591,-1.8727028011  
 H,0,1.1941432839,-0.0752727893,-2.015161872  
 H,0,2.4499354058,1.2556840168,-0.0791903895  
 H,0,0.695593523,2.63483255,1.3088039962

### MPW3LYP6-31+G(d,p)

CpTsmpw3lyp

E(RmPW+HF-LYP) = -388.202482494

Zero-point correction= 0.187819 (Hartree/Particle)  
 Thermal correction to Energy= 0.195879  
 Thermal correction to Enthalpy= 0.196823  
 Thermal correction to Gibbs Free Energy= 0.155214  
 Sum of elec / zero-point Energies= -388.014663  
 Sum of elec / thermal Energies= -388.006604  
 Sum of elec / thermal Enthalpies= -388.005659  
 Sum of elec / thermal Free Energies= -388.047268

| E (Thermal) | CV             | S        |
|-------------|----------------|----------|
| KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol- |
| Kelvin      |                |          |
| Total       | 122.916        | 33.402   |
| 87.573      |                |          |

C,0,-0.5092699536,-0.5504417357,1.3735640961  
 C,0,-1.2117843268,-0.7411175877,0.1513953885  
 C,0,-0.5837118417,-1.9654862312,-0.5094385045  
 C,0,0.7697193669,-1.9987290338,0.1468408721  
 C,0,0.7165881575,-1.2695352976,1.307599749  
 H,0,-0.570486776,-1.9453851813,-1.6029139429  
 H,0,-1.1578893054,-2.8573672587,-0.2071614286  
 C,0,-0.6783472922,0.6802767862,-1.0572252027  
 C,0,-0.8644549373,1.9188769219,-0.1845921344  
 C,0,0.4909382884,2.0393401615,0.4572657012  
 C,0,1.3998676546,1.3377002403,-0.2933715111  
 C,0,0.7225831704,0.5573270917,-1.2713689413  
 H,0,-1.7067227399,1.8720828466,0.5115852039  
 H,0,-1.0346314036,2.7867903149,-0.8435832308  
 H,0,1.5920131369,-2.6247724593,-0.17904841  
 H,0,1.512070661,-1.19950098,2.0419400873  
 H,0,-0.8387265099,0.0532804461,2.2091977194  
 H,0,-2.2901293707,-0.6039260864,0.1083051169  
 H,0,-1.3787996063,0.4858110284,-1.8665804269  
 H,0,1.199012373,-0.0416636092,-2.0365688983  
 H,0,2.4726843455,1.3278222127,-0.1323755314  
 H,0,0.7183968754,2.6991852212,1.2862218934

### PBE1KCIS6-31+G(d,p)

pbekcisPS

E(RPBE+HF-KCIS) = -387.714293023

Zero-point correction= 0.188050 (Hartree/Particle)  
 Thermal correction to Energy= 0.196144  
 Thermal correction to Enthalpy= 0.197088  
 Thermal correction to Gibbs Free Energy= 0.155431  
 Sum of elec / zero-point Energies= -387.526243  
 Sum of elec / thermal Energies= -387.518149  
 Sum of elec / thermal Enthalpies= -387.517205  
 Sum of elec / thermal Free Energies= -387.558862

| E (Thermal) | CV             | S        |
|-------------|----------------|----------|
| KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol- |
| Kelvin      |                |          |
| Total       | 123.082        | 33.545   |
| 87.675      |                |          |

C,0,-0.5063435098,-0.5525959274,1.3715508799  
 C,0,-1.2166727153,-0.7583541271,0.1703040246  
 C,0,-0.5864747684,-1.9613720083,-0.5025962123  
 C,0,0.7639642657,-2.0004964901,0.1423675362  
 C,0,0.723420424,-1.2657895349,1.2962002242  
 H,0,-0.5817066688,-1.9370248956,-1.5966227594  
 H,0,-1.1547767437,-2.8590899806,-0.2034743132  
 C,0,-0.667580341,0.6977053119,-1.073319906  
 C,0,-0.860639269,1.9147974728,-0.1909306212

C,0,0.4837618213,2.0406864505,0.4555463226  
 C,0,1.3954546214,1.3340307978,-0.2808115823  
 C,0,0.7227307612,0.5595846971,-1.2678862091  
 H,0,-1.7084025173,1.8633078389,0.4991099109  
 H,0,-1.0299012449,2.7887684811,-0.8435128367  
 H,0,1.5832463503,-2.6293472404,-0.189385476  
 H,0,1.5269356398,-1.190005742,2.0226289471  
 H,0,-0.8270014901,0.0591732539,2.2065518314  
 H,0,-2.2921037403,-0.6005435457,0.1137290489  
 H,0,-1.3756352706,0.482469371,-1.8714355232  
 H,0,1.2045884523,-0.0469969786,-2.0256338589  
 H,0,2.4674316872,1.3186333024,-0.1084554487  
 H,0,0.7046242225,2.7030273037,1.2857636858

### BB1K\6-31+G(d,p)

TSBB1K

E(RB+HF-B95) = -387.997623583

Zero-point correction= 0.192703 (Hartree/Particle)  
 Thermal correction to Energy= 0.200623  
 Thermal correction to Enthalpy= 0.201568  
 Thermal correction to Gibbs Free Energy= 0.160520  
 Sum of elec / zero-point Energies= -387.804920  
 Sum of elec / thermal Energies= -387.797000  
 Sum of elec / thermal Enthalpies= -387.796056  
 Sum of elec / thermal Free Energies= -387.837103

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 125.893                 |                      | 32.385              |
| 86.392 |                         |                      |                     |

C,0,0.7214696007,0.1178307322,1.3445885402  
 C,0,0.8003808603,-1.0450466728,0.5686042938  
 C,0,1.8550131248,-0.8017141229,-0.4782047492  
 C,0,1.8933020193,0.6875443517,-0.5138512421  
 C,0,1.3505078848,1.1688307488,0.6344051274  
 H,0,1.6702403975,-1.2832066533,-1.4356286238  
 H,0,2.8136621648,-1.1761148686,-0.1015716142  
 C,0,-0.8003808603,-1.0450466728,-0.5686042938  
 C,0,-1.8550131248,-0.8017141229,0.4782047492  
 C,0,-1.8933020193,0.6875443517,0.5138512421  
 C,0,-1.3505078848,1.1688307488,-0.6344051274  
 C,0,-0.7214696007,0.1178307322,-1.3445885402  
 H,0,-1.6702403975,-1.2832066533,1.4356286238  
 H,0,-2.8136621648,-1.1761148686,0.1015716142  
 H,0,2.4159524505,1.2639825778,-1.2598897101  
 H,0,1.3332504099,2.2058139095,0.9312976165  
 H,0,0.2617678951,0.204175441,2.3145036095  
 H,0,0.6783080852,-2.0260954433,1.0066458772  
 H,0,-0.6783080852,-2.0260954433,-1.0066458772  
 H,0,-0.2617678951,0.204175441,-2.3145036095  
 H,0,-1.3332504099,2.2058139095,-0.9312976165  
 H,0,-2.4159524505,1.2639825778,1.2598897101

### O3LYP\6-31+G(d,p)

TSO3LYP

E(R03+HF-V5LYP) = -388.063014051

Zero-point correction= 0.187344 (Hartree/Particle)  
 Thermal correction to Energy= 0.195544  
 Thermal correction to Enthalpy= 0.196488  
 Thermal correction to Gibbs Free Energy= 0.155189  
 Sum of elec / zero-point Energies= -387.875670  
 Sum of elec / thermal Energies= -387.867470  
 Sum of elec / thermal Enthalpies= -387.866526

Sum of elec / thermal Free Energies= -387.907825

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 122.706                 |                      | 33.785              |
| 86.921 |                         |                      |                     |

C,0,0.7906972127,0.125033317,1.3587642696  
 C,0,0.819174495,-1.0390182909,0.5518347005  
 C,0,1.9016355274,-0.8051601082,-0.4912270252  
 C,0,2.0125319114,0.690821755,-0.4915567264  
 C,0,1.4557414166,1.1754030201,0.6646463776  
 H,0,1.718318481,-1.2595699584,-1.4685601546  
 H,0,2.8420576153,-1.2364352083,-0.1082916259  
 C,0,-0.819174495,-1.0390182909,-0.5518347005  
 C,0,-1.9016355274,-0.8051601082,-0.4912270252  
 C,0,-2.0125319114,0.690821755,0.4915567264  
 C,0,-1.4557414166,1.1754030201,-0.6646463776  
 C,0,-0.7906972127,0.125033317,-1.3587642696  
 H,0,-1.718318481,-1.2595699584,1.4685601546  
 H,0,-2.8420576153,-1.2364352083,0.1082916259  
 H,0,2.5649120225,1.2637053655,-1.2280940622  
 H,0,1.4762817665,2.2120388079,0.9859251816  
 H,0,0.3201236923,0.215616271,-2.3297470749  
 H,0,0.702976287,-2.0264349707,0.9937827879  
 H,0,-0.702976287,-2.0264349707,-0.9937827879  
 H,0,-0.3201236923,0.215616271,-2.3297470749  
 H,0,-1.4762817665,2.2120388079,-0.9859251816  
 H,0,-2.5649120225,1.2637053655,1.2280940622

### BP86\6-31+G(d,p)

TSBP86

E(RB-P86) = -388.198930004

Zero-point correction= 0.182083 (Hartree/Particle)  
 Thermal correction to Energy= 0.190478  
 Thermal correction to Enthalpy= 0.191423  
 Thermal correction to Gibbs Free Energy= 0.149876  
 Sum of elec / zero-point Energies= -388.016847  
 Sum of elec / thermal Energies= -388.008452  
 Sum of elec / thermal Enthalpies= -388.007507  
 Sum of elec / thermal Free Energies= -388.049054

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|--------|-------------------------|----------------------|---------------------|
| Total  | 119.527                 |                      | 35.000              |
| 87.442 |                         |                      |                     |

C,0,0.7788616419,0.1262694502,1.3668394118  
 C,0,0.836969074,-1.0525744944,0.5754802099  
 C,0,1.907873647,-0.8115770466,-0.4874947755  
 C,0,1.9945808772,0.694916476,-0.5051319265  
 C,0,1.4278244868,1.1864151034,0.6539092237  
 H,0,1.7153680088,-1.2827724861,-1.4659753736  
 H,0,2.8692878015,-1.228059199,-0.1124832096  
 C,0,-0.836969074,-1.0525744944,-0.5754802099  
 C,0,-1.907873647,-0.8115770466,0.4874947755  
 C,0,-1.9945808772,0.694916476,0.5051319265  
 C,0,-1.4278244868,1.1864151034,-0.6539092237  
 C,0,-0.7788616419,0.1262694502,-1.3668394118  
 H,0,-1.7153680088,-1.2827724861,1.4659753736  
 H,0,-2.8692878015,-1.228059199,0.1124832096  
 H,0,2.5418657411,1.2725509221,-1.2538849955  
 H,0,1.4280781687,2.2352691258,0.9641229898  
 H,0,0.2961053792,0.2235778969,2.340977984  
 H,0,0.7100044565,-2.0480157484,1.0168861448  
 H,0,-0.7100044565,-2.0480157484,-1.0168861448



H,0,-0.2961053792,0.2235778969,-2.3409777984  
 H,0,-1.4280781687,2.2352691258,-0.9641229898  
 H,0,-2.5418657411,1.2725509221,1.2538849955

### PW91\6-31+G(d,p)

TSPW91

E(RPW91-PW91) = -388.042854528

Zero-point correction= 0.183038 (Hartree/Particle)  
 Thermal correction to Energy= 0.191400  
 Thermal correction to Enthalpy= 0.192344  
 Thermal correction to Gibbs Free Energy= 0.150861  
 Sum of elec / zero-point Energies= -387.859817  
 Sum of elec / thermal Energies= -387.851455  
 Sum of elec / thermal Enthalpies= -387.850511  
 Sum of elec / thermal Free Energies= -387.891993

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol- |
|--------|-------------------------|----------------------|---------------|
| Kelvin |                         |                      |               |
| Total  | 120.105                 |                      | 34.825        |
| 87.307 |                         |                      |               |

C,0,0.7762289483,0.1261785499,1.3644632336  
 C,0,0.8394977708,-1.0507698379,0.5790311952  
 C,0,1.9033992357,-0.810339023,-0.4844585567  
 C,0,1.9898590982,0.6923915886,-0.5040442093  
 C,0,1.4220582922,1.1846610643,0.6506355014  
 H,0,1.7090455364,-1.2816416032,-1.4599135069  
 H,0,2.8639985202,-1.2247029554,-0.1124844698  
 C,0,-0.8394977708,-1.0507698379,-0.5790311952  
 C,0,-1.9033992357,-0.810339023,0.4844585567  
 C,0,-1.9898590982,0.6923915886,0.5040442093  
 C,0,-1.4220582922,1.1846610643,-0.6506355014  
 C,0,-0.7762289483,0.1261785499,-1.3644632336  
 H,0,-1.7090455364,-1.2816416032,1.4599135069  
 H,0,-2.8639985202,-1.2247029554,0.1124844698  
 H,0,2.53466514,1.2678174253,-1.2528467386  
 H,0,1.4186871389,2.2321091313,0.9572353408  
 H,0,0.2921023742,0.2248622912,2.3353471688  
 H,0,0.7062124538,-2.0445666311,1.0160670845  
 H,0,-0.7062124538,-2.0445666311,-1.0160670845  
 H,0,-0.2921023742,0.2248622912,-2.3353471688  
 H,0,-1.4186871389,2.2321091313,-0.9572353408  
 H,0,-2.53466514,1.2678174253,1.2528467386

### Cyclopentadiene

#### B3LYP/6-31G\*

E(RB+HF-LYP) = -194.101058102

Zero-point correction= 0.092894 (Hartree/Particle)  
 Thermal correction to Energy= 0.097037  
 Thermal correction to Enthalpy= 0.097981  
 Thermal correction to Gibbs Free Energy= 0.066297  
 Sum of elec / zero-point Energies= -194.008164  
 Sum of elec / thermal Energies= -194.004021  
 Sum of elec / thermal Enthalpies= -194.003077  
 Sum of elec / thermal Free Energies= -194.034761

|        | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol- |
|--------|-------------------------|----------------------|---------------|
| Kelvin |                         |                      |               |
| Total  | 60.892                  |                      | 15.532        |
| 66.686 |                         |                      |               |

C,0,0.6060113819,0.8584337704,-0.6085373113  
 C,0,0.6994883093,0.7087826711,0.7287459978  
 C,0,-0.151571919,-0.4119606018,1.1532588261  
 C,0,-0.761654919,-0.942830538,0.0737003299  
 C,0,-0.3364714453,-0.1822536595,-1.1556434048  
 H,0,1.1132278349,1.5965117921,-1.2193869712  
 H,0,1.3017843824,1.309771887,1.4025751874  
 H,0,-0.2587531789,-0.7445209875,2.1808302064  
 H,0,-1.4508669347,-1.7794626404,0.0596005501  
 H,0,-1.1937654504,0.2708997447,-1.6772984333  
 H,0,0.1535649003,-0.8342296489,-1.8954671653

### Endo dimer of cyclopentadiene

#### B3LYP/6-31G\*

CpDimerEndo631Gd

E(RB+HF-LYP) = -388.228021536

Zero-point correction= 0.194205 (Hartree/Particle)  
 Thermal correction to Energy= 0.201239  
 Thermal correction to Enthalpy= 0.202183  
 Thermal correction to Gibbs Free Energy= 0.162958  
 Sum of elec / zero-point Energies= -388.033816  
 Sum of elec / thermal Energies= -388.026782  
 Sum of elec / thermal Enthalpies= -388.025838  
 Sum of elec / thermal Free Energies= -388.065064

|        | E (Thermal)<br>KCAL/MOL | CV<br>CAL/MOL-KELVIN | S<br>CAL/MOL- |
|--------|-------------------------|----------------------|---------------|
| KELVIN |                         |                      |               |
| TOTAL  | 126.279                 |                      | 30.939        |
| 82.557 |                         |                      |               |

C,0,-2.2560796181,0.1595921422,0.3493194822  
 C,0,-1.6403945249,-1.1672889872,-0.0326081215  
 H,0,-1.434749192,-1.7848405253,0.8533933432  
 C,0,-0.3450759904,-0.7770532259,-0.7952740327  
 C,0,-0.3050239297,0.7963961086,-0.8251589038  
 C,0,-1.5482884357,1.2067777352,-0.0829254095  
 H,0,-2.3216804355,-1.7571566192,-0.66194982  
 C,0,1.0324682994,-1.1386134646,-0.128744484  
 H,0,-0.358276236,-1.1854702563,-1.8110943292  
 C,0,1.0942774603,1.1210533929,-0.1637957775  
 H,0,-0.2969582286,1.1925227969,-1.850095823  
 H,0,-1.8184142029,2.2476486912,0.079802303  
 H,0,-3.1809562898,0.2272855508,0.9178658985  
 H,0,1.4496015073,2.1379079118,-0.3500354419  
 C,0,1.031306395,0.6861758346,1.2918152891  
 C,0,1.9288537341,-0.0415445365,-0.7572886234  
 H,0,1.3390645009,-2.177532876,-0.2785436268  
 C,0,0.998456771,-0.6533087818,1.3142995126  
 H,0,0.9214482296,1.3584540958,2.1367244088  
 H,0,0.8643717918,-1.2898566977,2.1831431289  
 H,0,2.9571823829,-0.063799768,-0.3824489039  
 H,0,1.9363652065,-0.0582796084,-1.8545947262

#### B3LYP/6-31+G\*\*

CpDimerEndo631+Gdp

E(RB+HF-LYP) = -388.257581818

Zero-point correction= 0.193122 (Hartree/Particle)  
 Thermal correction to Energy= 0.200200  
 Thermal correction to Enthalpy= 0.201144  
 Thermal correction to Gibbs Free Energy= 0.161855  
 Sum of elec / zero-point Energies= -388.064460  
 Sum of elec / thermal Energies= -388.057382

Sum of elec / thermal Enthalpies= -388.056438  
 Sum of elec / thermal Free Energies= -388.095727

| E (Thermal) | CV             | S        |
|-------------|----------------|----------|
| KCAL/MOL    | CAL/MOL-KELVIN | CAL/MOL- |
| KELVIN      |                |          |
| TOTAL       | 125.627        | 31.237   |
| 82.691      |                |          |

C,0,-2.2624581629,0.1586363266,0.345274822  
 C,0,-1.6428640825,-1.1680844622,-0.0342785148  
 H,0,-1.4401347381,-1.7834693626,0.8532747917  
 C,0,-0.3452772362,-0.7775302015,-0.7936362675  
 C,0,-0.305049998,0.7964134642,-0.8229013197  
 C,0,-1.550601055,1.2079275849,-0.0833749905  
 H,0,-2.3214177739,-1.7576311036,-0.66544887  
 C,0,1.0337933732,-1.1396426453,-0.1277190555  
 H,0,-0.3568357954,-1.1862859055,-1.809005039  
 C,0,1.09601433,1.1219574815,-0.1630393772  
 H,0,-0.2971858327,1.1936987808,-1.8467063367  
 H,0,-1.8222784936,2.2477017692,0.0803842198  
 H,0,-3.1882994205,0.2279332807,0.9110340128  
 H,0,1.4500433622,2.1385931201,-0.3499440478  
 C,0,1.0360100143,0.6879418369,1.2931736044  
 C,0,1.9291682553,-0.041657959,-0.7591181683  
 H,0,1.3397622798,-2.1782530385,-0.2774511851  
 C,0,1.0022066087,-0.6542468789,1.3158208136  
 H,0,0.9293922096,1.3582815107,2.1393031789  
 H,0,0.8705160737,-1.2883031368,2.1861290905  
 H,0,2.9579646345,-0.0638212636,-0.3868647661  
 H,0,1.9328212128,-0.0587319338,-1.8559143283

C,0,0.9988947527,-0.6522235351,1.3134229927  
 H,0,0.9241865724,1.3527521094,2.1362252954  
 H,0,0.8673568824,-1.2845008708,2.1823452839  
 H,0,2.9542545205,-0.0627577044,-0.3845950372  
 H,0,1.9327011137,-0.057885419,-1.8524841739

### VRI on B3LYP/6-31G\* surface

|   |          |          |          |
|---|----------|----------|----------|
| C | -0.73992 | 0.11798  | -1.36316 |
| C | -0.76762 | -1.05277 | -0.53173 |
| C | -1.88547 | -0.80127 | 0.48432  |
| C | -1.93504 | 0.70283  | 0.49523  |
| C | -1.39489 | 1.16999  | -0.67807 |
| H | -1.72469 | -1.26804 | 1.46124  |
| H | -2.83214 | -1.20212 | 0.08355  |
| C | 0.76762  | -1.05278 | 0.53172  |
| C | 1.88547  | -0.80127 | -0.48432 |
| C | 1.93503  | 0.70283  | -0.49523 |
| C | 1.39489  | 1.16998  | 0.67808  |
| C | 0.73992  | 0.11797  | 1.36316  |
| H | 1.72469  | -1.26803 | -1.46124 |
| H | 2.83215  | -1.20212 | -0.08356 |
| H | -2.48066 | 1.2895   | 1.22602  |
| H | -1.40507 | 2.20574  | -1.00421 |
| H | -0.29082 | 0.18708  | -2.34577 |
| H | -0.70357 | -2.03602 | -0.99785 |
| H | 0.70357  | -2.03603 | 0.99783  |
| H | 0.29082  | 0.18706  | 2.34578  |
| H | 1.40507  | 2.20573  | 1.00423  |
| H | 2.48065  | 1.28951  | -1.22601 |

### B3LYP/6-311+G\*\*

CpDimerEndo6311+Gdp  
 E(RB+HF-LYP) = -388.327940775

Zero-point correction= 0.192621 (Hartree/Particle)  
 Thermal correction to Energy= 0.199693  
 Thermal correction to Enthalpy= 0.200637  
 Thermal correction to Gibbs Free Energy= 0.161367  
 Sum of elec / zero-point Energies= -388.135319  
 Sum of elec / thermal Energies= -388.128248  
 Sum of elec / thermal Enthalpies= -388.127303  
 Sum of elec / thermal Free Energies= -388.166574

| E (Thermal) | CV             | S        |
|-------------|----------------|----------|
| KCAL/MOL    | CAL/MOL-KELVIN | CAL/MOL- |
| KELVIN      |                |          |
| TOTAL       | 125.309        | 31.247   |
| 82.652      |                |          |

C,0,-2.2569529075,0.1601868988,0.3463044117  
 C,0,-1.6401532309,-1.1657600711,-0.0332952889  
 H,0,-1.4384576226,-1.7798844186,0.8525618344  
 C,0,-0.3444944436,-0.7775794085,-0.7934475939  
 C,0,-0.3051637785,0.7948251607,-0.8229660415  
 C,0,-1.5484568323,1.2051389446,-0.0824314287  
 H,0,-2.3192394919,-1.7524137887,-0.6628052208  
 C,0,1.0335834159,-1.13868781,-0.1284677127  
 H,0,-0.3573928114,-1.1853105571,-1.806365788  
 C,0,1.0942546489,1.1211413789,-0.1636099591  
 H,0,-0.2992985264,1.1907565807,-1.844592779  
 H,0,-1.8198584317,2.2428485565,0.0808810042  
 H,0,-3.1800317061,0.2300861172,0.9124305078  
 H,0,1.4469580849,2.1359753097,-0.3482844247  
 C,0,1.0317240342,0.6848965082,1.2910882834  
 C,0,1.9282989287,-0.0410756324,-0.7580708462  
 H,0,1.3396138901,-2.1748405193,-0.2764774018

## M. Listing of Dynamics Programs for Program Suite PROGDYN

version 0.9.3, March, 2009

The end of this section shows program changes used for special experiments.

### 1. Program progdynstarterHP

```
#!/bin/bash
# This is the master control program for
dynamics, in the form of a Unix Shell
Script.
#
# Necessary input files:
# freqinHP - This is the
standard output from a Gaussian 98 or 03
frequency calculation using freq=hpmodes.
# progdyn.conf - This is a file giving a
variety of configuration options, called
on by many of the subprograms.
#
# Optional input:
# isomernumber - A number in file
isomernumber provides a start for
numbering runs.
# detour - A signal file that, by
existing, signals the program to do a
side calculations
# nogo - A signal file that, by existing,
signals the program to stop between
points
# methodfile - a file that contains lines
that go at the end of the Gaussian input
file
# cannontraj - a file that contains
initial x, y, and z velocities to be
added to the normal velocities generated
by proggenHP.
# These are used for shooting a structure
toward another structure.
#
# Programs called:
# proggenHP - An awk program that
starts a trajectory, giving each mode its
zero point energy (if a quasiclassical
calculation) plus random additional
excitations depending on the temperature.
# proglstpoint - Awk program that
creates the first Gaussian input file for
each run
# prog2ndpoint - Awk program that
creates the second Gaussian input file
for each run
# progdynb - Awk program that creates
subsequent Gaussian input files until
trajectory is completed.
# proganal - A program to analyze the
latest point and see if a trajectory is
done. This program must be redone for
each new system. Elaborate changes are
often programmed into proganal, such as
```

```
the automatic changing of configuration
variables.
# randgen - A program that generates
random numbers between 0 and 1. These
are generated all at once and stored in a
file for use by proggenHP.
#
# Output files
# isomernumber - A running tab of the run
number
# geoRecord - A record of all the
starting positions and velocities.
# geoPlusVel - Created by proggen, this
gives starting position and velocities
for current run.
# g03.com - Created by proglstpoint,
prog2ndpoint, and progdynb, this is the
latest input
# file for Gaussian03 for current
run and latest point.
# olddynrun and olderdynrun - files
containing the last two outputs from
Gaussian, for creation
# of the next point
# dyn - A record of all of the Gaussian
outputs.
# dynfollowfile - A short record of the
runs and their results.
# skipstart - A signal file that, by
existing, tells progdynstarterHP that we
are in the middle of a run.
# diagnostics - optional output that
follows which subprograms are running and
configuration variables, decided by
variable in progdyn.conf
# vellist - optional output that list the
velocities of each atom, decided by
variable in progdyn.conf
# Echeck - After the first point of a
trajectory runs, prog2ndpoint checks to
see if the total potential energy +
kinetic energy is sufficiently close to
# the energy desired based on the
original design that assumed the harmonic
approximation. The output of this check
is placed into Echeck, and proganal will
start a new run if the energy is too far
off.
# A number of files starting with 'temp'
are created then later erased.

#progdynstarterHP, made to use
high=precision modes from Gaussian freq
output
#updated to create a random number file
temp811 that is used by proggenHP
#version September 16, 2005, made for
workstations
#version August 2007 to allow periodic
copying of g03.log to dyn putting it
under control of progdynb
#version Feb 2008 moves variables like
the scratch directory and location of
randgen to the beginning
```

```

#version March 2008 added proganal
reporting to points 1 and 2
#version Jan 2009 fixed bug generator of
having proganal run twice in checking for
complete runs
#
OUTLINE
# A. initilize to perform Gaussian jobs
and know where we are
#   start loop
# B. if no file named "skipstart" then
generate a new isomer. Get rid of
skipstart to start new isomer.
#
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAA
#origdir, randdir, scratchdir, g03root,
logfile, freqfile, programdir, all may
need varied from system to system and
assigned here or by program calling this
one
export g03root=/apps/lms/g03_E01_pre
. $g03root/g03/bsd/g03.profile
origdir=`pwd`
cd $origdir
logfile=docslog
randdir=~/.bin
scratchdir=/tmp/$PBS_JOBID
programdir=~/.bin2
freqfile=~/.bin2/freqinHP

rm -f nogo # assume that if someone is
starting a job, they want it to go.
rm -f diagnostics # contains extra info
from start of progFS

while (true)
do
#
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBB
if (test -f skipstart) then
echo "skipping start and continuing
from previous runs"
else
# change from older versions - freqin and
most other files are in origdir.
Advantage is compartmentalization.
# Also allows separate configurations for
separate runs, so we can move to using
config files.
# Disadvantage is multiple copies of
files.
cd $origdir
echo 3 > runpointnumber
$randdir/randgen > temp811
# lets keep the next 8 lines as the only
difference between progdynstarter and
progdynstarterHP
awk '/      1      2      3
4/,/Harmonic frequencies/ {print}'
$freqfile > temp401

```

```

awk '/Frequencies --/ {print $3;print
$4;print $5;print $6;print $7}' temp401 >
tempfreqs
awk '/Reduced masses/ {print $4;print
$5;print $6;print $7;print $8}' temp401 >
tempredmass
awk '/Force constants/ {print
$4;print $5;print $6;print $7;print $8}'
temp401 > tempfrc
awk '/0/ && ((length($1) < 2) && ($1
< 4)) {print}' temp401 > tempmodes
awk '/has atomic number/ {print}'
$freqfile > tempmasses
awk '/Standard orientation:/,/tional
const/ {if ($3==0) print}' $freqfile >
tempstangeos
awk -f $programdir/proggenHP
$freqfile > geoPlusVel
if (test -f isomernumber) then
cp isomernumber temp533
awk 'BEGIN {getline;i=$1+1;print
i}' temp533 > isomernumber
rm temp533
else
echo 1 > isomernumber
fi
rm g03.com
awk -f $programdir/proglstpoint
geoPlusVel > g03.com
# TO DO - put error checking in
proglstpoint, prog2ndpoint, and progdynb
so no g03.com unless things are ok
if (test -s g03.com) then
rm tempfreqs tempredmass tempfrc
tempmodes tempstangeos tempmasses temp401
temp811
cat isomernumber >> geoRecord
cat geoPlusVel >> geoRecord
cat g03.com
rm -f goingwell
cd $scratchdir
$g03root/g03/g03 $origdir/g03.com >
$origdir/g03.log
cd $origdir
grep 'Normal termination' g03.log >
goingwell
if (test -s goingwell) then
cat g03.log >> dyn
awk -f $programdir/proganal
g03.log >> dynfollowfile
cp g03.log olderdynrun
else
break
fi
else
break
fi
rm g03.com
awk -f $programdir/prog2ndpoint
g03.log > g03.com
if (test -s g03.com) then
rm -f goingwell
cd $scratchdir

```

```

    $g03root/g03/g03 $origdir/g03.com >
$origdir/g03.log
    cd $origdir
    grep 'Normal termination' g03.log >
goingwell
    if (test -s goingwell) then
        cp g03.log olddynrun
        cat g03.log >> dyn
        awk -f $programdir/proganal
g03.log >> dynfollowfile
# old program progdyn replaced here with
commands from progdyn
    awk '/Input
orientation/,/Distance matrix/ {print}'
olddynrun > temp101
    awk '/ 0 / {print}' temp101
> old
    awk '/Input
orientation/,/Distance matrix/ {print}'
olderdynrun > temp102
> older
    awk -f $programdir/progdynb
olddynrun > g03.com
    rm -f temp101 temp102 old older
tempchk
    else
        break
    fi
    else
        break
    fi
# we've just completed a start, so lets
skipstart until instructed otherwise
    echo "skipping start" > skipstart
fi

while (true)
do
#increment runpointnumber
    if (test -f runpointnumber) then
        cp runpointnumber temp533
        awk 'BEGIN {getline;i=$1+1;print
i}' temp533 > runpointnumber
        rm temp533
    else
        echo 4 > runpointnumber
    fi
# this loop always starts with a g03.com
in place - because of the loss of former
program progdyn, I
# may have to worry about how each it is
to restart from a bad run
    rm -f goingwell
    cd $scratchdir
    $g03root/g03/g03 $origdir/g03.com >
$origdir/g03.log
    cd $origdir
    grep 'Normal termination' g03.log >
goingwell
    if (test -s goingwell) then
        cp olddynrun olderdynrun
        cp g03.log olddynrun
# old program progdyn replaced here too

```

```

    awk '/Input orientation/,/Distance
matrix/ {print}' olddynrun > temp101
    awk '/ 0 / {print}' temp101 >
old
    awk '/Input orientation/,/Distance
matrix/ {print}' olderdynrun > temp102
    awk '/ 0 / {print}' temp102 >
older
    awk -f $programdir/progdynb
olddynrun > g03.com
    rm -f temp101 temp102 old older
tempchk
# line removed to move the command under
control of progdynb    cat g03.log >>
dyn
    else
        break
    fi

# here is a cool link that lets you
interrupt the dynamics with a short job,
then
# it automatically goes back to the
dynamics just make the file 'detour' and
it
# will delete detour, run run.com, then
go back to dynamics
    if (test -f detour) then
        rm detour
        date >> $logfile
        cat run.com >> $logfile
        cp run.log temp.log
        cd $scratchdir
        $g03root/g03/g03 $origdir/run.com >
$origdir/run.log
        cd $origdir
    fi

#stop it all nicely by creating a nogo
file
    if (test -f nogo) then
        break
    fi

#figure out if this isomer is done
    awk -f $programdir/proganal g03.log
>> dynfollowfile
    rm -f tempdone
    tail -2 dynfollowfile > temp281
    awk '/XXXX/ {print}' temp281 >
tempdone
    rm temp281
    if (test -s tempdone) then
        rm -f skipstart
        rm -f olddynrun
        rm -f olderdynrun
        rm -f geoPlusVel
        break
    fi
done

# We've got to break a second time to get
out of this loop

```

```

# if we really want to quit.  Otherwise,
it will start over
# at the top
if (test -f nogo) then
    break
fi
if (test -s goingwell) then
    echo "probably starting a new point"
else
    break
fi
done
exit 0

```

## 2. Program proggenHP

```

# Jan 2009 - a number of little changes
to improve reporting, precision, etc,
specification of displacement on
particular modes
# Jan 2009 cannonball trajectories.  adds
desired energy to initial velocities
based on file cannontraj, so one can
shoot toward a ts
# updated Nov 2008 to incorporate running
DRPs
# updated Nov 2008 to allow for start
without an initial freq calc using
classical = 2
# updated Aug 2008 added to atom list to
handle a large number of atoms without
changes needed
# updated June 2008 to incorporate new
method for choosing displacements with
initialdis 2
# updated Jan 17 2008 - bug fix for > 99
atoms, 300 excitations of low modes
possible
# version August 2007 - incorporates
classical trajectory calculation option
#also allows listing of number of
imaginary frequencies
# version Sept 16, 2005 - incorporate
searchdir but not yet rotation
# now reads random numbers from temp811,
starting at a random place
# The input files are generated before
this and are tempfreqs, tempredmass,
# tempfrfc, tempmodes, and tempstangeos.
# It will count the number of atoms.

# default parameters, including
quassiclassical, no displacements,
transition state, not a DRP
# do not change these - rather, change
progdyn.conf to set the parameters
initialDis=0; timestep=1E-15;
scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0;
cannonball=0
charge=0; multiplicity=1; method="HF/3-
21G"; memory=20000000

```

```

diag=1; checkpoint="g03.chk";
searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1;
title1="you"; title2="need"
title3="a"; title4="progdyn.conf";
processors=1; highlevel=999
conver1=4.184E26 #dividing by this
converts amu angs^2 /s^2 to kcal/mol

#initialization and constants
i=1;j=1;k=1
c=29979245800; h=6.626075E-34;
avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0;
classicalSpacing=4
zpeGauss=0; zpeGaussK=0; zpePlusE=0;
potentialE=0

# read progdyn.conf for configuration
info
blankLineTester=10
while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity")
multiplicity=$2
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="initialdis") initialDis=$2
    if ($1=="timestep") timestep=$2
    if ($1=="scaling") scaling=$2
    if ($1=="temperature") temp=$2
    if ($1=="searchdir") searchdir=$2
    if ($1=="classical") classical=$2
    if ($1=="numimag") numimag=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="boxon") boxon=$2
    if ($1=="boxsize") boxsize=$2
    if ($1=="DRP") DRP=$2; if (DRP==1)
classical=2 #this lets one start a DRP
from a point that is not a freq calc
    if ($1=="maxAtomMove") maxAtomMove=$2
    if ($1=="cannonball") cannonball=$2
    if ($1=="displacements")
disMode[$2]=$3
    if ($1=="title") {
        title1=$2
        title2=$3
        title3=$4
        title4=$5
    }
    blankLineTester=length($0)
}

if (diag>=1) print "*****
starting proggen *****" >>
"diagnostics"
if (diag>=1) print
"method,charge,multiplicity,memory" >>
"diagnostics"

```

```

if (diag>=1) print
method,charge,multiplicity,memory >>
"diagnostics"
if (diag>=1) print
"processors,checkpoint,title,initialdis,t
imestep,scaling,temperature" >>
"diagnostics"
if (diag>=1) print
processors,checkpoint,title1,title2,title
3,title4,initialDis,timestep,scaling,temp
>> "diagnostics"
if (diag>=1) print
"classical,numimag,highlevel,boxon,boxsiz
e,DRP,maxAtomMove,cannonball" >>
"diagnostics"
if (diag>=1) print
classical,numimag,highlevel,boxon,boxsize
,DRP,maxAtomMove,cannonball >>
"diagnostics"

# put geometries into array, also figure
out number of atoms
# note that this picks out the last
geometry in a file, assuming
# that if there is an optimization
followed by a freq, nothing else follows
# kludgy - repeats last line twice - must
be a better way
do {
  getline < "tempstangeos"
  if (oldline==$0) $0=""
  oldline=$0
  atom = $1
  if (atom>numAtoms) numAtoms=atom
  atNum[atom]=$2
  geoArr[atom,1]=$4; geoArr[atom,2]=$5;
geoArr[atom,3]=$6
  velArr[atom,1]=0; velArr[atom,2]=0;
velArr[atom,3]=0
}
while (length($0) > 0)

#output the number of atoms, used in many
routines
print numAtoms

# put in atomic symbols and atomic
weights - assigns a default mass but then
reads it from tempmasses when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1)
{atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2)
{atSym[i]="He";atWeight[i]=4.0026}
  if (atNum[i]==3)
{atSym[i]="Li";atWeight[i]=6.941}
  if (atNum[i]==4)
{atSym[i]="Be";atWeight[i]=9.012}
  if (atNum[i]==5)
{atSym[i]="B";atWeight[i]=10.811}
  if (atNum[i]==6)
{atSym[i]="C";atWeight[i]=12.}

  if (atNum[i]==7)
{atSym[i]="N";atWeight[i]=14.007}
  if (atNum[i]==8)
{atSym[i]="O";atWeight[i]=15.9994}
  if (atNum[i]==9)
{atSym[i]="F";atWeight[i]=18.9984}
  if (atNum[i]==10)
{atSym[i]="Ne";atWeight[i]=20.1797}
  if (atNum[i]==11)
{atSym[i]="Na";atWeight[i]=22.989}
  if (atNum[i]==12)
{atSym[i]="Mg";atWeight[i]=24.305}
  if (atNum[i]==13)
{atSym[i]="Al";atWeight[i]=26.98154}
  if (atNum[i]==14)
{atSym[i]="Si";atWeight[i]=28.0855}
  if (atNum[i]==15)
{atSym[i]="P";atWeight[i]=30.9738}
  if (atNum[i]==16)
{atSym[i]="S";atWeight[i]=32.066}
  if (atNum[i]==17)
{atSym[i]="Cl";atWeight[i]=35.4527}
  if (atNum[i]==18)
{atSym[i]="Ar";atWeight[i]=39.948}
  if (atNum[i]==19)
{atSym[i]="K";atWeight[i]=39.0983}
  if (atNum[i]==20)
{atSym[i]="Ca";atWeight[i]=40.078}
  if (atNum[i]==34)
{atSym[i]="Se";atWeight[i]=78.96}
  if (atNum[i]==35)
{atSym[i]="Br";atWeight[i]=79.904}
  if (atNum[i]==46)
{atSym[i]="Pd";atWeight[i]=106.42}
  if (atNum[i]==53)
{atSym[i]="I";atWeight[i]=126.90447}
# gets actual weight from freqinHP when
possible so a prior calc with
readisotopes gets you isotopic
substitution
  if ((i<100) && ($9>0)) atWeight[i]=$9
  if ((i>99) && ($8>0)) atWeight[i]=$8

  if ((diag>1) && (i==1)) print
"atNum[i],atSym[i],atWeight[i],geoArr[i,1
],geoArr[i,2],geoArr[i,3]" >>
"diagnostics"
  if (diag>1) print
atNum[i],atSym[i],atWeight[i],geoArr[i,1
],geoArr[i,2],geoArr[i,3] >> "diagnostics"
}

# read in frequencies, scale them, read
in Reduced masses, read in force
#constants, replace negative frequencies
by 4 wavenumbers
numFreq=3*numAtoms-6
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfreqs"
  freq[i]=$0*scaling
  if (freq[i]<0) freq[i]=4
}
for (i=1;i<=numFreq;i++) {

```

```

$0=""
getline < "tempredmass"
redMass[i]=$0
if (redMass[i]=="") redMass[i]=1.
}
for (i=1;i<=numFreq;i++) {
$0=""
getline < "tempfrc"
frc[i]=$0
if (frc[i]=="") frc[i]=0.0001
if (frc[i]==0) frc[i]=0.0001
if ((diag>1) && (i==1)) print
"freq[i],redMass[i],frc[i]" >>
"diagnostics"
if (diag>1) print
freq[i],redMass[i],frc[i] >>
"diagnostics"
}

# read in the modes - note that
trajectories always need a freq calc with
freq=hpmodes unless classical=2
for (i=1;i<=numFreq;i+=5) {
for (j=1;j<=(3*numAtoms);j++) {
getline < "tempmodes"
mode[i,$2,$1]=$4;
mode[i+1,$2,$1]=$5; mode[i+2,$2,$1]=$6;
mode[i+3,$2,$1]=$7; mode[i+4,$2,$1]=$8
}
}
if (diag>2) {for (i=1;i<=numFreq;i++)
{print
mode[i,1,1],mode[i,1,2],mode[i,1,3] >>
"modesread"}}}

# if doing a cannonball trajectory, read
in the vector
if (cannonball>0) {
for (i=1;i<=numAtoms;i++) {
getline < "cannontraj"
cannonArr[i,1]=$1;
cannonArr[i,2]=$2; cannonArr[i,3]=$3
}
}

# collect a series of random numbers from
file temp811, generated from an outside
random number generator called by
prodynstarterHP
# read from temp811, starting at a random
place
srand(); tester=rand()*1000
for (i=1;i<=tester;i++) getline <
"temp811"
for (i=1;i<=numFreq;i++) {
getline < "temp811"; randArr[i]=$1
getline < "temp811"; randArrB[i]=$1
getline < "temp811"; randArrC[i]=$1
}
# for a QM distribution for a harmonic
oscillator in its ground state, we want
to generate a set of random numbers

#between -1 and 1 weighted such that
numbers toward the center are properly
more common
i=1
while (i<=numFreq) {
getline < "temp811"
tempNum=2*($1-.5)
prob=exp(-(tempNum^2))
getline < "temp811"
if ($1<prob) {
randArrD[i]=tempNum
i++
}
}

# to start without normal modes or
frequencies we need to just pick a random
direction for the motion of each atom,
requiring 3N random numbers
for (i=1;i<=numAtoms;i++) {
for (j=1;j<=3;j++) {
getline < "temp811"
if ($1>0.5) randArrE[i,j]=1
if ($1<.5) randArrE[i,j]=-1
}
}

# determine energy in each normal mode
for (i=1;i<=numFreq;i++) {
zpeJ[i]=0.5*h*c*freq[i] #units J
per molecule
#if classical, treat as modes spaced by
classicalSpacing wavenumbers
if (classical==1)
zpeJ[i]=0.5*h*c*classicalSpacing # the
zpe is not used when classical but the
spacing is used to calculate the E in
mode
zpeK[i]=zpeJ[i]*avNum/4184 #units
kcal/mol
if (temp<10) vibN[i]=0 # avoids
working with very small temperatures - if
the temp is too low, it just acts like 0
K
if (temp>=10) {
zpeRat[i]=exp((-
2*zpeK[i])/(RgasK*temp))
if (zpeRat[i]==1)
zpeRat[i]=.9999999999
Q[i]=1/(1-zpeRat[i])
newRand=randArr[i]
vibN[i]=0
tester=1/Q[i]
# get up to 1000 excitations of low
modes
for (j=1;j<=(1000*zpeRat[i]+2);j++)
{
if (newRand>tester) vibN[i]++
}
tester=tester+((zpeRat[i]^j)/Q[i])
}
}
}

```



```

# figure out mode energies and maximum
classical shift and then actual shift
# also calculated total energy desired
for molecule
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
  modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1)
# units here are mDyne Angstroms for
compatability with Gaussian force
constants
  if (classical==1)
modeEn[i]=(zpeJ[i]*1E18)*2*vibN[i] #no
zpe when classical
  modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
  if (classical==1)
modeEnK[i]=zpeK[i]*2*vibN[i] #no
zpe when classical
  desiredModeEnK=desiredModeEnK +
modeEnK[i]
# no 1/2 hv for imaginary frequencies
# treating modes with frequencies <10 as
translations, ignoring their zero point
energies
  if (freq[i]<10)
modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i])
  maxShift[i]=(2*modeEn[i]/frc[i])^0.5
  if (initialDis==2)
shift[i]=maxShift[i]*randArrD[i]
  if (initialDis==1)
shift[i]=maxShift[i]*(2*(randArrC[i]-
0.5))
  if (initialDis==0) shift[i]=0
# lines below allow for setting of
displacement mode for individual modes;
use disMode 10 to turn off displacements
for a mode
  if (disMode[i]==2)
shift[i]=maxShift[i]*randArrD[i]
  if (disMode[i]==1)
shift[i]=maxShift[i]*(2*(randArrC[i]-
0.5))
  if (disMode[i]==10) shift[i]=0
# no displacements along imaginary
frequencies and very low ones - it is
better to treat these
# as translations - employing a shift can
give you initial weird geometries
  if (freq[i]<10) shift[i]=0
  if (numimag==1) shift[1]=0
  if (numimag==2) shift[2]=0
}
for (i=1;i<=numFreq;i++) {
  if ((diag>1) && (i==1)) print
"zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],m
odeEn[i],maxShift[i],shift[i]" >>
"diagnostics"
  if (diag>1) print
zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],mo
deEn[i],maxShift[i],shift[i] >>
"diagnostics"
}

# multiply each of the modes by its shift
and add them up

for (i=1;i<=numFreq;i++) {
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {

shiftMode[i,j,k]=mode[i,j,k]*shift[i]
geoArr[j,k]=geoArr[j,k]+shiftMode[i,j,k]
    }
  }
}

#output the new geometry.
for (j=1;j<=numAtoms;j++) {
  printf("%2s % .7f % .7f % .7f %9.5f
\n",atSym[j],geoArr[j,1],geoArr[j,2],geoA
rr[j,3],atWeight[j])
}

#now start toward velocities
for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-
0.5*frc[i]*shift[i]^2) # the 100000
converts to g angstrom^2 s^2

vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.
5 # in angstrom / s
#use searchdir in progdyn.conf to control
the direction for trajectories started
from a saddle point
  if (numimag>1) numimag=1 #only the
first freq can be sent in the searchdir
direction, the rest go in a random
direction
  if (i>numimag) {
    if (randArrB[i]<0.5) vel[i]=-vel[i]
  }
  if (i==numimag) {
    if (searchdir=="negative") vel[i]=-
vel[i]
  }
  if ((diag>1) && (i==1)) print "vel[i]"
>> "diagnostics"
  if (diag>1) print vel[i] >>
"diagnostics"
}
# the next line can be uncommented and
set so as to make a particular mode
velocity either positive or negative
# if (vel[2]<0) vel[2]=-vel[2]

# multiply each of the modes by its
velocity and add them up
for (i=1;i<=numFreq;i++) {
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {

velMode[i,j,k]=mode[i,j,k]*vel[i]*timeste
p
velArr[j,k]=velArr[j,k]+velMode[i,j,k]
    }
  }
}

```

```

# to start without normal modes or
frequencies we figure out the energy per
atom based on 1/2RT in degree of freedom
if (classical==2) {
    degFreedomEnK=temp*RgasK

degFreedomEnJ=degFreedomEnK/(avNum/4184)
    cartEn=degFreedomEnJ*1E18
    kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ,
cartEn, kinEnCart
    for (i=1;i<=numAtoms;i++) {
        for (j=1;j<=3;j++) {

velArr[i,j]=randArrE[i,j]*timestep*(2*kin
EnCart/(atWeight[i]/avNum))^0.5
            if (DRP==1) velArr[i,j]=0
        }
    }

# calculate the KE in the modes at this
point
KEinitmodes=0
for (j=1;j<=numAtoms;j++) {
    KEinitmodes=KEinitmodes +
0.5*atWeight[j]*(velArr[j,1]^2 +
velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
}

# if doing a cannonball, adjust
multiplier until extra energy is correct
if (cannonball>0) {
    multiplier=1; tester=0; tolerance=.1
    while (tester==0) {
        KEinittotal=0
        for (j=1;j<=numAtoms;j++) {

cannonvelArr[j,1]=velArr[j,1]+multiplier*
cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*
cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*
cannonArr[j,3]
            KEinittotal=KEinittotal +
0.5*atWeight[j]*(cannonvelArr[j,1]^2 +
cannonvelArr[j,2]^2 +
cannonvelArr[j,3]^2)/((timestep^2)*conver
1)
        }
        if
(KEinittotal>(KEinitmodes+cannonball+tole
rance)) multiplier=multiplier*0.98901364
        if
(KEinittotal<(KEinitmodes+cannonball-
tolerance)) multiplier=multiplier*1.01
        if
((KEinittotal<(KEinitmodes+cannonball+tol
erance)) &&
(KEinittotal>(KEinitmodes+cannonball-
tolerance))) tester=1
    }
    for (j=1;j<=numAtoms;j++) {

velArr[j,1]=velArr[j,1]+multiplier*cannon
Arr[j,1];
velArr[j,2]=velArr[j,2]+multiplier*cannon
Arr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannon
Arr[j,3]
        }

#output the velocities and calculate the
total kinetic energy overall
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
    KEinittotal=KEinittotal +
0.5*atWeight[j]*(velArr[j,1]^2 +
velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
    printf("%.8f % .8f % .8f
\n",velArr[j,1],velArr[j,2],velArr[j,3])
}

#anything else I add to the file will not
affect the trajectories but will keep a
record and be good for analysis
for (i=1;i<=numFreq;i++) {
    if (initialDis==0) printf("%.6f %
.6f %4i % 1.4e % .6f %1i\n",
randArr[i], randArrB[i], vibN[i], vel[i],
shift[i], disMode[i])
    if (initialDis==1) printf("%.6f %
.6f %4i % 1.4e % .6f %1i\n",
randArr[i], randArrC[i], vibN[i], vel[i],
shift[i], disMode[i])
    if (initialDis==2) printf("%.6f %
.6f %4i % 1.4e % .6f %1i\n",
randArr[i], randArrD[i], vibN[i], vel[i],
shift[i], disMode[i])
}
print "temp ",temp
print "initialDis",initialDis
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "%.3f"
print "Total mode energy
desired=",desiredModeEnK
print "KE initial from
modes=",KEinitmodes," KE initial
total=",KEinittotal
if (cannonball>0) print
"cannonball",cannonball," cannon
Energy=",KEinittotal-KEinitmodes
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP,"
maxAtomMove",maxAtomMove
} # End of BEGIN

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"

```

```

print "Gaussian
zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol
E + zpe=",zpePlusE," potential
E=",potentialE
print "" #will use blank line to mark end
of geoPlusVel file
}

```

### 3. Program prog1stpoint

```

BEGIN {
# Jan 2009 - a number of little changes
to improve reporting, precision, etc
# aug 2008 added to atom list so handles
H to Cl without change needed
# version Feb 2008 incorporates
methodfile, boxon and boxsize, though
this point unaffected by box
# version Jan 2008 - allows for ONIOM
jobs, fixed atoms
# version Sept 2005 - incorportates
meth3, meth4, meth5, meth6, but not yet
rotation
# this program creates the first input
file for g03
# the title should be changed as
appropriate
# the isomer number comes from a file
isomernumber

# default parameters, including
quassiclassical, no displacements,
transition state, not a DRP
# do not change these - rather, change
progdyn.conf to set the parameters
initialDis=0; timestep=1E-15;
scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0;
cannonball=0
charge=0; multiplicity=1; method="HF/3-
21G"; memory=20000000
diag=1; checkpoint="g03.chk";
searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1;
title1="you"; title2="need"
title3="a"; title4="progdyn.conf";
processors=1; highlevel=999

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34;
avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

# read progdyn.conf for configuration
info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2

```

```

  if ($1=="charge") charge=$2
  if ($1=="multiplicity")
multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="methodfile")
methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
  }
  blankLineTester=length($0)
}

if (diag==1) print "*****
starting prog1stpoint *****"
>> "diagnostics"
if (diag==1) print
"method,charge,multiplicity,memory" >>
"diagnostics"
if (diag==1) print
method,charge,multiplicity,memory >>
"diagnostics"
if (diag==1) print
"processors,checkpoint,title" >>
"diagnostics"
if (diag==1) print
processors,checkpoint,title1,title2,title
3,title4 >> "diagnostics"

getline < "isomernumber"
isomernum = $1
print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk="
checkpoint
print "#p " method " force
scf=(tight,nosym) "
#print "IOp(3/76=0572004280)" #for mPW1K
in g03
if (meth2=="unrestricted") print
"guess=mix" #for unrestricted
calculations
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
# make the title four words exactly,
leaving out spaces if necessary
print title1,title2,title3,title4

```

```

print "runpoint 1"
print "runisomer ", isomernum
print ""
print charge,multiplicity
}

(/H / || /He / || /Li / || /Be / || /B /
|| /C / || /N / || /O / || /F / || /Ne /
|| /Na / || /Mg / || /Al / || /Si / || /P
/ || /S / || /Cl /) {
  atomnumber++
  printf("%s %.7f %.7f
%.7f", $1,$2,$3,$4)
  if (atomnumber>highlevel) printf(
%s", "M")
  print ""
}

END {
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
  }
}
print ""
}

```

#### 4. Program prog2ndpoint

```

BEGIN {
# aug 2008 added to atom list so handles
1 to 17 without change needed
# version Feb 2008 incorporates
methodfile, boxon and boxsize, though
this point unaffected by box
# version Jan 2008 - allows for ONIOM
jobs, fixed atoms
# version Sept 9, 2005 - incorportates
meth3, meth4, meth5, meth6, but not yet
rotation
# read progdyn.conf for configuration
info

# default parameters, including
quassiclassical, no displacements,
transition state, not a DRP
# do not change these - rather, change
progdyn.conf to set the parameters
initialDis=0; timestep=1E-15;
scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0;
cannonball=0
charge=0; multiplicity=1; method="HF/3-
21G"; memory=20000000
diag=1; checkpoint="g03.chk";
searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1;
title1="you"; title2="need"

```

```

title3="a"; title4="progdyn.conf";
processors=1; highlevel=999

```

```

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34;
avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity")
multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="DRP") DRP=$2
  if ($1=="methodfile")
methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
  }
  blankLineTester=length($0)
}

```

```

if (diag>=1) print "*****
starting prog2ndpoint *****"
>> "diagnostics"
if (diag>=1) print
"method,charge,multiplicity,memory" >>
"diagnostics"
if (diag>=1) print
method,charge,multiplicity,memory >>
"diagnostics"
if (diag>=1) print
"processors,checkpoint,title" >>
"diagnostics"
if (diag>=1) print
processors,checkpoint,title1,title2,title
3,title4 >> "diagnostics"

```

```

#get the isomer number from file
getline < "isomernumber"
isomernum = $1

```

```

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk="
checkpoint
print "#p " method " force
scf=(tight,nosym) "
if (meth2=="unrestricted") print
"guess=mix" #for unrestricted
calculations
if (meth2=="read") print "guess=tcheck"
#for reading orbitals from check,
sometimes faster, sometimes not
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
print title1,title2,title3,title4
print "runpoint 2"
print "runisomer ", isomernum
print ""
print charge,multiplicity

# ok, now we have to figure the second
point. this should be
#  $x(t) = x + v*t + 1/2*F*t^2/m$ 
# so we need to set up arrays for
position, velocity, and force
getline < "geoPlusVel"
numAtoms=$1
# first the geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$ (1+j)
  }
}
#now we go ahead and add the velocities
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    arr[i,j]=$j+geoArr[i,j]
  }
  if ((diag>1) && (i==1)) print
"geometry after adding velocities" >>
"diagnostics"
  if (diag>1) print
arr[i,1],arr[i,2],arr[i,3] >>
"diagnostics"
}

#pull out other information useful for
testing whether total energy is right or
bad
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
  if ($4=="desired=") desiredModeEnK=$5
  if ($4=="modes=") {
    KEinitmodes=$5
    KEinittotal=$9
  }
  if ($11=="potential") potentialE=$13

  blankLineTester=length($0)
}
} # end of BEGIN

/SCF Done/ {
print "trajectory #",isomernum >>
"Echeck"
newPotentialE=$5
newPotentialEK=(newPotentialE-
potentialE)*627.509
print "point 1 potential
E=",newPotentialEK," point 1 kinetic
E=",KEinittotal,"
Total=",newPotentialEK+KEinittotal >>
"Echeck"
print "desired total energy=",
desiredModeEnK >> "Echeck"
if
((newPotentialEK+KEinittotal)>(desiredMod
eEnK+1)) print "XXXX bad total Energy" >>
"Echeck"
if
((newPotentialEK+KEinittotal)<(desiredMod
eEnK-1)) print "XXXX bad total Energy" >>
"Echeck"
}

# now we go ahead and translate the
forces and add them
(/
1 / || / 2 /
|| / 3 / || / 4 /
|| / 5 / || / 6 /
|| / 7 / || / 8 /
|| / 9 / || / 10 /
|| / 11 / || / 12 /
|| / 13 / || / 14 /
|| / 15 / || / 16 /
|| / 17 /) && length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$ (2+j) #the raw units
of the forces are Hartree/Bohr
}
if ((diag>1) && (i==1)) print
"i,weight[i],forceArr[i,1],forceArr[i,2],
forceArr[i,3]" >> "diagnostics"
if (diag>1) print
i,weight[i],forceArr[i,1],forceArr[i,2],f
orceArr[i,3] >> "diagnostics"
}

END {
# turn the forces into motion
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    # conversions here take force to
J/angstrom, 1E20 converts to kg angstroms
/ s^2, then mult time (s^s) and divide by
weight in kg to get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.
509*(4184/(0.529177*avNum))*(timestep^2)/
(weight[i]/(avNum*1000))

```

```

# for simplicity, DRPs will throw away
the forces at the second pont. This
means that if we are not at a
saddlepoint, point 2 = point 1 but this
is a minor waste
    if (DRP==1) forceArr[i,j]=0
    arr[i,j]=arr[i,j]+forceArr[i,j]
# if atoms are fixed, replace calcd new
position by original position
    if ((i==fixedatom1) ||
(i==fixedatom2) || (i==fixedatom3) ||
(i==fixedatom4)) arr[i,j]=geoArr[i,j]
    }
    if ((diag>1) && (i==1)) print
"i,weight[i],forceArr[i,1],forceArr[i,2],
forceArr[i,3]" >> "diagnostics"
    if (diag>1) print
i,weight[i],forceArr[i,1],forceArr[i,2],f
orceArr[i,3] >> "diagnostics"
    printf("%s %.7f %.7f
%.7f",atSym[i],arr[i,1],arr[i,2],arr[i,3]
)
    if (i>highlevel) printf(" %s","M")
    print ""
}
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
        getline < "methodfile"
        print $0
    }
}
print ""
}

```

## 5. Program progdynb

```

BEGIN { #this is the main routine for
generating new .com files by the Verlet
algorithm
# Jan 2009 - a number of little changes
to improve reporting, precision, etc
# Nov 2008 added ability to handle DRPs
# Aug 2008 added long list of atoms to
handle 1-17 without change
# May 2008 added option to put out
velocities in vellist - make diag=2
# version Feb 2008 incorporates
methodfile, boxon and boxsize
# version Jan 2008 incorporates fixed
atoms, oniom, and velocity damping
# version August 2007 incorporates
keepevery to decrease size of dyn file
# version Sept 11, 2005 - incorporatates
meth3, meth4, meth5, meth6, but not yet
rotation

# default parameters, including
quassiclassical, no displacements,
transition state, not a DRP

```

```

# do not change these - rather, change
progdyn.conf to set the parameters
initialDis=0; timestep=1E-15;
scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0;
cannonball=0
charge=0; multiplicity=1; method="HF/3-
21G"; memory=20000000
diag=1; checkpoint="g03.chk";
searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1;
title1="you"; title2="need"
title3="a"; title4="progdyn.conf";
processors=1; highlevel=999

```

```

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34;
avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0
OFS=" "

#allow for damping from file named
damping, but limit its range
damping=1
DRP=0
getline < "damping"
if (($1>0.05) && ($1<2.1)) damping=$1

```

```

# read progdyn.conf for configuration
info
blankLineTester=10
while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity")
multiplicity=$2
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="method3") meth3=$2
    if ($1=="method4") meth4=$2
    if ($1=="method5") meth5=$2
    if ($1=="method6") meth6=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="keepevery") keepevery=$2
    if ($1=="fixedatom1") fixedatom1=$2
    if ($1=="fixedatom2") fixedatom2=$2
    if ($1=="fixedatom3") fixedatom3=$2
    if ($1=="fixedatom4") fixedatom4=$2
    if ($1=="boxon") boxon=$2
    if ($1=="boxsize") boxsize=$2
    if ($1=="DRP") DRP=$2
    if ($1=="maxAtomMove") maxAtomMove=$2
    if ($1=="methodfile")
methodfilelines=$2
    if ($1=="killcheck") killcheck=$2
    if ($1=="title") {
        title1=$2
    }
}

```

```

        title2=$3
        title3=$4
        title4=$5
    }
    blankLineTester=length($0)
}

if (diag>=1) print "*****
starting progdynb *****" >>
"diagnostics"
if (diag>=1) print
"method,charge,multiplicity,memory" >>
"diagnostics"
if (diag>=1) print
method,charge,multiplicity,memory >>
"diagnostics"
if (diag>=1) print
"processors,checkpoint,title" >>
"diagnostics"
if (diag>=1) print
processors,checkpoint,title1,title2,title
3,title4 >> "diagnostics"

# get number of atoms and weights from
geoPlusVel, and previous geometries from
old and older
getline < "geoPlusVel"
numAtoms=$1
for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
    weight[i]=$5; atSym[i]=$1
}

for (at=1;at<=numAtoms;at++) {
    getline < "old"
    oldarr[at,1]=$4; oldarr[at,2]=$5;
oldarr[at,3]=$6
}

for (at=1;at<=numAtoms;at++) {
    getline < "older"
    olderarr[at,1]=$4; olderarr[at,2]=$5;
olderarr[at,3]=$6
}

#for DRPs read in oldAdjForces and
maxAtomMove
if (DRP==1) {
    for (at=1;at<=numAtoms;at++) {
        getline < "oldAdjForces"
        oldForce[at,1]=$1;
oldForce[at,2]=$2; oldForce[at,3]=$3
    }
    getline < "maxMove"
    if (($1<maxAtomMove) && ($1>0))
maxAtomMove=$1
}

# record atom velocities for IVR
analysis. This is actually the velocity
in the previous run, which is the easiest
to calculate.
getline < "isomernumber"
isomernum = $1

getline < "runpointnumber"
runpointnum = $1
if (diag==3) print "runpoint
",runpointnum-1,"runisomer ",isomernum >>
"vellist"
for (at=1;at<=numAtoms;at++) {
    atomVel=((oldarr[at,1]-
olderarr[at,1])^2 + (oldarr[at,2]-
olderarr[at,2])^2 +(oldarr[at,3]-
olderarr[at,3])^2)^.5
    if (diag==3) print atomVel >> "vellist"
}

#must adjust next line for weird atoms
(/          1      / || /          2      /
|| /          3      / || /          4      /
|| /          5      / || /          6      /
|| /          7      / || /          8      /
|| /          9      / || /         10      /
|| /         11      / || /         12      /
|| /         13      / || /         14      /
|| /         15      / || /         16      /
|| /         17      /) && length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
    forceArr[i,j]=$ (2+j) #the raw units
of the forces are Hartree/Bohr
}
if ((diag>1) && (i==1)) print
"i,weight[i],forceArr[i,1],forceArr[i,2],
forceArr[i,3]" >> "diagnostics"
if (diag>1) print
i,weight[i],forceArr[i,1],forceArr[i,2],f
orceArr[i,3] >> "diagnostics"
}

END {
#####routine for
DRPs#####
if (DRP==1) {
    maxForce=0;oscillTest=0
    for (i=1;i<=numAtoms;i++) {
        for (j=1;j<=3;j++) {
# conversions here take force to
J/angstrom, 1E20 converts to kg angstroms
/ s^2, then mult time (s^s) and divide by
weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*
(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))

oscillTest=oscillTest+forceArr[i,j]*oldFo
rce[i,j]
            if (forceArr[i,j]>maxForce)
maxForce=forceArr[i,j]
            if ((0-forceArr[i,j])>maxForce)
maxForce=-forceArr[i,j]
        }
        if (i==1) printf("% .8f % .8f % .8f
\n",forceArr[1,1],forceArr[1,2],forceArr[
1,3]) > "oldAdjForces"

```





```

int main(void)
{
    int count=1;
    srand48(time (0));
    while (count<=10000)
    {
        d = drand48();
        printf ("%%.20f\n", d);
        count++;
    }
    return 0;
}

```

### 7. Program proganal

```

BEGIN {
getline < "isomernumber"
isomer=$1
}

/ CpDim/ {
    printf("%s %s %s %s %s %s
", $1,$2,$3,$4,$6,$8)
    runpoint=$6
    isomer=$8
}

/ 1 C 0.000000/,/ 6 H
0.000000/ {
    if ($1==8) CCset=$4
    if ($1==10) CCh=$3
    if ($1==12) CCl=$6
}

END {
    printf("%s %.3f %s %.3f %s %.3f
", "CCset", CCset, "CCh", CCh, "CCl", CCl)
    if (runpoint>500) {
        print "Too many points. XXXX"
        movedyn(isomer)
    }
    if (CCset>2.2) {
        print "Dead starting material
XXXX"
        killdyn(isomer)
    }
    if ((CCset<1.7) && (CCh<2.2)) {
        print "Heavy carbon reacted
XXXX"
        movedyn(isomer)
    }
    if ((CCset<1.7) && (CCl<2.2)) {
        print "Light carbon reacted
XXXX"
        movedyn(isomer)
    }
    system("date")
    if (runpoint>2) system("tail -1 Echeck
| grep XXXX")
}

function movedyn(isomer) {
    if (isomer==1) system("mv dyn dyn1")
    if (isomer==2) system("mv dyn dyn2")
    if (isomer==3) system("mv dyn dyn3")

```

```

    if (isomer==4) system("mv dyn dyn4")
    if (isomer==5) system("mv dyn dyn5")
    if (isomer==6) system("mv dyn dyn6")
    if (isomer==7) system("mv dyn dyn7")
    if (isomer==8) system("mv dyn dyn8")
    if (isomer==9) system("mv dyn dyn9")
    if (isomer==10) system("mv dyn dyn10")
    if (isomer==11) system("mv dyn dyn11")
    if (isomer==12) system("mv dyn dyn12")
    if (isomer==13) system("mv dyn dyn13")
    if (isomer==14) system("mv dyn dyn14")
    if (isomer==15) system("mv dyn dyn15")
    if (isomer==16) system("mv dyn dyn16")
    if (isomer==17) system("mv dyn dyn17")
    if (isomer==18) system("mv dyn dyn18")
    if (isomer==19) system("mv dyn dyn19")
    if (isomer==20) system("mv dyn dyn20")
    if (isomer==21) system("mv dyn dyn21")
    if (isomer==22) system("mv dyn dyn22")
    if (isomer==23) system("mv dyn dyn23")
    if (isomer==24) system("mv dyn dyn24")
    if (isomer==25) system("mv dyn dyn25")
    if (isomer==26) system("mv dyn dyn26")
    if (isomer==27) system("mv dyn dyn27")
    if (isomer==28) system("mv dyn dyn28")
    if (isomer==29) system("mv dyn dyn29")
    if (isomer==30) system("mv dyn dyn30")
}

```

```

function killdyn(isomer) {
    system("rm -f dyn")
}

```

```

function moveold(isomer) {
    if (isomer==1) system("cp old* n1")
    if (isomer==2) system("cp old* n2")
    if (isomer==3) system("cp old* n3")
    if (isomer==4) system("cp old* n4")
    if (isomer==5) system("cp old* n5")
    if (isomer==6) system("cp old* n6")
    if (isomer==7) system("cp old* n7")
    if (isomer==8) system("cp old* n8")
    if (isomer==9) system("cp old* n9")
    if (isomer==10) system("cp old* n10")
    if (isomer==11) system("cp old* n11")
    if (isomer==12) system("cp old* n12")
    if (isomer==13) system("cp old* n13")
    if (isomer==14) system("cp old* n14")
    if (isomer==15) system("cp old* n15")
    if (isomer==16) system("cp old* n16")
    if (isomer==17) system("cp old* n17")
    if (isomer==18) system("cp old* n18")
    if (isomer==19) system("cp old* n19")
    if (isomer==20) system("cp old* n20")
    if (isomer==21) system("cp old* n21")
    if (isomer==22) system("cp old* n22")
    if (isomer==23) system("cp old* n23")
    if (isomer==24) system("cp old* n24")
    if (isomer==25) system("cp old* n25")
    if (isomer==26) system("cp old* n26")
    if (isomer==27) system("cp old* n27")
    if (isomer==28) system("cp old* n28")
    if (isomer==29) system("cp old* n29")
    if (isomer==30) system("cp old* n30")
}

```

}

## 8. progdyn.conf

```
#conf file for dynamics. This is read by
awk programs proglstpoint, prog2ndpoint,
and progdynb.
#The programs won't read anything past
the first blank line,
#and this file must end with a blank
line. You can add to these comments but
#don't use keywords as the first word on
a line. Don't delete lines - the program
#has no built in default values if they
aren't here.
#values here are read repeatedly and can
be changed in the middle of runs
method B3LYP/6-31G*
method2 restricted #The options here are
restricted, unrestricted, and read.
#If the method is U..., put unrestricted
here and the .com files will have in them
guess=mix.
#If you put read here, the .com files
will contain guess=tcheck, which
sometimes makes things faster, sometimes
not.
charge 0
multiplicity 1
memory 100000000
killcheck 1
#checkpoint dyn20.chk #uses one
checkpoint file repeatedly
processors 1
diagnostics 0 # 1 prints out extra stuff
to a file "diagnostics", 2 adds
velocities to a file "vellist"
title CpDim76C4 B3631Gd 298QC dis=2 # the
title must be exactly four words
initialdis 2
timestep 1E-15
scaling 1.0
temperature 298.15
#add extra lines to .com files to
implement things like the iop for mPW1k
#Leave the second word blank if you are
not going to use them. otherwise any word
you put in will end up in the com file
#only a single term with no spaces can be
added, one per method line
#method3 IOp(3/76=0572004280)
#add the line below with big structures
to get it to put out the distance matrix
and the input orientation
#method3 iop(2/9=2002)
#method4 scrf=(pcm,solvent=dms0,read)
#method5 and method6 are placed at the
end of the file instead of in the keyword
section
method5
method6
#for more complicated ends of .com files,
it will be necessary to put the ends in a
file
```

```
#methodfile 1
#searchdir says what direction to follow
the mode associated with the imaginary
frequency.
#put as values the words "negative" or
"positive"
searchdir negative
#for quassiclassical dynamics, the
default, use 0. for classical dynamics,
use 1 below
#if there are no normal modes and the
velocities are to be generated from
scratch, use classical=2
classical 0
#to run a DRP use 'DRP 1' in the line
below, otherwise leave it at 0
#treatment of starting saddlepoints not
yet implemented
#if DRP shows oscillations then decrease
maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
# to fire a structure toward a ts, make a
file cannontraj with initial velocities
and set cannonball to the amount of extra
energy you want to put in
#cannonball 10
#line below gives number of negative
frequencies - if 0, treats as ground
state and direction of all modes is
random
#if 1, negative freq will go direction of
searchdir
#if 2, only lowest freq will go direction
of searchdir and other imag mode will go
in random direction
numimag 1
# the line below tells progdynb how often
to write g03.log to file dyn, after the
first two points. Use 1 for most
dynamics
# until excessive, but use a higher
integer if doing long term classical
dynamics.
keepevery 5
# for ONIOM jobs, the following line
states the number of highlevel atoms,
which must come before the medium level
atoms
# make this number 999 if not ONIOM
highlevel 999
#use fixedatom1, fixedatom2, fixedatom3,
fixedatom4 to fix atoms in space.
#note that fixing one atom serves no
useful purpose and messes things up,
while
#fixing two atoms fixes one distance, and
#fixing three has the effect of fixing
three distances, not just two
#in current form fixed atoms only are
meant to work with no displacements, that
is, initialdis=0
#fixedatom1 2
#fixedatom2 3
```

```
#fixedatom3 19
#dynamics with solvent molecules tends to
blast molecules away. Because of this,
#it would be good to have a pressure and
periodic boundary conditions, etc, but
until
#I learn how to do this, I can just
restrict the molecules to a box
#atoms outside this box get bounced. Set
box size so as to fit the entire initial
molecule but not have too much extra room
#the box does not affect anything until
progdynb
boxon 0
boxsize 7.5
# you can set the initialdis of
particular modes by using a series of
lines of the format
# displacements NumberOfMode
InitialDisForThatMode, as in the line
below. You should be able to do as many
of these as you like
# you might consider this for rotations
where a straight-line displacement goes
wrong at large displacements
#displacements 86 2
```

```
#updated Aug 9, 2007 to include the
possibility of classical dynamics by the
keyword classical
#updated Jan 2008 to include fixed atoms,
ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile
parameter
# updated Nov 2008 to allow for start
without an initial freq calc using
classical = 2
```

## 9. Program modifications used in calculational experiments

Classical trajectories were accessed from the standard code above using classical 1 in progdyn.conf.

```
To start trajectories with carbon 12 then
switch to using carbon 140 with constant
momentum, lines as shown below, modified
slightly for each carbon, were added to
proggenHP at line 335:
# ***** this section changed for special
experiment for cyclopentadiene. do not
use this for other cases
atWeight[1]=140.0001
# ***** line below added for special
experiment switching mass from 12 to 140,
keeping momenta the same
velArr[1,1]=velArr[1,1]/11.66667;
velArr[1,2]=velArr[1,2]/11.66667;
velArr[1,3]=velArr[1,3]/11.66667
```

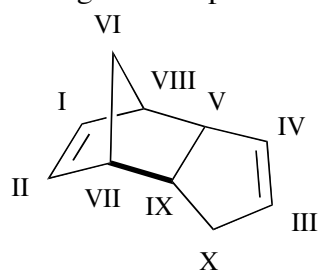
```
To start trajectories with carbon 140
then switch to using carbon 12 with
constant momentum, lines as shown below
were added to proggenHP. At line 123,
the addition was:
# ***** line below is commented out
for special experiment switching weights
- do not use for regular runs
# if ((i<100) && ($9>0)) atWeight[i]=$9
at line 340, the addition was:
# ***** line below added for special
experiment switching mass from 140 to 12,
keeping momenta the same
velArr[4,1]=11.66667*velArr[4,1];
velArr[4,2]=11.66667*velArr[4,2];
velArr[4,3]=11.66667*velArr[4,3]
```

```
To equalize the sampling of trajectories
with positive and negative signs for the
velocities of the lowest-energy real
vibrational mode, the line 476 of
proggenHP was uncommented, using either:
if (vel[2]<0) vel[2]=-vel[2]
or
if (vel[2]>0) vel[2]=-vel[2]
to obtain trajectories of a desired sign.
```

## N. NMR Raw Integrations and Isotope Effect Calculations

### 1. $^{13}\text{C}$ NMR Raw Integrations

The roman numerals on the figure below are ordered to correspond to the  $^{13}\text{C}$  peaks from left to right (high  $\delta$  to low  $\delta$ ) in the  $^{13}\text{C}$  NMR spectrum of a highly concentrated sample. (Peaks II, III, and IV are close and their order under other conditions can be different.) The integrations in the table below are given in this order. The numbers provided are taken from a total of 84 spectra, arising from 6 spectra for each of 7 equilibrated and non-equilibrated (kinetic dimer) samples.



| Sample:    | A            | A                | B            | B                | C            | C                | D            |
|------------|--------------|------------------|--------------|------------------|--------------|------------------|--------------|
|            | equilibrated | non-equilibrated | equilibrated | non-equilibrated | equilibrated | non-equilibrated | equilibrated |
| SPECTRUM 1 |              |                  |              |                  |              |                  |              |
| I          | 1037.31      | 1027.59          | 1021.39      | 1014.27          | 1015.69      | 1010.31          | 1009.80      |
| II         | 1035.53      | 1033.09          | 1039.73      | 1045.17          | 1033.55      | 1041.76          | 1042.83      |
| III        | 1050.04      | 1050.45          | 1061.06      | 1057.17          | 1053.60      | 1052.41          | 1046.09      |
| IV         | 1057.36      | 1046.37          | 1062.86      | 1059.66          | 1064.78      | 1053.43          | 1071.33      |
| V          | 1030.91      | 1012.80          | 1089.68      | 1084.53          | 1081.71      | 1060.65          | 1081.60      |
| VI         | 1019.21      | 1015.71          | 1068.09      | 1066.28          | 1073.01      | 1074.70          | 1066.70      |
| VII        | 1000.27      | 993.47           | 1040.68      | 1043.84          | 1030.28      | 1022.50          | 1035.36      |
| VIII       | 1024.93      | 1004.13          | 1050.86      | 1039.63          | 1051.66      | 1035.69          | 1050.32      |
| IX         | 988.77       | 972.59           | 1020.76      | 1017.27          | 1011.99      | 986.84           | 1015.05      |
| X          | 1000.00      | 1000.00          | 1000.00      | 1000.00          | 1000.00      | 1000.00          | 1000.00      |
| SPECTRUM 2 |              |                  |              |                  |              |                  |              |
| I          | 1033.88      | 1026.66          | 1011.98      | 1015.02          | 1001.99      | 1008.73          | 1015.01      |
| II         | 1033.27      | 1034.80          | 1039.12      | 1040.11          | 1027.86      | 1047.56          | 1046.68      |
| III        | 1046.04      | 1048.39          | 1055.23      | 1057.11          | 1035.48      | 1061.12          | 1047.66      |
| IV         | 1055.86      | 1043.56          | 1056.54      | 1058.40          | 1063.29      | 1050.87          | 1077.97      |
| V          | 1028.25      | 1009.93          | 1083.34      | 1075.42          | 1079.89      | 1069.88          | 1089.92      |
| VI         | 1020.65      | 1015.51          | 1065.77      | 1064.30          | 1070.53      | 1070.85          | 1067.67      |
| VII        | 998.96       | 992.56           | 1036.79      | 1037.43          | 1033.50      | 1030.37          | 1040.22      |
| VIII       | 1021.64      | 1004.41          | 1045.55      | 1039.64          | 1059.07      | 1038.45          | 1049.93      |
| IX         | 988.75       | 971.32           | 1013.91      | 1007.58          | 999.12       | 996.23           | 1018.21      |
| X          | 1000.00      | 1000.00          | 1000.00      | 1000.00          | 1000.00      | 1000.00          | 1000.00      |
| SPECTRUM 3 |              |                  |              |                  |              |                  |              |
| I          | 1032.46      | 1029.58          | 1013.45      | 1017.98          | 1003.47      | 1007.46          | 1017.48      |
| II         | 1033.04      | 1035.42          | 1040.24      | 1045.18          | 1031.96      | 1038.07          | 1045.36      |
| III        | 1046.34      | 1047.56          | 1057.21      | 1058.17          | 1041.91      | 1054.35          | 1052.59      |

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| IV   | 1053.84 | 1046.81 | 1054.23 | 1065.89 | 1057.59 | 1055.74 | 1082.41 |
| V    | 1027.37 | 1011.60 | 1085.91 | 1079.69 | 1074.32 | 1064.87 | 1090.27 |
| VI   | 1017.68 | 1012.82 | 1067.03 | 1066.39 | 1075.54 | 1069.40 | 1076.16 |
| VII  | 995.17  | 991.48  | 1037.88 | 1042.49 | 1028.35 | 1034.63 | 1037.70 |
| VIII | 1020.75 | 1006.26 | 1047.54 | 1040.58 | 1050.59 | 1038.35 | 1051.16 |
| IX   | 985.56  | 973.87  | 1019.30 | 1015.65 | 996.95  | 990.66  | 1023.68 |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## SPECTRUM 4

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| I    | 1030.29 | 1031.01 | 1011.05 | 1017.83 | 1005.25 | 1002.22 | 1016.83 |
| II   | 1030.22 | 1036.73 | 1039.22 | 1047.27 | 1027.24 | 1032.63 | 1049.53 |
| III  | 1047.39 | 1050.36 | 1051.78 | 1063.54 | 1048.73 | 1057.09 | 1054.73 |
| IV   | 1053.88 | 1044.83 | 1057.23 | 1064.72 | 1052.16 | 1063.07 | 1078.73 |
| V    | 1024.50 | 1011.61 | 1083.61 | 1084.69 | 1071.19 | 1064.86 | 1091.65 |
| VI   | 1017.99 | 1018.44 | 1060.54 | 1070.21 | 1071.99 | 1072.06 | 1066.96 |
| VII  | 996.70  | 992.75  | 1034.61 | 1042.45 | 1021.67 | 1028.95 | 1037.32 |
| VIII | 1019.85 | 1006.68 | 1045.05 | 1046.37 | 1047.97 | 1038.22 | 1055.15 |
| IX   | 984.77  | 974.89  | 1015.77 | 1015.49 | 1001.70 | 999.95  | 1019.71 |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## SPECTRUM 5

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| I    | 1032.21 | 1030.84 | 1018.13 | 1014.74 | 1004.96 | 1013.50 | 1018.88 |
| II   | 1031.91 | 1037.79 | 1045.70 | 1043.68 | 1032.72 | 1035.37 | 1049.65 |
| III  | 1047.23 | 1051.51 | 1057.51 | 1053.94 | 1044.33 | 1057.12 | 1056.35 |
| IV   | 1054.22 | 1046.32 | 1059.80 | 1056.21 | 1052.77 | 1062.85 | 1078.00 |
| V    | 1025.51 | 1012.48 | 1087.81 | 1073.34 | 1077.62 | 1066.92 | 1087.38 |
| VI   | 1017.46 | 1018.24 | 1070.69 | 1064.47 | 1074.09 | 1074.28 | 1073.29 |
| VII  | 995.44  | 994.89  | 1040.64 | 1037.03 | 1026.31 | 1027.82 | 1041.53 |
| VIII | 1019.38 | 1005.64 | 1051.21 | 1039.99 | 1045.00 | 1041.17 | 1053.54 |
| IX   | 987.76  | 974.87  | 1020.56 | 1012.28 | 1007.30 | 996.77  | 1021.86 |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## SPECTRUM 6

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| I    | 1032.93 | 1026.79 | 1018.63 | 1015.71 | 1001.77 | 1013.35 | 1012.98 |
| II   | 1033.08 | 1033.86 | 1044.27 | 1047.23 | 1013.15 | 1042.79 | 1043.11 |
| III  | 1044.67 | 1048.90 | 1057.13 | 1059.55 | 1028.11 | 1053.04 | 1050.41 |
| IV   | 1052.89 | 1043.10 | 1057.82 | 1060.96 | 1054.65 | 1056.19 | 1074.07 |
| V    | 1028.53 | 1009.34 | 1088.01 | 1078.67 | 1069.76 | 1067.34 | 1089.49 |
| VI   | 1017.18 | 1014.85 | 1067.66 | 1063.71 | 1059.08 | 1067.26 | 1073.14 |
| VII  | 996.39  | 988.99  | 1041.38 | 1042.38 | 1010.02 | 1028.80 | 1033.32 |
| VIII | 1020.42 | 1002.81 | 1049.49 | 1038.95 | 1043.18 | 1038.30 | 1049.14 |
| IX   | 985.93  | 969.95  | 1016.43 | 1013.28 | 987.97  | 995.44  | 1015.24 |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

| Sample:    | D<br>non-<br>equilibrated | E<br>equilibrated | E<br>non-<br>equilibrated | F<br>equilibrated | F<br>non-<br>equilibrated | G<br>equilibrated | G<br>non-<br>equilibrated |
|------------|---------------------------|-------------------|---------------------------|-------------------|---------------------------|-------------------|---------------------------|
| SPECTRUM 1 |                           |                   |                           |                   |                           |                   |                           |
| I          | 1014.30                   | 1014.37           | 1004.28                   | 1003.42           | 1004.42                   | 1016.53           | 1010.93                   |
| II         | 1061.45                   | 1024.58           | 1026.04                   | 1003.02           | 1010.09                   | 1021.41           | 1007.18                   |
| III        | 1058.61                   | 1046.38           | 1047.44                   | 1014.03           | 1019.59                   | 1024.17           | 1030.96                   |
| IV         | 1078.93                   | 1054.13           | 1044.51                   | 1008.84           | 1013.80                   | 1037.48           | 1034.82                   |
| V          | 1084.85                   | 1079.73           | 1067.52                   | 995.42            | 985.38                    | 1011.87           | 991.27                    |
| VI         | 1070.93                   | 1069.52           | 1066.98                   | 1000.52           | 999.01                    | 1009.51           | 1005.17                   |

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| VII  | 1037.75 | 1031.16 | 1034.11 | 977.31  | 961.22  | 983.00  | 962.91  |
| VIII | 1041.61 | 1052.78 | 1041.08 | 982.73  | 973.70  | 1004.45 | 978.72  |
| IX   | 1016.60 | 1007.77 | 1008.06 | 984.92  | 954.42  | 987.75  | 955.57  |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## SPECTRUM 2

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| I    | 1012.77 | 1011.28 | 1009.32 | 1002.98 | 1006.09 | 1015.56 | 1016.84 |
| II   | 1057.48 | 1024.68 | 1029.20 | 1005.70 | 1008.85 | 1014.69 | 1021.69 |
| III  | 1062.10 | 1043.36 | 1044.11 | 1009.08 | 1020.36 | 1018.16 | 1038.44 |
| IV   | 1068.66 | 1050.30 | 1045.88 | 1008.83 | 1016.16 | 1036.08 | 1040.20 |
| V    | 1080.95 | 1079.96 | 1071.43 | 995.76  | 982.50  | 1010.07 | 1002.02 |
| VI   | 1068.82 | 1068.57 | 1062.99 | 1000.20 | 1003.81 | 1009.05 | 1013.82 |
| VII  | 1038.45 | 1028.24 | 1035.79 | 973.24  | 958.80  | 982.55  | 967.63  |
| VIII | 1040.40 | 1048.87 | 1041.04 | 977.64  | 972.79  | 993.81  | 991.88  |
| IX   | 1012.58 | 1009.70 | 1007.74 | 983.23  | 959.69  | 985.99  | 965.93  |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## SPECTRUM 3

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| I    | 1011.97 | 1008.28 | 1007.93 | 1006.01 | 1005.38 | 1016.68 | 1013.90 |
| II   | 1054.32 | 1023.51 | 1030.54 | 1007.63 | 1011.65 | 1013.81 | 1022.27 |
| III  | 1058.97 | 1043.76 | 1046.50 | 1012.53 | 1022.64 | 1017.09 | 1029.80 |
| IV   | 1065.62 | 1047.06 | 1045.48 | 1010.18 | 1017.26 | 1036.28 | 1043.14 |
| V    | 1084.04 | 1076.71 | 1072.32 | 1002.62 | 988.24  | 1005.08 | 985.20  |
| VI   | 1069.56 | 1067.38 | 1064.55 | 1004.64 | 1003.18 | 1009.18 | 1012.63 |
| VII  | 1042.18 | 1027.89 | 1035.42 | 978.06  | 960.73  | 983.06  | 967.52  |
| VIII | 1046.71 | 1047.76 | 1040.65 | 987.46  | 971.78  | 996.18  | 976.80  |
| IX   | 1012.92 | 1003.66 | 1009.25 | 987.92  | 962.60  | 984.00  | 959.52  |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## SPECTRUM 4

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| I    | 1010.60 | 1001.11 | 997.75  | 1000.70 | 1003.33 | 1013.33 | 1029.68 |
| II   | 1052.61 | 1014.42 | 1018.30 | 1005.29 | 1007.91 | 1014.13 | 1032.95 |
| III  | 1055.53 | 1040.19 | 1046.23 | 1009.90 | 1020.55 | 1016.32 | 1039.97 |
| IV   | 1081.77 | 1041.08 | 1037.60 | 1004.05 | 1009.99 | 1028.04 | 1041.65 |
| V    | 1077.71 | 1075.44 | 1065.17 | 999.08  | 985.79  | 1008.34 | 1001.84 |
| VI   | 1066.74 | 1063.32 | 1061.40 | 995.28  | 1000.84 | 1006.60 | 1020.18 |
| VII  | 1029.58 | 1019.34 | 1024.71 | 977.10  | 960.57  | 980.51  | 980.34  |
| VIII | 1042.38 | 1044.12 | 1032.39 | 984.21  | 972.02  | 994.30  | 995.98  |
| IX   | 1012.56 | 1004.51 | 1004.35 | 988.03  | 955.84  | 987.39  | 968.79  |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## SPECTRUM 5

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| I    | 1011.02 | 999.90  | 996.25  | 997.39  | 1005.93 | 1016.67 | 1020.94 |
| II   | 1049.42 | 1015.46 | 1018.35 | 994.68  | 1013.76 | 1020.52 | 1019.13 |
| III  | 1052.57 | 1040.06 | 1043.77 | 1004.69 | 1023.61 | 1022.47 | 1033.49 |
| IV   | 1072.81 | 1038.87 | 1037.06 | 1006.89 | 1017.22 | 1036.66 | 1038.11 |
| V    | 1079.29 | 1075.90 | 1065.06 | 995.62  | 990.96  | 1007.39 | 994.68  |
| VI   | 1066.82 | 1064.74 | 1059.90 | 995.47  | 1004.40 | 1012.77 | 1010.12 |
| VII  | 1038.47 | 1018.92 | 1024.60 | 972.79  | 962.25  | 982.17  | 973.10  |
| VIII | 1039.47 | 1043.92 | 1033.49 | 983.09  | 974.35  | 997.82  | 980.66  |
| IX   | 1014.81 | 1003.76 | 1004.33 | 977.57  | 960.68  | 989.37  | 965.97  |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## SPECTRUM 6

|      |         |         |         |         |         |         |         |
|------|---------|---------|---------|---------|---------|---------|---------|
| I    | 1015.20 | 997.27  | 995.26  | 1001.16 | 1010.23 | 1014.56 | 1020.80 |
| II   | 1054.76 | 1012.11 | 1020.50 | 999.83  | 1019.47 | 1013.26 | 1022.62 |
| III  | 1055.99 | 1039.89 | 1045.58 | 1009.24 | 1024.05 | 1019.33 | 1035.52 |
| IV   | 1067.63 | 1038.60 | 1035.98 | 1016.03 | 1020.07 | 1027.88 | 1040.49 |
| V    | 1077.81 | 1070.24 | 1067.37 | 996.58  | 987.00  | 1006.78 | 993.17  |
| VI   | 1064.12 | 1059.64 | 1061.62 | 997.81  | 1003.87 | 1010.21 | 1009.96 |
| VII  | 1034.43 | 1016.27 | 1024.60 | 977.72  | 959.29  | 977.44  | 976.52  |
| VIII | 1035.88 | 1042.78 | 1033.68 | 981.72  | 977.51  | 995.70  | 993.13  |
| IX   | 1012.41 | 1001.14 | 1005.08 | 984.94  | 960.38  | 986.62  | 963.64  |
| X    | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 | 1000.00 |

## 2. $^{13}\text{C}$ NMR Peak Ratios

For each of the 84 spectra, simple peak ratios were calculated for the pair of peaks arising from competing positions. These ratios, their average values, and standard deviations are given in the table below. The particular peak ratios taken are given in the left-hand column.

| Sample A |        | equilibrated |        |        |        |        |         |        |  |
|----------|--------|--------------|--------|--------|--------|--------|---------|--------|--|
|          | fid1   | fid2         | fid3   | fid4   | fid5   | fid6   | average | stdev  |  |
| IV/I     | 1.0193 | 1.0213       | 1.0207 | 1.0229 | 1.0213 | 1.0193 | 1.0208  | 0.0014 |  |
| V/II     | 0.9955 | 0.9951       | 0.9945 | 0.9944 | 0.9938 | 0.9956 | 0.9948  | 0.0007 |  |
| III/VIII | 1.0245 | 1.0239       | 1.0251 | 1.0270 | 1.0273 | 1.0238 | 1.0253  | 0.0016 |  |
| VI/X     | 1.0192 | 1.0207       | 1.0177 | 1.0180 | 1.0175 | 1.0172 | 1.0184  | 0.0013 |  |
| VII/IX   | 1.0116 | 1.0103       | 1.0097 | 1.0121 | 1.0078 | 1.0106 | 1.0104  | 0.0015 |  |

| Sample A |        | NON-equilibrated |        |        |        |        |         |        |  |
|----------|--------|------------------|--------|--------|--------|--------|---------|--------|--|
|          | fid1   | fid2             | fid3   | fid4   | fid5   | fid6   | average | stdev  |  |
| IV/I     | 1.0183 | 1.0165           | 1.0167 | 1.0134 | 1.0150 | 1.0159 | 1.0160  | 0.0017 |  |
| V/II     | 0.9804 | 0.9760           | 0.9770 | 0.9758 | 0.9756 | 0.9763 | 0.9768  | 0.0018 |  |
| III/VIII | 1.0461 | 1.0438           | 1.0410 | 1.0434 | 1.0456 | 1.0460 | 1.0443  | 0.0020 |  |
| VI/X     | 1.0157 | 1.0155           | 1.0128 | 1.0184 | 1.0182 | 1.0149 | 1.0159  | 0.0021 |  |
| VII/IX   | 1.0215 | 1.0219           | 1.0181 | 1.0183 | 1.0205 | 1.0196 | 1.0200  | 0.0016 |  |

| Sample B |        | equilibrated |        |        |        |        |         |        |  |
|----------|--------|--------------|--------|--------|--------|--------|---------|--------|--|
|          | fid1   | fid2         | fid3   | fid4   | fid5   | fid6   | average | stdev  |  |
| IV/I     | 1.0406 | 1.0440       | 1.0402 | 1.0457 | 1.0409 | 1.0385 | 1.0417  | 0.0027 |  |
| V/II     | 1.0480 | 1.0426       | 1.0439 | 1.0427 | 1.0403 | 1.0419 | 1.0432  | 0.0026 |  |
| III/VIII | 1.0097 | 1.0093       | 1.0092 | 1.0064 | 1.0060 | 1.0073 | 1.0080  | 0.0016 |  |
| VI/X     | 1.0681 | 1.0658       | 1.0670 | 1.0605 | 1.0707 | 1.0677 | 1.0666  | 0.0034 |  |
| VII/IX   | 1.0195 | 1.0226       | 1.0182 | 1.0185 | 1.0197 | 1.0245 | 1.0205  | 0.0025 |  |

| Sample B |        | NON-equilibrated |        |        |        |        |         |        |  |
|----------|--------|------------------|--------|--------|--------|--------|---------|--------|--|
|          | fid1   | fid2             | fid3   | fid4   | fid5   | fid6   | average | stdev  |  |
| IV/I     | 1.0448 | 1.0427           | 1.0471 | 1.0461 | 1.0409 | 1.0446 | 1.0443  | 0.0022 |  |
| V/II     | 1.0377 | 1.0339           | 1.0330 | 1.0357 | 1.0284 | 1.0300 | 1.0331  | 0.0035 |  |
| III/VIII | 1.0169 | 1.0168           | 1.0169 | 1.0164 | 1.0134 | 1.0198 | 1.0167  | 0.0020 |  |
| VI/X     | 1.0663 | 1.0643           | 1.0664 | 1.0702 | 1.0645 | 1.0637 | 1.0659  | 0.0024 |  |
| VII/IX   | 1.0261 | 1.0296           | 1.0264 | 1.0265 | 1.0244 | 1.0287 | 1.0270  | 0.0019 |  |

| Sample C | lots of drift + peak splitting |        |        |        |        |        | average | stdev  |        |
|----------|--------------------------------|--------|--------|--------|--------|--------|---------|--------|--------|
|          | equilibrated                   | fid1   | fid2   | fid3   | fid4   | fid5   |         |        | fid6   |
| IV/I     |                                | 1.0483 | 1.0612 | 1.0539 | 1.0467 | 1.0476 | 1.0528  | 1.0517 | 0.0055 |
| V/II     |                                | 1.0466 | 1.0506 | 1.0410 | 1.0428 | 1.0435 | 1.0559  | 1.0467 | 0.0056 |
| III/VIII |                                | 1.0018 | 0.9777 | 0.9917 | 1.0007 | 0.9994 | 0.9856  | 0.9928 | 0.0097 |
| VI/X     |                                | 1.0730 | 1.0705 | 1.0755 | 1.0720 | 1.0741 | 1.0591  | 1.0707 | 0.0059 |
| VII/IX   |                                | 1.0181 | 1.0344 | 1.0315 | 1.0199 | 1.0189 | 1.0223  | 1.0242 | 0.0070 |

| Sample C | NON-equilibrated |        |        |        |        |        | average | stdev  |
|----------|------------------|--------|--------|--------|--------|--------|---------|--------|
|          | fid1             | fid2   | fid3   | fid4   | fid5   | fid6   |         |        |
| IV/I     | 1.0427           | 1.0418 | 1.0479 | 1.0607 | 1.0487 | 1.0423 | 1.0473  | 0.0072 |
| V/II     | 1.0181           | 1.0213 | 1.0258 | 1.0312 | 1.0305 | 1.0235 | 1.0251  | 0.0051 |
| III/VIII | 1.0161           | 1.0218 | 1.0154 | 1.0182 | 1.0153 | 1.0142 | 1.0168  | 0.0028 |
| VI/X     | 1.0747           | 1.0709 | 1.0694 | 1.0721 | 1.0743 | 1.0673 | 1.0714  | 0.0029 |
| VII/IX   | 1.0361           | 1.0343 | 1.0444 | 1.0290 | 1.0312 | 1.0335 | 1.0347  | 0.0053 |

| Sample D | equilibrated |        |        |        |        |        | average | stdev  |
|----------|--------------|--------|--------|--------|--------|--------|---------|--------|
|          | fid1         | fid2   | fid3   | fid4   | fid5   | fid6   |         |        |
| IV/I     | 1.0609       | 1.0620 | 1.0638 | 1.0609 | 1.0580 | 1.0603 | 1.0610  | 0.0019 |
| V/II     | 1.0372       | 1.0413 | 1.0430 | 1.0401 | 1.0359 | 1.0445 | 1.0403  | 0.0033 |
| III/VIII | 0.9960       | 0.9978 | 1.0014 | 0.9996 | 1.0027 | 1.0012 | 0.9998  | 0.0025 |
| VI/X     | 1.0667       | 1.0677 | 1.0762 | 1.0670 | 1.0733 | 1.0731 | 1.0707  | 0.0040 |
| VII/IX   | 1.0200       | 1.0216 | 1.0137 | 1.0173 | 1.0192 | 1.0178 | 1.0183  | 0.0027 |

| Sample D | NON-equilibrated |        |        |        |        |        | average | stdev  |
|----------|------------------|--------|--------|--------|--------|--------|---------|--------|
|          | fid1             | fid2   | fid3   | fid4   | fid5   | fid6   |         |        |
| IV/I     | 1.0637           | 1.0552 | 1.0530 | 1.0704 | 1.0611 | 1.0516 | 1.0592  | 0.0072 |
| V/II     | 1.0220           | 1.0222 | 1.0282 | 1.0238 | 1.0285 | 1.0219 | 1.0244  | 0.0031 |
| III/VIII | 1.0163           | 1.0209 | 1.0117 | 1.0126 | 1.0126 | 1.0194 | 1.0156  | 0.0039 |
| VI/X     | 1.0709           | 1.0688 | 1.0696 | 1.0667 | 1.0668 | 1.0641 | 1.0678  | 0.0024 |
| VII/IX   | 1.0208           | 1.0255 | 1.0289 | 1.0168 | 1.0233 | 1.0218 | 1.0229  | 0.0041 |

| Sample E | equilibrated |        |        |        |        |        | average | stdev  |
|----------|--------------|--------|--------|--------|--------|--------|---------|--------|
|          | fid1         | fid2   | fid3   | fid4   | fid5   | fid6   |         |        |
| IV/I     | 1.0392       | 1.0386 | 1.0385 | 1.0399 | 1.0390 | 1.0414 | 1.0394  | 0.0011 |
| V/II     | 1.0538       | 1.0539 | 1.0520 | 1.0602 | 1.0595 | 1.0574 | 1.0561  | 0.0034 |
| III/VIII | 0.9939       | 0.9947 | 0.9962 | 0.9962 | 0.9963 | 0.9972 | 0.9958  | 0.0012 |
| VI/X     | 1.0695       | 1.0686 | 1.0674 | 1.0633 | 1.0647 | 1.0596 | 1.0655  | 0.0037 |
| VII/IX   | 1.0232       | 1.0184 | 1.0241 | 1.0148 | 1.0151 | 1.0151 | 1.0184  | 0.0043 |

| Sample E | NON-equilibrated |        |        |        |        |        | average | stdev  |
|----------|------------------|--------|--------|--------|--------|--------|---------|--------|
|          | fid1             | fid2   | fid3   | fid4   | fid5   | fid6   |         |        |
| IV/I     | 1.0401           | 1.0362 | 1.0373 | 1.0399 | 1.0410 | 1.0409 | 1.0392  | 0.0020 |
| V/II     | 1.0404           | 1.0410 | 1.0405 | 1.0460 | 1.0459 | 1.0459 | 1.0433  | 0.0029 |
| III/VIII | 1.0061           | 1.0029 | 1.0056 | 1.0134 | 1.0099 | 1.0115 | 1.0083  | 0.0040 |
| VI/X     | 1.0670           | 1.0630 | 1.0646 | 1.0614 | 1.0599 | 1.0616 | 1.0629  | 0.0025 |
| VII/IX   | 1.0258           | 1.0278 | 1.0259 | 1.0203 | 1.0202 | 1.0194 | 1.0232  | 0.0037 |



| Sample F |        | equilibrated |        |        |        |        |         |        |  |
|----------|--------|--------------|--------|--------|--------|--------|---------|--------|--|
|          | fid1   | fid2         | fid3   | fid4   | fid5   | fid6   | average | stdev  |  |
| IV/I     | 1.0054 | 1.0058       | 1.0041 | 1.0033 | 1.0095 | 1.0149 | 1.0072  | 0.0043 |  |
| V/II     | 0.9924 | 0.9901       | 0.9950 | 0.9938 | 1.0009 | 0.9968 | 0.9948  | 0.0037 |  |
| III/VIII | 1.0319 | 1.0322       | 1.0254 | 1.0261 | 1.0220 | 1.0280 | 1.0276  | 0.0039 |  |
| VI/X     | 1.0005 | 1.0002       | 1.0046 | 0.9953 | 0.9955 | 0.9978 | 0.9990  | 0.0036 |  |
| VII/IX   | 0.9923 | 0.9898       | 0.9900 | 0.9889 | 0.9951 | 0.9927 | 0.9915  | 0.0023 |  |

| Sample F |        | NON-equilibrated |        |        |        |        |         |        |  |
|----------|--------|------------------|--------|--------|--------|--------|---------|--------|--|
|          | fid1   | fid2             | fid3   | fid4   | fid5   | fid6   | average | stdev  |  |
| IV/I     | 1.0093 | 1.0100           | 1.0118 | 1.0066 | 1.0112 | 1.0097 | 1.0098  | 0.0018 |  |
| V/II     | 0.9755 | 0.9739           | 0.9769 | 0.9781 | 0.9775 | 0.9681 | 0.9750  | 0.0037 |  |
| III/VIII | 1.0471 | 1.0489           | 1.0523 | 1.0499 | 1.0506 | 1.0476 | 1.0494  | 0.0019 |  |
| VI/X     | 0.9990 | 1.0038           | 1.0032 | 1.0008 | 1.0044 | 1.0039 | 1.0025  | 0.0021 |  |
| VII/IX   | 1.0071 | 0.9991           | 0.9981 | 1.0050 | 1.0016 | 0.9989 | 1.0016  | 0.0037 |  |

| Sample G |        | equilibrated |        |        |        |        |         |        |  |
|----------|--------|--------------|--------|--------|--------|--------|---------|--------|--|
|          | fid1   | fid2         | fid3   | fid4   | fid5   | fid6   | average | stdev  |  |
| IV/I     | 1.0206 | 1.0202       | 1.0193 | 1.0145 | 1.0197 | 1.0131 | 1.0179  | 0.0032 |  |
| V/II     | 0.9907 | 0.9954       | 0.9914 | 0.9943 | 0.9871 | 0.9936 | 0.9921  | 0.0030 |  |
| III/VIII | 1.0196 | 1.0245       | 1.0210 | 1.0222 | 1.0247 | 1.0237 | 1.0226  | 0.0020 |  |
| VI/X     | 1.0095 | 1.0091       | 1.0092 | 1.0066 | 1.0128 | 1.0102 | 1.0096  | 0.0020 |  |
| VII/IX   | 0.9952 | 0.9965       | 0.9990 | 0.9930 | 0.9927 | 0.9907 | 0.9945  | 0.0030 |  |

| Sample G |        | NON-equilibrated |        |        |        |        |         |        |  |
|----------|--------|------------------|--------|--------|--------|--------|---------|--------|--|
|          | fid1   | fid2             | fid3   | fid4   | fid5   | fid6   | average | stdev  |  |
| IV/I     | 1.0236 | 1.0230           | 1.0288 | 1.0116 | 1.0168 | 1.0193 | 1.0205  | 0.0060 |  |
| V/II     | 0.9842 | 0.9807           | 0.9637 | 0.9699 | 0.9760 | 0.9712 | 0.9743  | 0.0075 |  |
| III/VIII | 1.0534 | 1.0469           | 1.0543 | 1.0442 | 1.0539 | 1.0427 | 1.0492  | 0.0052 |  |
| VI/X     | 1.0052 | 1.0138           | 1.0126 | 1.0202 | 1.0101 | 1.0100 | 1.0120  | 0.0050 |  |
| VII/IX   | 1.0077 | 1.0018           | 1.0083 | 1.0119 | 1.0074 | 1.0134 | 1.0084  | 0.0041 |  |

### 3. $^{13}\text{C}$ Ratios for Individual Samples

The table below first gives a column that corresponds to the “apparent” preference for  $^{13}\text{C}$  in the x position over the x’ position. This column arises from taking ratios of the averages for equilibrated versus non-equilibrated samples in the table above. To get the direction of the effect right, the first three numbers ( $e/e'$ ,  $d/d'$ ,  $a/a'$ ) are equilibrated / non-equilibrated while the last two ( $b/b'$ ,  $c/c'$ ) are non-equilibrated/equilibrated. The second column gives a corrected x/x’  $^{13}\text{C}$  ratio that has allowed for the calculated equilibrium isotope effects (given in another section)

affecting the equilibrated samples. The third column gives a propagated standard deviation on the measurements, derived in a normal way, i.e., for  $z=x/y$ ,  $\Delta z = z * ((\Delta x/x)^2 + (\Delta y/y)^2)^{1/2}$ .

|          | Apparent<br><sup>13</sup> C ratio | Corrected <sup>13</sup> C ratio for<br>equilibrium isotope effect | Standard<br>deviation |
|----------|-----------------------------------|---|-----------------------|
| Sample A |                                   |   |                       |
| e/e'     | 1.005                             | 1.004   | 0.002                 |
| d/d'     | 1.018                             | 1.019   | 0.002                 |
| a/a'     | 0.982                             | 0.980   | 0.002                 |
| b/b'     | 0.998                             | 0.999   | 0.002                 |
| c/c'     | 1.010                             | 1.010   | 0.002                 |
| Sample B |                                   |   |                       |
| e/e'     | 0.997                             | 0.996   | 0.003                 |
| d/d'     | 1.010                             | 1.011   | 0.004                 |
| a/a'     | 0.991                             | 0.990   | 0.003                 |
| b/b'     | 0.999                             | 1.001   | 0.004                 |
| c/c'     | 1.006                             | 1.007   | 0.003                 |
| Sample C |                                   |   |                       |
| e/e'     | 1.004                             | 1.003   | 0.009                 |
| d/d'     | 1.021                             | 1.022   | 0.007                 |
| a/a'     | 0.976                             | 0.975   | 0.010                 |
| b/b'     | 1.001                             | 1.002   | 0.006                 |
| c/c'     | 1.010                             | 1.011   | 0.009                 |
| Sample D |                                   |   |                       |
| e/e'     | 1.002                             | 1.001   | 0.007                 |
| d/d'     | 1.016                             | 1.016   | 0.004                 |
| a/a'     | 0.984                             | 0.983   | 0.004                 |
| b/b'     | 0.997                             | 0.999   | 0.004                 |
| c/c'     | 1.004                             | 1.005   | 0.005                 |
| Sample E |                                   |   |                       |
| e/e'     | 1.000                             | 0.999   | 0.002                 |
| d/d'     | 1.012                             | 1.013   | 0.004                 |
| a/a'     | 0.988                             | 0.986   | 0.004                 |
| b/b'     | 0.998                             | 0.999   | 0.004                 |
| c/c'     | 1.005                             | 1.006   | 0.006                 |
| Sample F |                                   |   |                       |
| e/e'     | 0.997                             | 0.996   | 0.005                 |
| d/d'     | 1.020                             | 1.021   | 0.005                 |
| a/a'     | 0.979                             | 0.978   | 0.004                 |
| b/b'     | 1.004                             | 1.005   | 0.004                 |
| c/c'     | 1.010                             | 1.011   | 0.004                 |
| Sample G |                                   |   |                       |
| e/e'     | 0.997                             | 0.996   | 0.007                 |
| d/d'     | 1.018                             | 1.019   | 0.008                 |
| a/a'     | 0.975                             | 0.973   | 0.005                 |
| b/b'     | 1.002                             | 1.004   | 0.005                 |
| c/c'     | 1.014                             | 1.015   | 0.005                 |

#### **4. <sup>13</sup>C Ratios and KIEs**

The <sup>13</sup>C ratios given in the main text are calculated as the average of the values of the table above. The 95% confidence limits given in the main text are calculated in a standard way for seven measurements and 6 degrees of freedom: uncertainty = std dev \* 2.447 / (7<sup>1/2</sup>). The KIEs given in the main text are the reciprocal of the <sup>13</sup>C ratios.