Popular Integration Grids Can Result in Large Errors in DFT-Computed Free Energies

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Density functional theory (DFT) has emerged as a powerful tool for analyzing (bio-)organic and organometallic systems and proved remarkably accurate in computing the small free energy differences that underpin many chemical phenomena (e.g. regio- and stereoselective reactions). We show that the lack of rotational invariance of popular DFT integration grids reveals large uncertainties in computed free energies for some isomerizations, torsional barriers, and regio- and stereoselective reactions. The result is that predictions based on DFT-computed free energies for systems with very low-frequency vibrational modes can change qualitatively depending on molecular orientation. For example, for a metal-free propargylation of benzaldehyde, predicted enantioselectivities based on B97-D/def2-TZVP free energies using a popular pruned (75,302) integration grid can vary from 62:38 to 99:1 by simply rotating the transition state structures. Relative free energies for the regiocontrolling transition state structures for an Ir-catalyzed C–H functionalization reaction computed using M06/6-31G(d,p)/LANL2DZ and the same grid can vary by more than 5 kcal/mol, resulting in predicted regioselectivities that range anywhere from 14:86 to >99:1. Errors of these magnitudes occur for different functionals and basis sets, are potentially widespread among modern applications of DFT, and can be reduced by using much denser integration grids than commonly employed.

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Popular Integration Grids Can Result in Large Errors in DFT-Computed Free Energies

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Abstract

Density functional theory (DFT) has emerged as a powerful tool for analyzing (bio-)organic and organometallic systems and proved remarkably accurate in computing the small free energy differences that underpin many chemical phenomena (*e.g.* regio- and stereoselective reactions). We show that the lack of rotational invariance of popular DFT integration grids reveals large uncertainties in computed free energies for some isomerizations, torsional barriers, and regio- and stereoselective reactions. The result is that predictions based on DFT-computed free energies for systems with very low-frequency vibrational modes can change qualitatively depending on molecular orientation. For example, for a metal-free propargylation of benzaldehyde, predicted enantioselectivities based on B97-D/def2-TZVP free energies using a popular pruned (75,302) integration grid can vary from 62:38 to 99:1 by simply rotating the transition state structures. Relative free energies for the regiocontrolling transition state structures for an Ir-catalyzed C–H functionalization reaction computed using M06/6-31G(*d,p*)/LANL2DZ and the same grid can vary by more than 5 kcal mol^{−1}, resulting in predicted regioselectivities that range anywhere from 14:86 to >99:1. Errors of these magnitudes occur for different functionals and basis sets, are potentially widespread among modern applications of DFT, and can be reduced by using much denser integration grids than commonly employed.

Introduction

Density functional theory (DFT) is widely used to understand and predict the properties and reactivity of complex (bio-)organic and organometallic systems,¹⁻⁹ particularly among non-experts. Many of these applications require accuracies in relative free energies (ΔG or $\Delta\Delta G$) that are smaller than the quantities of interest, which are often only a few kcal mol⁻¹. For instance, in the context of regio- and stereoselective reactions, a 1 kcal mol⁻¹ change in relative free energy barriers can be the difference between modest and high selectivity.³ Several recent reviews have highlighted the many challenges faced in achieving such accuracy,^{2,10-12} and errors arising from the choice of DFT functional and basis set are widely appreciated among users. However, there is an additional source of potentially significant errors in DFT free energies that goes largely unnoticed—the integration grid.

The evaluation of integrals over the exchange-correlation potential in DFT requires a numerical integration scheme, which is accomplished in most quantum chemistry programs using atom-centered grids comprising N^r shells of N^Ω points denoted as (N^r, N^Ω) . Integration grid errors can significantly impact energies and other molecular properties, particularly for newer functionals.^{10,13-28} For example, in 2010, Wheeler and Houk²⁴ reported large grid errors in isomerization energies of small organic molecules when members of the M06 suite of functionals²⁹ were paired with the SG-1 grid [a pruned (50,194) grid].³⁰ In 2016, Head-Gordon and co-workers²⁶ assessed grid errors across a wider array of Minnesota functionals, finding that atomization energies are often converged with a (75,302) grid (similar to the ‘fine’ grid in Gaussian) for all but two of these functionals and fully converged for all of them with a (99,590) grid (*i.e.* an ‘ultrafine’ grid). In light of the grid sensitivity of electronic energies from some DFT functionals, there have been recent efforts to account for this in the development and (re)parameterization of DFT functionals^{25,27-28,31} and Herbert *et al.*³² have developed standardized grids designed to provide accurate energies for modern DFT functionals.

These previous discussions of grid errors primarily concerned electronic energies. Here, we show that popular grids can lead to even larger errors in *free energies*, with harrowing implications for DFT studies of organic and organometallic systems. These errors arise from the sensitivity of the entropic component of the free energy to small variations in the values of low-frequency vibrational modes but are distinct from errors due to the treatment of these modes as harmonic oscillators. Moreover, they occur using different DFT functionals and basis sets and require at least a (99,590) grid to be resolved in many cases.

Results and Discussion

In the absence of an external field, the energy of a molecule should be independent of its orientation relative to the lab-fixed Cartesian coordinate system. However, because the atom-centered integration grids used in most quantum chemistry packages are anchored to the Cartesian axes, DFT energies typically lack invariance with respect to rigid-body rotations. While this has been known for decades,^{30,33-35} some users are not aware of this shortcoming because many quantum chemistry codes automatically reorient molecules such that the principle axes are aligned with the Cartesian axes (the so-called ‘standard orientation’). Luckily, this lack of rotational invariance has negligible impact on relative electronic energies, at least for small systems and some DFT functionals (*vide infra*). For instance, the B97-D/def2-TZVP electronic energy (E) of 2-butyne relative to 1,3-butadiene (reaction 1) is plotted in Figure 1A as a function of the rotation of 2-butyne around an axis perpendicular to the molecule using a pruned (75,302) grid. The variation in this relative energy is 0.01 kcal mol⁻¹.

However, first and second derivatives of the DFT energy with respect to nuclear displacements also lack rotational invariance. The result is that both the geometries of stationary points and the values of harmonic vibrational frequencies depend on the molecular orientation. For example, in the case of 2-butyne, the B97-D/def2-TZVP value for the methyl rocking mode using a pruned (75,302) grid, which is the default in Gaussian09³⁶ and has been recommended by Herbert *et al.*³² for B97-derived functionals, varies from 31*i* to 29 cm⁻¹ upon rotation (see Figure 1B). In other words, the very nature of this stationary point on this DFT potential energy surface depends on the molecular orientation, even if the geometry is tightly optimized at each orientation. In terms of zero-point vibrational corrected energies and thermal enthalpies, such fluctuations in low-frequency vibrational modes are typically inconsequential (if one excludes orientations for which there is an anomalous imaginary mode). On the other hand, the impact on free energies is substantial due to the sensitivity of the entropic component to small vibrational frequencies within the standard rigid-rotor/harmonic-oscillator (RRHO) approximation. For example, using this (75,302) grid and excluding the orientations for which the low-frequency mode is imaginary, there is ~1 kcal mol⁻¹ variation in ΔG for reaction 1 (see Figure 1A).

Figure 1. A) B97-D/def2-TZVP energy (E) and free energy (G) of reaction 1 as a function of rotation of D_{3h}-symmetric 2-butyne around the indicated axis using a (75,302) grid. Free energies for orientations at which the low-lying frequency is imaginary are omitted. The grid-converged values are indicated with dotted lines. B) Low-frequency vibration for 2-butyne as a function of the indicated rotation using a (75,302) grid. The grid-converged value is indicated with a dotted line. C) Distribution of RRHO free energies for reaction 1 across 50 representative orientations using four popular integration grids.

Variations in both vibrational frequencies and free energies exhibit a 90° periodicity (see Figures 1A and B), mirroring the octahedral symmetry of the atom-centered grids.³⁷ To assess how these errors behave for different grids, the distribution of free energies for reaction 1 across 50 representative orientations of 2-butyne are plotted for four popular integration grids in Figure

1C. The extent of variations in ΔG contracts with increasing grid size, and by the (99,590) grid becomes negligible. In other words, the lack of rotational invariance can be used as a gauge of the grid errors for a given free energy difference. Similar variations occur using other functionals and basis sets [see SI Figure S1 for data using B97-D,³⁸⁻³⁹ B3LYP,⁴⁰ PBE,⁴¹ ω B97X-D,⁴² and M06-2X⁴³ paired with 6-31G(d), cc-pVTZ, and def2-TZVP]⁴⁴⁻⁴⁵ and different electronic structure packages.⁴⁶

Of course, the real culprit is the RRHO approximation, which should not be used for low-frequency vibrational modes. Instead, these modes should be projected out of the hessian and treated separately as, for example, hindered rotors.⁴⁷⁻⁵⁰ While such treatments are feasible for simple molecules such as 2-butyne, they are impractical for the large systems on which DFT methods are most often applied because the problematic modes rarely involve simple combinations of internal coordinates. Instead, users tend to employ more approximate treatments of the entropic contribution of low-frequency vibrations. Chief among these are the quasi-harmonic approximation of Cramer and Truhlar⁵¹ and the quasi-RRHO approximation of Grimme.⁵² In the former, vibrational frequencies below some cutoff value (typically 100 cm⁻¹) are changed to that cutoff value and the RRHO formulae applied. In the latter, the entropic contributions of vibrational frequencies below some cutoff (again, typically 100 cm⁻¹) are interpolated between those from an effective free-rotor and the RRHO limit. Figure 1A shows that the use of the quasi-RRHO approach reduces variations in ΔG for reaction 1 by limiting the impact of low-frequency vibrations. The quasi-harmonic approximation all but eliminates these variations because the most problematic mode is consistently below the cutoff value, so is shifted to a constant value of 100 cm⁻¹. However, grid errors in quasi-harmonic free energies will remain in cases in which one or more vibrational frequencies exhibit variability around the cutoff value (*vide infra*).

Such grid errors are not isolated to reaction 1 but will occur for any transformation in which one or more molecules exhibit low frequency vibrational modes.⁵³ This includes many of the organic and organometallic molecules studied using DFT,¹⁻⁹ which tend to exhibit large-amplitude rocking motions with very low frequencies (<50 cm⁻¹). Moreover, variations in DFT-computed free energies upon rotations can be substantial, resulting in uncertainties in free energies that can overshadow quantities of interest. Scheme 1 shows four systems that highlight the potential impacts of these grid errors, spanning a range of molecular sizes and complexities. Reaction 2 concerns the relative free energy (ΔG) of the atropisomeric HIV integrase inhibitor **1**

and its diastereomer (**1'**),⁵⁴ while quantifying the rate of reaction 3 requires the torsional free energy barrier ($\Delta G^\ddagger$) of 4,4'-dimethyl-1,1'-biphenyl. Predicting the selectivity of reactions 4 and 5 requires relative free energies ($\Delta\Delta G^\ddagger$) for competing transition state (TS) structures leading to alternative products. In particular, the stereoselective addition of allenyltrichlorosilane to benzaldehyde catalyzed by a 2,2'-biquinoline-*N,N'*-dioxide⁵⁵⁻⁵⁸ (reaction 4) depends on the relative free energy of TS structures leading to enantiomeric products. In reaction 5, Ir can catalyze the C–H functionalization of indole at either C₂ or C₇ depending on the relative free energy of the corresponding TS structures.⁵⁹ Free energy swings of ± 2 kcal mol⁻¹ can be catastrophic for predicting the outcome of reactions such as 4 and 5 because of the exponential dependence of selectivities on $\Delta\Delta G^\ddagger$.³ For each of these transformations, we quantified uncertainties in the energy, enthalpy, and free energy due to integration grid errors by sampling representative orientations, fully optimizing the geometry for each orientation (see Computational Methods for details).

Scheme 1. Representative transformations for which accurate relative free energies are required.

Table 1. Grid converged energy, enthalpy, and free energy differences and minimum and maximum values across representative orientations for four pruned integration grids for reactions 1-5, in kcal mol⁻¹.

Reaction	Grid Converged Value ^a	SG-1		(75,302)		(99,590)		(175,974)	
		Min	Max	Min	Max	Min	Max	Min	Max
Electronic Energy									
(1)	10.1	10.1	10.2	10.1	10.1	10.1	10.1	10.1	10.1
(2)	1.1	0.7	1.5	0.9	1.2	1.1	1.1	1.1	1.1
(3)	2.0	1.6	2.2	1.9	2.0	2.0	2.0	2.0	2.0
(4)	0.5	-0.2	1.2	0.3	0.8	0.5	0.6	0.5	0.5
(5)	1.3	0.1	2.0	0.9	1.6	1.2	1.4	1.3	1.3
Enthalpy (298K)									
(1)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
(2)	1.1	0.6	1.5	0.9	1.4	1.0	1.2	1.0	1.1
(3)	1.4	1.2	2.8	1.3	1.5	1.3	1.4	1.4	1.4
(4)	0.7	0.1	1.2	0.6	0.9	0.6	0.7	0.6	0.7
(5)	1.2	0.1	3.0	0.8	2.1	1.1	1.5	1.2	1.3
Free Energy (RRHO Approximation)									
(1)	8.9	8.2	9.6	8.4	9.2	8.9	9.0	8.9	9.0
(2)	0.7	-0.6	2.8	0.0	2.4	0.5	1.5	0.4	1.1
(3)	2.6	1.0	3.3	0.8	3.5	2.4	3.1	2.5	2.8
(4)	1.4	-1.1	2.6	0.3	2.6	0.8	2.1	1.0	1.8
(5)	1.3	-0.7	6.2	-1.1	5.2	0.4	3.5	0.6	1.7
Free Energy (Quasi-RRHO Approximation) ⁵²									
(1)	9.5	9.1	9.8	9.2	9.6	9.5	9.5	9.5	9.5
(2)	0.9	-0.1	2.4	0.4	2.0	0.7	1.4	0.6	1.2
(3)	2.4	1.5	2.7	1.5	2.8	2.2	2.6	2.3	2.5
(4)	1.0	-0.5	2.0	0.3	1.7	0.7	1.3	0.8	1.2
(5)	1.3	-0.5	5.3	-0.3	4.3	0.8	2.7	0.8	1.5
Free Energy (Quasi-harmonic Approximation) ⁵¹									
(1)	9.7	9.6	9.8	9.7	9.7	9.7	9.7	9.7	9.7
(2)	1.0	0.1	2.3	0.7	1.8	0.9	1.5	0.8	1.3
(3)	2.4	1.6	2.8	2.3	2.6	2.4	2.5	2.4	2.5
(4)	0.8	-0.3	1.8	0.3	1.3	0.6	0.9	0.6	0.9
(5)	1.2	-0.6	4.7	-0.1	3.9	0.6	2.3	0.8	1.4

^aRotationally averaged energy differences using a (175,974) grid.

Table 1 contains grid-converged energies, enthalpies, and free energies (using the RRHO, quasi-RRHO, and quasi-harmonic approximations)⁵¹⁻⁵² for reactions 1-5 as well as the minimum and maximum values that can be obtained by varying one or both molecular orientations using four popular integration grids. For several of these reactions there are large variations in the relative electronic energies, particularly using the SG-1 grid. While these variations are due to previously documented grid errors, their implications for predictions of reaction outcomes should not be overlooked. For instance, using the SG-1 grid, the overall sign of the electronic energy difference between the two stereocontrolling TS structures for reaction 4 can vary. In other words, using this grid one cannot confidently predict which of the stereoisomeric products will be preferentially formed. As reported by Head-Gordon and co-workers²⁶ for atomization

energies, these errors in E are essentially converged by the (99,590) grid. Variations in relative enthalpies are slightly larger, and there are troublingly large swings in computed values using both the SG-1 and (75,302) grids. For instance, the relative enthalpy of the regiocontrolling TS structures for reaction 5 can fall anywhere between 0.8 and 2.1 kcal mol⁻¹, preventing any quantitative prediction of regioselectivity.

Figure 2. Distribution of RRHO free energy differences across all combinations of sampled orientations for the two structures for reactions (A) 2, (B) 3, (C) 4, and (D) 5.

Variations in free energies are even larger and more slowly convergent with respect to grid size. Moreover, while the quasi-RRHO and quasi-harmonic approximations reduce the ranges of free energy differences, they remain significant (see Table 1). To provide a better feel for the spread of possible computed free energy differences using different popular grids, the

distributions of free energy values across different orientations for reactions 2-5 are shown in Figure 2. In all cases, the spread of free energy differences computed using the SG-1 and (75,302) grids are substantial. Moreover, for some of these reactions one can obtain *qualitatively* different results using a given level of theory by considering different molecular orientations. For example, using a (75,302) grid the computed torsional free energy barrier for reaction 3 can be anywhere from 0.8 kcal mol⁻¹ to 3.5 kcal mol⁻¹, corresponding to two orders of magnitude in terms of reaction rate. Even worse, the relative free energies of the HIV integrase inhibitor **1**, relative its diastereomer (reaction 2), can vary from -1.1 kcal mol⁻¹ to +2.6 kcal mol⁻¹ using the SG-1 grid. This is particularly important, because it was found experimentally that the biologically active form of this potential drug (**1**) was the less stable diastereomer, necessitating the development of a complex stereoselective synthesis of the desired molecule.⁶⁰

Figure 3. RRHO free energy difference between the stereocontrolling TS structures for reaction 4 for three levels of theory using a pruned (75,302) grid for different orientations of TS(R) and TS(S) in its standard orientation.

The variations in $\Delta\Delta G^\ddagger$ for reactions 4 and 5 are particularly large, which does not bode well for predictions of selectivity. For example, for reaction 4, RRHO $\Delta\Delta G^\ddagger$ values at the B97-D/def2-TZVP level of theory using a pruned (75,302) grid range from 0.3 kcal mol⁻¹ to 2.6 kcal mol⁻¹ depending on the TS orientations. In other words, one can predict selectivities for this reaction that range anywhere from 62:38 to 99:1 by choosing different molecular orientations. Using the SG-1 grid, predicted selectivities can range from 14:86 to 99:1. Even with the (99,590) and (175,974) grids, $\Delta\Delta G^\ddagger$ still varies by 1.2 and 0.8 kcal mol⁻¹, respectively, leading to

unacceptably large uncertainties in predicted enantioselectivities for this simple organocatalytic reaction. Similar variations in $\Delta\Delta G^\ddagger$ for this reaction arise using other popular functionals paired with a pruned (75,302) grid (See Figure 3). In the standard orientation (rotation angle of 0°) these three DFT methods provide consistent $\Delta\Delta G^\ddagger$ values of 0.85 ± 0.15 kcal mol $^{-1}$. However, rotating TS(R) by only 5° results in divergent stereoselectivity predictions. The result is that the molecular orientation has a far greater impact on the predicted selectivity of this reaction than the choice of exchange-correlation functional.

Variations in the free energy difference between the regiocontrolling TS structures for reaction 5 span more than 6 kcal mol $^{-1}$ for the SG-1 and (75,302) grids. For instance, using the (75,302) grid, this free energy difference can fall anywhere from -1.1 to $+5.2$ kcal mol $^{-1}$. Figure 4 shows the energy, enthalpy, and RRHO free energy of TS(C₇) in a fixed orientation relative to different orientations of TS(C₂) using a pruned (75,302) grid. By varying just one TS structure, $\Delta\Delta G^\ddagger$ values fluctuate between ± 1 kcal mol $^{-1}$, again highlighting the sensitivity of DFT free energies to even small changes in orientation. Even with the very large (174,975) grid the $\Delta\Delta G^\ddagger$ values for reaction 5 can vary by more than 1 kcal mol $^{-1}$.

Figure 4. M06/6-31G(d,p)/LANL2DZ energy (E), enthalpy (H), and RRHO free energy (G) of TS(C₇) relative to TS(C₂) using a pruned (75,302) grid for different orientations of TS(C₂) and the pictured orientation of TS(C₇), which is rotated 15° from the standard orientation (grid-converged values indicated with dotted lines).

The lack of rotational invariance of DFT energies, gradients, and vibrational frequencies is widely acknowledged,³³⁻³⁵ and documentation for many quantum chemistry packages include caveats regarding the sensitivity of vibrational frequencies to integration grids. For instance, starting with Gaussian98, a (99,590) grid has been recommended for computing ‘very low frequency modes.’ Similarly, the Orca manual advises users to assess the convergence of vibrational frequencies with respect to integration grid. Unfortunately, these sage pieces of advice seem to have gone largely unheeded among users, as evidenced by a lack of discussion of grids in otherwise comprehensive recent reviews covering the challenges of accurately modeling complex organic and organometallic systems.^{2,10-12}

One means of dealing with the lack of rotational invariance is to use the ‘standard orientation’ in all computations. Equivalently, the atom-centered integration grids can be rotated with the molecule.³⁴ Along the same lines, the Orca manual warns against the use of ‘grossly different orientations’ when computing relative energies of similar molecules. These approaches all rest on the assumption that similar orientations will minimize grid errors in computed free energies. Table 2 lists errors in RRHO free energies for reactions 1-5 using the standard orientation, relative to grid-converged values. In most cases, the errors in the standard orientation are large, particularly for the smaller grids. For example, using the SG-1 grid, $\Delta\Delta G^\ddagger$ for reaction 5 is 1.5 kcal mol⁻¹ from the grid-converged value of 1.3 kcal mol⁻¹. While the errors are smaller for the other reactions and grids, they are not negligible until reaching the (175,974) grid. In other words, the use of a standard orientation (or equivalently, rotating the atom-centered grids with the molecule) does not minimize these grid errors. Similarly, the use of ‘similar orientations’ does not necessarily lead to error cancelation. This can be seen explicitly in Figure 5, which shows the relative free energies of the two regiocontrolling TS structures for reaction 5 as they are rotated simultaneously around the indicated axes starting from their respective standard orientations. Even using a (99,590) grid, there is more than 2 kcal mol⁻¹ variation in the free energy difference between these regiocontrolling TS structures.

Table 2. Errors in RRHO free energy differences for reactions 1-5 using the standard orientation, relative to grid-converged values, in kcal mol⁻¹.

Reaction	SG-1	(75,302)	(99,590)	(175,974)
(1)	0.5	-0.1	0.0	0.0
(2)	0.8	-0.1	0.2	-0.1
(3)	0.0	-0.8	-0.1	0.0
(4)	-0.9	-0.4	0.3	0.0
(5)	1.5	0.6	0.6	-0.2

Figure 5. M06/6-31G(d,p)/LANL2DZ energy (E), enthalpy (H), and RRHO free energy (G) of TS(C₇) relative to TS(C₂) for simultaneous rotation of TS(C₂) and TS(C₇) around the indicated axis starting from the standard orientation (pictured) using a pruned (99,590) grid. Grid-converged values indicated with dotted lines.

Conclusions

The evaluation of accurate relative free energies is vital for many applications of quantum chemistry to (bio-)organic and organometallic systems.¹⁻⁹ We showed that the lack of rotational invariance of popular integration grids can result in large uncertainties in DFT-computed free energy differences, with SG-1 and pruned (75,302) grids leading to errors exceeding 5 kcal mol⁻¹ in relative free energies for some systems. As the default in Gaussian09 and many other codes, the latter grid is particularly widely used. While the reactions in Scheme 1 were chosen to highlight these errors, they are not atypical. Consequently, errors of this magnitude are potentially widespread among modern DFT applications and can easily overshadow chemically

meaningful free energy differences. In some cases, the outcomes of reactions predicted based on free energies using a given level of DFT theory can vary *qualitatively* depending on molecular orientation. Relative enthalpies, on the other hand, are far less sensitive to grids, and often provide closer agreement with experiment than ostensibly more physically meaningful free energies. In fact, one hallmark of the grid errors detailed above is a qualitative difference between relative enthalpies and free energies.

The underlying source of these errors is the unphysically large contribution of low-frequency vibrational modes to the entropic component of the free energy in the standard RRHO treatment. To this end, the quasi-harmonic and quasi-RRHO approximations⁵¹⁻⁵² reduce, but do not eliminate, these grid errors. At the same time, despite continued advances in more rigorous treatments of the entropic contributions of low-frequency vibrational modes,⁶¹⁻⁶² such approaches are still impractical for the organic and organometallic systems most often subject to DFT computations. Baik *et al.*¹¹ recently warned of the unphysical contributions of low frequency vibrational modes to the free energies in organometallic systems, showing that rotations of a Cp ring in a Rh-complex can lead to variations of nearly 2 kcal mol⁻¹ in the free energy. The grid errors discussed above are arguably more alarming, because they concern larger variations in free energies for rotations of the entire molecule.

The good news is that these errors are reduced substantially using a (99,590) grid in many cases. Consequently, this grid (which is the default in Gaussian16)⁶³ should be considered a minimal grid when using DFT to compute free energies of any system with low-frequency vibrational modes (< 100 cm⁻¹). However, given that errors of ~1 kcal mol⁻¹ remain for some systems even with larger grids, we implore users to compute free energies for several molecular orientations⁶⁴ using multiple integration grids in order to gauge the magnitude of grid errors and to guide the choice of the most appropriate integration grid for a given problem. Quantum chemistry applications always require choices between accuracy and computational expediency, and users must strive to identify and minimize major sources of errors. Herein, we highlighted the choice of integration grid as an often-overlooked source of error in DFT free energy computations. As long as predictions and interpretations based on DFT computed free energies are made with these potential errors in mind, DFT remains a powerful and indispensable tool for analyzing and even predicting the outcome of organic and organometallic reactions.

Theoretical Methods

Gas-phase energies, enthalpies (298K), and free energies (298K) for each energy minimum or TS structure for reactions 1-5 were computed for 25 (for reactions 2-4) or 50 (for reactions 1 and 5) representative orientations using four pruned⁶⁵ integration grids: (50,194), (75,302), (99,590), and (175,974) [the latter uses a (250,974) grid for Ir], accessible in Gaussian via the grid keywords ‘SG1grid,’ ‘Fine,’ ‘Ultrafine,’ and ‘Superfine.’ These orientations were generated by performing independent rigid body rotations around the three principle axes in 10° (or 5°) increments up to 80° (or 85°) starting from the respective standard orientations using AaronTools.⁶⁶ For reaction 1, only the orientation of 2-butyne was varied, because the free energy of 1,3-butadiene is essentially constant across different orientations. For each orientation, the geometry was fully optimized using the corresponding integration grid such that the maximum and RMS gradients were below 1.5×10^{-5} and 1.0×10^{-5} hartree/bohr, respectively. Harmonic vibrational frequencies were then computed via analytic second derivatives. By default, Gaussian uses smaller grids in the solution of the CPHF equations than requested for the SCF equations (the ‘Fine’ grid for a ‘superfine’ SCF grid, ‘SG-1’ for the ‘ultrafine’ SCF grid, and ‘coarse’ for the others); however, the use of larger grids for the CPHF equations does not appear to eliminate these errors (see SI Figure S3). It should also be noted that if geometries were not re-optimized at each orientation, the observed variations in enthalpies and free energies were even larger and there were often many superfluous imaginary vibrational modes. Grid-converged values of energies, enthalpies, and free energies were obtained by averaging the corresponding quantity using a (175,974) grid across all combinations of sampled orientations. In Table 1, the minimum and maximum energy differences correspond to the extreme energy differences across all sampled orientations. For orientations for which the correct rotational symmetry number was not automatically recognized, we manually appended the corresponding correction to the entropy. Quasi-RRHO and quasi-harmonic free energies were computed using AaronTools.⁶⁶

The data in Table 1 for reactions 1-4 were computed at the B97-D/def2-TZVP level of theory using density fitting. It should be noted that the documented grid errors are independent of whether density fitting is used (see SI Figure S4). Additional data for reaction 4 were also computed using B3LYP/6-31G(d) and M06-2X/6-31G(d) for Figure 3. Data for reaction 5 were computed using M06 paired with the LANL2DZ/HayWadt basis set/ECP on Ir and the 6-31G(*d,p*) basis set on all other atoms,^{43,67} following Ref 59. For reaction 4, initial TS structures

were taken from Ref 56; initial TS structures for reaction 5 were taken from Ref 59. Predicted selectivities for reactions 4 and 5 assume Curtin-Hammett conditions. The computations presented above were performed using Gaussian09;³⁶ selected data were also computed using Orca⁶⁸ (see SI). Molecular structure figures were generated using CYLView.⁶⁹

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Supporting Information Available: Additional computational data and figures, absolute energies, Cartesian coordinates.

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Supporting Information

Popular Integration Grids Can Result in Large Errors in DFT-Computed Free Energies

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Contents

	<u>page</u>
Figure S1. Low-lying frequency of 2-butyne as a function of orientation using four DFT functionals and three basis sets	2
Figure S2. Low-lying frequency of 2-butyne as a function of orientation computed with Orca	3
Figure S3. Variations in free energy difference for reaction 5 using pruned and unpruned (75,302) grids.	3
Figure S4. Low-lying frequency of 2-butyne as a function of orientation with and without density fitting	3
Tables S2-S5: Absolute energies, enthalpies, and free energies for reaction 1	4
Tables S6-S13: Absolute energies, enthalpies, and free energies for reaction 2	12
Tables S14-S21: Absolute energies, enthalpies, and free energies for reaction 3	28
Tables S22-S29: Absolute energies, enthalpies, and free energies for reaction 4	44
Tables S30-S37: Absolute energies, enthalpies, and free energies for reaction 5	60

Figure S1. Low-lying frequency of D_{3h} -symmetric 2-butyne as a function of rotations around the indicated axis using B3LYP, wB97X-D, PBE, M06-2X, and B97-D paired with the 6-31G(d), cc-pVTZ, and def2-TZVP basis sets and a (75,302) grid.

Figure S2. Low-lying frequency of 2-butyne as a function of rotations around the indicated axis at the B3LYP/def2-TZVP level of theory and two integration grids computed using Orca.

Figure S3. B3LYP/6-31G(d)/LANL2DZ RRHO free energy difference between regiocontrolling TS structures for reaction 5 using the ‘fine’ grid in Gaussian [a pruned (75,302) grid for the SCF and a pruned (35,110) grid for the CPHF equations] and an unpruned (75,302) grid for the SCF and CPHF equations.

Figure S4. Low-lying frequency of 2-butyne as a function of rotations around the indicated axis at the B97-D/def2-TZVP level of theory and a (75,302) grid with and without density fitting.

Absolute Energies, etc. for Reaction 1

Table S2. Values of the low-lying vibrational frequency (Freq, in cm^{-1}), energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for 2-butyne as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	Freq.	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	71.2	-155.922117	-155.833890	-155.866744	-155.866397	-155.866429
5	x	68.1	-155.922119	-155.833851	-155.866742	-155.866365	-155.866384
10	x	49.3	-155.922115	-155.833853	-155.867058	-155.866483	-155.866399
15	x	11.4	-155.922107	-155.833868	-155.868444	-155.867142	-155.866407
20	x	-52.0	-155.922094	-155.834817	-155.865712	-155.865716	-155.865714
25	x	-57.8	-155.922087	-155.834844	-155.865771	-155.865775	-155.865772
30	x	-28.4	-155.922107	-155.834846	-155.865784	-155.865787	-155.865786
35	x	49.7	-155.922126	-155.833878	-155.867089	-155.866518	-155.866436
40	x	41.3	-155.922127	-155.833847	-155.867188	-155.866515	-155.866359
45	x	15.8	-155.922124	-155.833844	-155.868072	-155.866925	-155.866338
50	x	41.3	-155.922127	-155.833847	-155.867188	-155.866515	-155.866359
55	x	49.7	-155.922126	-155.833878	-155.867089	-155.866518	-155.866436
60	x	-28.0	-155.922107	-155.834846	-155.865784	-155.865787	-155.865785
65	x	-57.8	-155.922087	-155.834844	-155.865771	-155.865775	-155.865772
70	x	-52.0	-155.922094	-155.834817	-155.865712	-155.865716	-155.865714
75	x	11.5	-155.922107	-155.833868	-155.868439	-155.867140	-155.866406
80	x	49.3	-155.922115	-155.833853	-155.867057	-155.866482	-155.866399
85	x	68.1	-155.922119	-155.833851	-155.866741	-155.866365	-155.866384
5	y	75.8	-155.922126	-155.833889	-155.866688	-155.866382	-155.866431
10	y	83.5	-155.922148	-155.833882	-155.866592	-155.866349	-155.866425
15	y	85.3	-155.922158	-155.833860	-155.866522	-155.866293	-155.866375
20	y	92.4	-155.922152	-155.833892	-155.866484	-155.866303	-155.866412
25	y	90.3	-155.922169	-155.833886	-155.866493	-155.866298	-155.866399
30	y	77.7	-155.922179	-155.833858	-155.866611	-155.866322	-155.866377
35	y	24.7	-155.922137	-155.833922	-155.867808	-155.866875	-155.866496

40	y	60.5	-155.922135	-155.833782	-155.866732	-155.866281	-155.866266
45	y	65.0	-155.922112	-155.833774	-155.866652	-155.866247	-155.866251
50	y	60.6	-155.922135	-155.833782	-155.866732	-155.866281	-155.866264
55	y	24.7	-155.922137	-155.833922	-155.867808	-155.866875	-155.866496
60	y	77.7	-155.922179	-155.833858	-155.866611	-155.866322	-155.866377
65	y	90.3	-155.922169	-155.833886	-155.866493	-155.866298	-155.866398
70	y	92.4	-155.922152	-155.833892	-155.866484	-155.866303	-155.866412
75	y	85.3	-155.922158	-155.833860	-155.866522	-155.866293	-155.866375
80	y	83.5	-155.922148	-155.833882	-155.866592	-155.866349	-155.866425
85	y	75.8	-155.922126	-155.833889	-155.866688	-155.866383	-155.866432
5	z	20.4	-155.922105	-155.833842	-155.867870	-155.866846	-155.866380
10	z	-28.6	-155.922092	-155.834774	-155.865673	-155.865677	-155.865673
15	z	8.4	-155.922089	-155.833883	-155.868752	-155.867304	-155.866428
20	z	-28.6	-155.922092	-155.834774	-155.865673	-155.865677	-155.865673
25	z	20.4	-155.922105	-155.833842	-155.867870	-155.866846	-155.866380
30	z	71.2	-155.922117	-155.833891	-155.866744	-155.866397	-155.866429
35	z	20.4	-155.922105	-155.833842	-155.867870	-155.866846	-155.866380
40	z	-28.6	-155.922092	-155.834774	-155.865673	-155.865677	-155.865673
45	z	8.4	-155.922089	-155.833883	-155.868752	-155.867304	-155.866428
50	z	-28.6	-155.922092	-155.834774	-155.865673	-155.865677	-155.865673
55	z	20.4	-155.922105	-155.833842	-155.867870	-155.866846	-155.866380
60	z	71.2	-155.922117	-155.833890	-155.866744	-155.866397	-155.866429
65	z	20.4	-155.922105	-155.833842	-155.867872	-155.866847	-155.866380
70	z	-28.6	-155.922092	-155.834774	-155.865673	-155.865677	-155.865673
75	z	8.6	-155.922089	-155.833883	-155.868737	-155.867297	-155.866429
80	z	-28.6	-155.922092	-155.834774	-155.865673	-155.865677	-155.865673
85	z	20.4	-155.922105	-155.833842	-155.867872	-155.866847	-155.866380
Butadiene			-155.938306	-155.849751	-155.881797	-155.881800	-155.881798

Table S3. Values of the low-lying vibrational frequency (Freq, in cm^{-1}), energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for 2-butyne as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	Freq.	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	23.9639	-155.922135	-155.833896	-155.867782	-155.866835	-155.866443
5	x	17.4613	-155.922133	-155.833878	-155.868052	-155.866953	-155.866414
10	x	-26.0115	-155.922127	-155.834833	-155.865737	-155.865741	-155.865738
15	x	-28.1806	-155.922129	-155.834837	-155.865741	-155.865745	-155.865742
20	x	23.5936	-155.922129	-155.833883	-155.867783	-155.866829	-155.866428
25	x	26.7550	-155.922124	-155.833879	-155.867661	-155.866768	-155.866426
30	x	18.8907	-155.922128	-155.833882	-155.867984	-155.866923	-155.866420
35	x	12.8685	-155.922135	-155.833878	-155.868335	-155.867089	-155.866408
40	x	10.2461	-155.922127	-155.833888	-155.868576	-155.867222	-155.866436
45	x	13.9687	-155.922120	-155.833887	-155.868291	-155.867085	-155.866443
50	x	10.1655	-155.922127	-155.833888	-155.868584	-155.867225	-155.866436
55	x	13.0231	-155.922135	-155.833878	-155.868323	-155.867084	-155.866409
60	x	18.8228	-155.922128	-155.833882	-155.867988	-155.866925	-155.866420
65	x	26.7446	-155.922124	-155.833879	-155.867661	-155.866768	-155.866426
70	x	23.6023	-155.922129	-155.833883	-155.867783	-155.866829	-155.866428
75	x	-28.0491	-155.922129	-155.834838	-155.865741	-155.865745	-155.865742
80	x	-26.0821	-155.922127	-155.834833	-155.865737	-155.865741	-155.865738
85	x	17.5992	-155.922133	-155.833878	-155.868044	-155.866949	-155.866413
5	y	27.2	-155.922132	-155.833887	-155.867651	-155.866766	-155.866432
10	y	23.3	-155.922129	-155.833886	-155.867799	-155.866837	-155.866430
15	y	7.7	-155.922133	-155.833893	-155.868851	-155.867357	-155.866436
20	y	30.9	-155.922136	-155.833885	-155.867522	-155.866700	-155.866422
25	y	26.3	-155.922130	-155.833887	-155.867683	-155.866781	-155.866430
30	y	29.8	-155.922129	-155.833884	-155.867564	-155.866725	-155.866431
35	y	29.0	-155.922136	-155.833880	-155.867574	-155.866721	-155.866415
40	y	37.2	-155.922131	-155.833882	-155.867347	-155.866620	-155.866423
45	y	43.7	-155.922124	-155.833880	-155.867202	-155.866560	-155.866429

50	y	37.2	-155.922131	-155.833882	-155.867347	-155.866620	-155.866423
55	y	29.0	-155.922136	-155.833880	-155.867574	-155.866721	-155.866415
60	y	29.8	-155.922129	-155.833884	-155.867564	-155.866725	-155.866431
65	y	26.3	-155.922130	-155.833887	-155.867682	-155.866781	-155.866430
70	y	30.8	-155.922136	-155.833885	-155.867525	-155.866701	-155.866422
75	y	7.7	-155.922133	-155.833893	-155.868847	-155.867355	-155.866436
80	y	23.4	-155.922129	-155.833886	-155.867795	-155.866835	-155.866431
85	y	27.3	-155.922132	-155.833887	-155.867647	-155.866764	-155.866431
5	z	29.8	-155.922134	-155.833892	-155.867573	-155.866733	-155.866439
10	z	17.5	-155.922132	-155.833891	-155.868077	-155.866977	-155.866438
15	z	35.2	-155.922132	-155.833886	-155.867409	-155.866652	-155.866431
20	z	17.4	-155.922132	-155.833891	-155.868079	-155.866978	-155.866438
25	z	29.8	-155.922134	-155.833892	-155.867574	-155.866734	-155.866439
30	z	24.0	-155.922135	-155.833896	-155.867780	-155.866834	-155.866443
35	z	29.8	-155.922134	-155.833892	-155.867574	-155.866734	-155.866439
40	z	17.4	-155.922132	-155.833891	-155.868079	-155.866978	-155.866438
45	z	35.2	-155.922132	-155.833886	-155.867409	-155.866652	-155.866431
50	z	17.5	-155.922132	-155.833891	-155.868077	-155.866977	-155.866438
55	z	29.8	-155.922134	-155.833892	-155.867573	-155.866733	-155.866439
60	z	24.0	-155.922135	-155.833896	-155.867782	-155.866835	-155.866443
65	z	29.8	-155.922134	-155.833892	-155.867573	-155.866733	-155.866439
70	z	17.4	-155.922132	-155.833891	-155.868078	-155.866978	-155.866438
75	z	35.2	-155.922132	-155.833886	-155.867408	-155.866652	-155.866431
80	z	17.4	-155.922132	-155.833891	-155.868078	-155.866978	-155.866438
85	z	29.8	-155.922134	-155.833892	-155.867573	-155.866733	-155.866439
Butadiene			-155.938267	-155.849800	-155.881935	-155.881935	-155.881936

Table S4. Values of the low-lying vibrational frequency (Freq, in cm^{-1}), energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for 2-butyne as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	Freq.	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	26.3	-155.922130	-155.833880	-155.867674	-155.866772	-155.866423
5	x	28.0	-155.922130	-155.833880	-155.867615	-155.866744	-155.866422
10	x	27.2	-155.922130	-155.833881	-155.867643	-155.866759	-155.866424
15	x	25.7	-155.922130	-155.833879	-155.867695	-155.866782	-155.866421
20	x	24.3	-155.922130	-155.833880	-155.867748	-155.866808	-155.866422
25	x	26.7	-155.922130	-155.833882	-155.867662	-155.866769	-155.866426
30	x	28.0	-155.922130	-155.833879	-155.867614	-155.866743	-155.866420
35	x	24.6	-155.922130	-155.833880	-155.867738	-155.866804	-155.866422
40	x	24.3	-155.922130	-155.833881	-155.867748	-155.866809	-155.866423
45	x	26.0	-155.922130	-155.833880	-155.867682	-155.866776	-155.866422
50	x	24.1	-155.922130	-155.833881	-155.867756	-155.866813	-155.866424
55	x	24.4	-155.922130	-155.833880	-155.867745	-155.866807	-155.866423
60	x	28.1	-155.922130	-155.833879	-155.867609	-155.866741	-155.866421
65	x	26.7	-155.922130	-155.833882	-155.867663	-155.866769	-155.866426
70	x	24.3	-155.922130	-155.833880	-155.867748	-155.866808	-155.866422
75	x	25.7	-155.922130	-155.833879	-155.867694	-155.866781	-155.866421
80	x	27.2	-155.922130	-155.833881	-155.867643	-155.866759	-155.866424
85	x	28.0	-155.922130	-155.833880	-155.867614	-155.866744	-155.866422
5	y	28.5	-155.922130	-155.833879	-155.867595	-155.866734	-155.866420
10	y	27.4	-155.922130	-155.833880	-155.867636	-155.866754	-155.866422
15	y	26.7	-155.922130	-155.833880	-155.867657	-155.866764	-155.866421
20	y	27.1	-155.922130	-155.833878	-155.867644	-155.866757	-155.866420
25	y	26.1	-155.922130	-155.833881	-155.867684	-155.866778	-155.866424
30	y	27.6	-155.922130	-155.833879	-155.867626	-155.866748	-155.866419
35	y	25.0	-155.922130	-155.833882	-155.867726	-155.866799	-155.866425
40	y	25.8	-155.922130	-155.833880	-155.867690	-155.866780	-155.866423
45	y	27.6	-155.922130	-155.833878	-155.867626	-155.866748	-155.866419

50	y	25.9	-155.922130	-155.833880	-155.867690	-155.866780	-155.866423
55	y	25.0	-155.922130	-155.833882	-155.867726	-155.866799	-155.866425
60	y	27.6	-155.922130	-155.833879	-155.867626	-155.866748	-155.866419
65	y	26.1	-155.922130	-155.833881	-155.867684	-155.866778	-155.866424
70	y	27.0	-155.922130	-155.833878	-155.867646	-155.866758	-155.866420
75	y	26.8	-155.922130	-155.833880	-155.867656	-155.866763	-155.866421
80	y	27.4	-155.922130	-155.833880	-155.867636	-155.866754	-155.866422
85	y	28.5	-155.922130	-155.833879	-155.867596	-155.866734	-155.866421
5	z	26.1	-155.922130	-155.833880	-155.867679	-155.866774	-155.866421
10	z	27.4	-155.922130	-155.833879	-155.867634	-155.866752	-155.866420
15	z	24.1	-155.922130	-155.833881	-155.867756	-155.866813	-155.866423
20	z	27.4	-155.922130	-155.833879	-155.867634	-155.866752	-155.866420
25	z	26.1	-155.922130	-155.833880	-155.867681	-155.866775	-155.866421
30	z	26.3	-155.922130	-155.833880	-155.867674	-155.866772	-155.866423
35	z	26.1	-155.922130	-155.833880	-155.867681	-155.866775	-155.866421
40	z	27.4	-155.922130	-155.833879	-155.867634	-155.866752	-155.866420
45	z	24.1	-155.922130	-155.833881	-155.867756	-155.866813	-155.866423
50	z	27.4	-155.922130	-155.833879	-155.867634	-155.866752	-155.866420
55	z	26.1	-155.922130	-155.833880	-155.867679	-155.866774	-155.866421
60	z	26.3	-155.922130	-155.833880	-155.867674	-155.866772	-155.866423
65	z	26.1	-155.922130	-155.833880	-155.867679	-155.866775	-155.866421
70	z	27.4	-155.922130	-155.833879	-155.867633	-155.866752	-155.866420
75	z	24.2	-155.922130	-155.833881	-155.867753	-155.866811	-155.866424
80	z	27.4	-155.922130	-155.833879	-155.867633	-155.866752	-155.866420
85	z	26.1	-155.922130	-155.833880	-155.867679	-155.866775	-155.866421
Butadiene			-155.938275	-155.849793	-155.881933	-155.881934	-155.881934

Table S5. Values of the low-lying vibrational frequency (Freq, in cm^{-1}), energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for 2-butyne as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	Freq.	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	26.5	-155.922129	-155.833881	-155.867667	-155.866770	-155.866422
5	x	26.0	-155.922129	-155.833881	-155.867687	-155.866780	-155.866423
10	x	26.8	-155.922129	-155.833881	-155.867655	-155.866764	-155.866423
15	x	26.0	-155.922129	-155.833881	-155.867685	-155.866779	-155.866424
20	x	26.4	-155.922129	-155.833881	-155.867673	-155.866773	-155.866423
25	x	27.1	-155.922130	-155.833880	-155.867646	-155.866759	-155.866423
30	x	24.8	-155.922129	-155.833882	-155.867733	-155.866802	-155.866424
35	x	26.1	-155.922129	-155.833881	-155.867684	-155.866778	-155.866424
40	x	25.7	-155.922129	-155.833881	-155.867697	-155.866785	-155.866424
45	x	25.5	-155.922129	-155.833881	-155.867704	-155.866788	-155.866423
50	x	25.7	-155.922129	-155.833881	-155.867698	-155.866785	-155.866424
55	x	26.1	-155.922129	-155.833881	-155.867683	-155.866778	-155.866424
60	x	24.8	-155.922129	-155.833882	-155.867732	-155.866802	-155.866424
65	x	27.1	-155.922130	-155.833880	-155.867646	-155.866759	-155.866423
70	x	26.4	-155.922129	-155.833881	-155.867673	-155.866773	-155.866423
75	x	26.0	-155.922129	-155.833881	-155.867686	-155.866779	-155.866424
80	x	26.8	-155.922129	-155.833881	-155.867655	-155.866764	-155.866423
85	x	25.9	-155.922129	-155.833881	-155.867689	-155.866781	-155.866423
5	y	25.7	-155.922129	-155.833881	-155.867697	-155.866785	-155.866424
10	y	26.5	-155.922129	-155.833881	-155.867666	-155.866769	-155.866423
15	y	27.3	-155.922129	-155.833881	-155.867639	-155.866756	-155.866423
20	y	26.7	-155.922129	-155.833881	-155.867660	-155.866767	-155.866423
25	y	26.0	-155.922129	-155.833882	-155.867688	-155.866780	-155.866425
30	y	27.0	-155.922129	-155.833881	-155.867648	-155.866761	-155.866423
35	y	26.6	-155.922129	-155.833881	-155.867664	-155.866769	-155.866424
40	y	27.5	-155.922130	-155.833881	-155.867632	-155.866753	-155.866423
45	y	24.2	-155.922129	-155.833882	-155.867753	-155.866812	-155.866424

50	y	27.6	-155.922130	-155.833881	-155.867629	-155.866751	-155.866423
55	y	26.6	-155.922129	-155.833881	-155.867664	-155.866769	-155.866424
60	y	27.2	-155.922129	-155.833881	-155.867643	-155.866758	-155.866423
65	y	25.9	-155.922129	-155.833882	-155.867689	-155.866781	-155.866425
70	y	26.6	-155.922129	-155.833881	-155.867663	-155.866768	-155.866423
75	y	27.3	-155.922129	-155.833881	-155.867639	-155.866756	-155.866423
80	y	26.5	-155.922129	-155.833881	-155.867669	-155.866770	-155.866424
85	y	25.7	-155.922129	-155.833881	-155.867697	-155.866785	-155.866424
5	z	25.9	-155.922129	-155.833881	-155.867690	-155.866781	-155.866423
10	z	26.8	-155.922129	-155.833881	-155.867656	-155.866764	-155.866424
15	z	25.9	-155.922129	-155.833881	-155.867689	-155.866781	-155.866423
20	z	26.8	-155.922129	-155.833881	-155.867656	-155.866764	-155.866424
25	z	26.0	-155.922129	-155.833881	-155.867687	-155.866780	-155.866423
30	z	26.5	-155.922129	-155.833881	-155.867667	-155.866769	-155.866422
35	z	26.0	-155.922129	-155.833881	-155.867687	-155.866780	-155.866423
40	z	26.8	-155.922129	-155.833881	-155.867656	-155.866764	-155.866424
45	z	25.9	-155.922129	-155.833881	-155.867689	-155.866781	-155.866423
50	z	26.8	-155.922129	-155.833881	-155.867656	-155.866764	-155.866424
55	z	25.9	-155.922129	-155.833881	-155.867690	-155.866781	-155.866423
60	z	26.5	-155.922129	-155.833881	-155.867667	-155.866770	-155.866422
65	z	25.9	-155.922129	-155.833881	-155.867690	-155.866781	-155.866423
70	z	26.8	-155.922129	-155.833881	-155.867656	-155.866764	-155.866424
75	z	26.0	-155.922129	-155.833881	-155.867685	-155.866779	-155.866424
80	z	26.8	-155.922129	-155.833881	-155.867656	-155.866764	-155.866424
85	z	25.9	-155.922129	-155.833881	-155.867690	-155.866781	-155.866423
Butadiene			-155.938275	-155.849791	-155.881931	-155.881931	-155.881931

Absolute Energies, etc. for Reaction 2

Table S6. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for **1** as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1454.481119	-1453.985339	-1454.073145	-1454.068519	-1454.068137
10	x	-1454.480765	-1453.984970	-1454.074151	-1454.068814	-1454.067971
20	x	-1454.481115	-1453.985429	-1454.073897	-1454.068915	-1454.068341
30	x	-1454.481093	-1453.985317	-1454.073299	-1454.068553	-1454.068110
40	x	-1454.480827	-1453.985133	-1454.074208	-1454.068979	-1454.068292
50	x	-1454.480989	-1453.985365	-1454.073858	-1454.068976	-1454.068474
60	x	-1454.481052	-1453.985275	-1454.074035	-1454.068968	-1454.068374
70	x	-1454.480843	-1453.985187	-1454.074083	-1454.069127	-1454.068513
80	x	-1454.480922	-1453.985295	-1454.074046	-1454.069061	-1454.068442
10	y	-1454.480805	-1453.985231	-1454.074340	-1454.069146	-1454.068411
20	y	-1454.480825	-1453.985306	-1454.074701	-1454.069434	-1454.068700
30	y	-1454.480827	-1453.985355	-1454.074340	-1454.069197	-1454.068495
40	y	-1454.481256	-1453.985290	-1454.072959	-1454.068341	-1454.067958
50	y	-1454.480959	-1453.985067	-1454.073397	-1454.068605	-1454.068152
60	y	-1454.480747	-1453.985571	-1454.074815	-1454.069819	-1454.069230
70	y	-1454.481205	-1453.985399	-1454.073795	-1454.069006	-1454.068626
80	y	-1454.481117	-1453.985321	-1454.073879	-1454.069095	-1454.068718
10	z	-1454.480810	-1453.985426	-1454.075259	-1454.069894	-1454.069093
20	z	-1454.480748	-1453.985392	-1454.075000	-1454.069720	-1454.069098
30	z	-1454.481252	-1453.985315	-1454.073558	-1454.068735	-1454.068338
40	z	-1454.480883	-1453.985277	-1454.073632	-1454.068946	-1454.068517
50	z	-1454.481096	-1453.985570	-1454.074912	-1454.069658	-1454.068929
60	z	-1454.481191	-1453.985464	-1454.074274	-1454.069268	-1454.068704
70	z	-1454.481089	-1453.985207	-1454.072776	-1454.068340	-1454.068012
80	z	-1454.480934	-1453.985176	-1454.074554	-1454.069233	-1454.068572

Table S7. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for **1** as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1454.480997	-1453.985391	-1454.074507	-1454.069453	-1454.068921
10	x	-1454.480875	-1453.985661	-1454.076020	-1454.070430	-1454.069519
20	x	-1454.480943	-1453.985520	-1454.075013	-1454.069793	-1454.069139
30	x	-1454.480942	-1453.985501	-1454.074750	-1454.069593	-1454.068959
40	x	-1454.480866	-1453.985586	-1454.076140	-1454.070401	-1454.069422
50	x	-1454.480945	-1453.985419	-1454.074423	-1454.069313	-1454.068680
60	x	-1454.480836	-1453.985682	-1454.076357	-1454.070572	-1454.069499
70	x	-1454.481012	-1453.985422	-1454.074767	-1454.069521	-1454.068860
80	x	-1454.480827	-1453.985478	-1454.075458	-1454.069960	-1454.069090
10	y	-1454.480840	-1453.985628	-1454.076630	-1454.070702	-1454.069555
20	y	-1454.480962	-1453.985474	-1454.075044	-1454.069724	-1454.068966
30	y	-1454.480908	-1453.985507	-1454.075145	-1454.069824	-1454.069088
40	y	-1454.480958	-1453.985512	-1454.075222	-1454.069806	-1454.069018
50	y	-1454.480897	-1453.985414	-1454.074482	-1454.069423	-1454.068817
60	y	-1454.480893	-1453.985494	-1454.075832	-1454.070147	-1454.069057
70	y	-1454.480976	-1453.985541	-1454.075297	-1454.069982	-1454.069333
80	y	-1454.480825	-1453.985466	-1454.075710	-1454.070105	-1454.069139
10	z	-1454.480918	-1453.985495	-1454.075272	-1454.069916	-1454.069166
20	z	-1454.480816	-1453.985433	-1454.075386	-1454.069862	-1454.068977
30	z	-1454.480955	-1453.985407	-1454.074534	-1454.069460	-1454.068862
40	z	-1454.480873	-1453.985476	-1454.075245	-1454.069842	-1454.069019
50	z	-1454.480924	-1453.985599	-1454.075255	-1454.069965	-1454.069259
60	z	-1454.480984	-1453.985388	-1454.074864	-1454.069523	-1454.068762
70	z	-1454.480979	-1453.985599	-1454.075214	-1454.069933	-1454.069219
80	z	-1454.480808	-1453.985385	-1454.075383	-1454.069873	-1454.068955

Table S8. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for **1** as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1454.480902	-1453.985522	-1454.075224	-1454.069885	-1454.069149
10	x	-1454.480891	-1453.985527	-1454.075535	-1454.070082	-1454.069283
20	x	-1454.480898	-1453.985538	-1454.075265	-1454.069929	-1454.069194
30	x	-1454.480891	-1453.985568	-1454.075517	-1454.070090	-1454.069321
40	x	-1454.480901	-1453.985547	-1454.075364	-1454.070012	-1454.069275
50	x	-1454.480898	-1453.985534	-1454.075339	-1454.069979	-1454.069239
60	x	-1454.480900	-1453.985548	-1454.075240	-1454.069939	-1454.069237
70	x	-1454.480885	-1453.985561	-1454.075635	-1454.070156	-1454.069330
80	x	-1454.480889	-1453.985509	-1454.075316	-1454.069936	-1454.069159
10	y	-1454.480898	-1453.985581	-1454.075564	-1454.070126	-1454.069334
20	y	-1454.480893	-1453.985550	-1454.075614	-1454.070150	-1454.069373
30	y	-1454.480883	-1453.985586	-1454.075585	-1454.070152	-1454.069360
40	y	-1454.480894	-1453.985566	-1454.075447	-1454.070059	-1454.069284
50	y	-1454.480894	-1453.985544	-1454.075258	-1454.069939	-1454.069226
60	y	-1454.480899	-1453.985596	-1454.075577	-1454.070143	-1454.069365
70	y	-1454.480890	-1453.985596	-1454.075782	-1454.070246	-1454.069365
80	y	-1454.480891	-1453.985506	-1454.075164	-1454.069854	-1454.069131
10	z	-1454.480884	-1453.985566	-1454.075662	-1454.070154	-1454.069300
20	z	-1454.480890	-1453.985597	-1454.075641	-1454.070192	-1454.069411
30	z	-1454.480892	-1453.985553	-1454.075491	-1454.070049	-1454.069244
40	z	-1454.480891	-1453.985520	-1454.075228	-1454.069892	-1454.069154
50	z	-1454.480897	-1453.985546	-1454.075409	-1454.070037	-1454.069304
60	z	-1454.480889	-1453.985548	-1454.075337	-1454.070002	-1454.069277
70	z	-1454.480903	-1453.985620	-1454.075756	-1454.070269	-1454.069452
80	z	-1454.480890	-1453.985563	-1454.075461	-1454.070086	-1454.069373

Table S9. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for **1** as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1454.480898	-1453.985517	-1454.075248	-1454.069908	-1454.069159
10	x	-1454.480900	-1453.985513	-1454.075237	-1454.069919	-1454.069197
20	x	-1454.480899	-1453.985527	-1454.075347	-1454.069987	-1454.069234
30	x	-1454.480898	-1453.985497	-1454.075237	-1454.069901	-1454.069154
40	x	-1454.480895	-1453.985519	-1454.075279	-1454.069943	-1454.069203
50	x	-1454.480899	-1453.985554	-1454.075358	-1454.070018	-1454.069293
60	x	-1454.480898	-1453.985513	-1454.075198	-1454.069876	-1454.069146
70	x	-1454.480899	-1453.985514	-1454.075285	-1454.069927	-1454.069169
80	x	-1454.480898	-1453.985572	-1454.075531	-1454.070114	-1454.069338
10	y	-1454.480898	-1453.985529	-1454.075344	-1454.069972	-1454.069199
20	y	-1454.480897	-1453.985533	-1454.075330	-1454.069978	-1454.069229
30	y	-1454.480899	-1453.985531	-1454.075296	-1454.069955	-1454.069212
40	y	-1454.480897	-1453.985538	-1454.075403	-1454.070016	-1454.069246
50	y	-1454.480899	-1453.985546	-1454.075396	-1454.070024	-1454.069268
60	y	-1454.480898	-1453.985497	-1454.075243	-1454.069894	-1454.069135
70	y	-1454.480897	-1453.985557	-1454.075547	-1454.070123	-1454.069343
80	y	-1454.480899	-1453.985489	-1454.075085	-1454.069804	-1454.069089
10	z	-1454.480897	-1453.985537	-1454.075287	-1454.069949	-1454.069206
20	z	-1454.480897	-1453.985552	-1454.075357	-1454.070000	-1454.069254
30	z	-1454.480900	-1453.985558	-1454.075454	-1454.070060	-1454.069298
40	z	-1454.480896	-1453.985560	-1454.075562	-1454.070128	-1454.069345
50	z	-1454.480895	-1453.985532	-1454.075416	-1454.070019	-1454.069243
60	z	-1454.480897	-1453.985542	-1454.075413	-1454.070020	-1454.069240
70	z	-1454.480896	-1453.985554	-1454.075411	-1454.070027	-1454.069257
80	z	-1454.480899	-1453.985507	-1454.075222	-1454.069889	-1454.069142

Table S10. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for **1'** as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1454.479660	-1453.983310	-1454.070728	-1454.066120	-1454.065628
10	x	-1454.479212	-1453.983555	-1454.072163	-1454.067328	-1454.066737
20	x	-1454.478941	-1453.983430	-1454.072729	-1454.067531	-1454.066679
30	x	-1454.479198	-1453.983837	-1454.072977	-1454.068003	-1454.067363
40	x	-1454.479186	-1453.983673	-1454.072946	-1454.067827	-1454.067072
50	x	-1454.479141	-1453.983578	-1454.072683	-1454.067723	-1454.067100
60	x	-1454.479562	-1453.983412	-1454.071398	-1454.066643	-1454.066098
70	x	-1454.478977	-1453.983293	-1454.072247	-1454.067120	-1454.066266
80	x	-1454.479261	-1453.983551	-1454.071828	-1454.067055	-1454.066464
10	y	-1454.479076	-1453.983889	-1454.073512	-1454.068256	-1454.067454
20	y	-1454.479143	-1453.983544	-1454.072716	-1454.067524	-1454.066686
30	y	-1454.479172	-1453.983936	-1454.073726	-1454.068536	-1454.067784
40	y	-1454.479241	-1453.983273	-1454.071622	-1454.066658	-1454.065907
50	y	-1454.479102	-1453.983394	-1454.071668	-1454.066843	-1454.066249
60	y	-1454.479284	-1453.983856	-1454.073775	-1454.068299	-1454.067245
70	y	-1454.479357	-1453.983701	-1454.072559	-1454.067548	-1454.066865
80	y	-1454.479030	-1453.983655	-1454.072430	-1454.067605	-1454.067019
10	z	-1454.479145	-1453.983510	-1454.072634	-1454.067472	-1454.066584
20	z	-1454.479217	-1453.983785	-1454.073422	-1454.068216	-1454.067444
30	z	-1454.479232	-1453.983466	-1454.071854	-1454.066943	-1454.066293
40	z	-1454.479357	-1453.983843	-1454.072927	-1454.068008	-1454.067367
50	z	-1454.479167	-1453.983618	-1454.073016	-1454.067673	-1454.066774
60	z	-1454.479204	-1453.983252	-1454.071852	-1454.066764	-1454.065985
70	z	-1454.479198	-1453.983773	-1454.073121	-1454.067967	-1454.067143
80	z	-1454.479133	-1453.983560	-1454.072461	-1454.067492	-1454.066770

Table S11. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for **1'** as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1454.479167	-1453.983713	-1454.073540	-1454.068151	-1454.067321
10	x	-1454.479214	-1453.983712	-1454.073393	-1454.068046	-1454.067097
20	x	-1454.479222	-1453.983796	-1454.073614	-1454.068281	-1454.067443
30	x	-1454.479232	-1453.983578	-1454.072739	-1454.067577	-1454.066821
40	x	-1454.479132	-1453.983872	-1454.074439	-1454.068748	-1454.067628
50	x	-1454.479227	-1453.983628	-1454.073380	-1454.067932	-1454.066910
60	x	-1454.479225	-1453.983719	-1454.073589	-1454.068154	-1454.067136
70	x	-1454.479160	-1453.983527	-1454.073278	-1454.067732	-1454.066630
80	x	-1454.479198	-1453.983700	-1454.073739	-1454.068200	-1454.067161
10	y	-1454.479168	-1453.983713	-1454.073835	-1454.068270	-1454.067170
20	y	-1454.479298	-1453.983764	-1454.073078	-1454.067857	-1454.067010
30	y	-1454.479119	-1453.983606	-1454.073217	-1454.067930	-1454.067084
40	y	-1454.479182	-1453.983731	-1454.073768	-1454.068305	-1454.067374
50	y	-1454.479207	-1453.983786	-1454.074080	-1454.068374	-1454.067129
60	y	-1454.479196	-1453.983730	-1454.073621	-1454.068161	-1454.067178
70	y	-1454.479155	-1453.983726	-1454.073642	-1454.068079	-1454.066962
80	y	-1454.479186	-1453.983640	-1454.073582	-1454.068122	-1454.067123
10	z	-1454.479230	-1453.983659	-1454.073506	-1454.068018	-1454.066967
20	z	-1454.479130	-1453.983725	-1454.074032	-1454.068376	-1454.067258
30	z	-1454.479221	-1453.983697	-1454.073374	-1454.068013	-1454.067175
40	z	-1454.479156	-1453.983662	-1454.073818	-1454.068208	-1454.067057
50	z	-1454.479211	-1453.983650	-1454.073598	-1454.068124	-1454.067152
60	z	-1454.479194	-1453.983742	-1454.074158	-1454.068514	-1454.067379
70	z	-1454.479106	-1453.983642	-1454.073440	-1454.068000	-1454.066988
80	z	-1454.479193	-1453.983703	-1454.074007	-1454.068396	-1454.067312

Table S12. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for **1'** as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1454.479175	-1453.983769	-1454.073777	-1454.068348	-1454.067385
10	x	-1454.479174	-1453.983670	-1454.073324	-1454.067980	-1454.067016
20	x	-1454.479182	-1453.983813	-1454.073790	-1454.068363	-1454.067373
30	x	-1454.479168	-1453.983818	-1454.074005	-1454.068485	-1454.067460
40	x	-1454.479185	-1453.983793	-1454.073880	-1454.068406	-1454.067385
50	x	-1454.479176	-1453.983774	-1454.073755	-1454.068299	-1454.067281
60	x	-1454.479176	-1453.983703	-1454.073346	-1454.067993	-1454.067020
70	x	-1454.479173	-1453.983756	-1454.073732	-1454.068312	-1454.067328
80	x	-1454.479188	-1453.983787	-1454.073743	-1454.068324	-1454.067350
10	y	-1454.479169	-1453.983706	-1454.073361	-1454.068002	-1454.067032
20	y	-1454.479167	-1453.983822	-1454.074193	-1454.068616	-1454.067579
30	y	-1454.479182	-1453.983753	-1454.073606	-1454.068236	-1454.067290
40	y	-1454.479180	-1453.983756	-1454.073531	-1454.068170	-1454.067211
50	y	-1454.479174	-1453.983741	-1454.073714	-1454.068309	-1454.067368
60	y	-1454.479175	-1453.983797	-1454.073755	-1454.068325	-1454.067348
70	y	-1454.479187	-1453.983749	-1454.073569	-1454.068184	-1454.067202
80	y	-1454.479170	-1453.983761	-1454.073774	-1454.068300	-1454.067248
10	z	-1454.479172	-1453.983768	-1454.073785	-1454.068344	-1454.067349
20	z	-1454.479180	-1453.983745	-1454.073645	-1454.068237	-1454.067258
30	z	-1454.479182	-1453.983707	-1454.073402	-1454.068029	-1454.067061
40	z	-1454.479175	-1453.983789	-1454.074011	-1454.068499	-1454.067507
50	z	-1454.479184	-1453.983759	-1454.073666	-1454.068271	-1454.067293
60	z	-1454.479175	-1453.983740	-1454.073577	-1454.068132	-1454.067094
70	z	-1454.479168	-1453.983836	-1454.074374	-1454.068712	-1454.067702
80	z	-1454.479172	-1453.983757	-1454.073936	-1454.068415	-1454.067351

Table S13. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for **1'** as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1454.479175	-1453.983832	-1454.074181	-1454.068628	-1454.067670
10	x	-1454.479174	-1453.983824	-1454.074155	-1454.068606	-1454.067634
20	x	-1454.479174	-1453.983798	-1454.073831	-1454.068369	-1454.067368
30	x	-1454.479175	-1453.983830	-1454.074082	-1454.068557	-1454.067559
40	x	-1454.479175	-1453.983781	-1454.073869	-1454.068390	-1454.067390
50	x	-1454.479175	-1453.983794	-1454.073960	-1454.068466	-1454.067483
60	x	-1454.479173	-1453.983797	-1454.073903	-1454.068420	-1454.067416
70	x	-1454.479178	-1453.983773	-1454.073733	-1454.068288	-1454.067286
80	x	-1454.479174	-1453.983878	-1454.074408	-1454.068774	-1454.067801
10	y	-1454.479176	-1453.983812	-1454.073948	-1454.068442	-1454.067409
20	y	-1454.479174	-1453.983813	-1454.073978	-1454.068471	-1454.067453
30	y	-1454.479174	-1453.983821	-1454.074101	-1454.068531	-1454.067463
40	y	-1454.479175	-1453.983835	-1454.074144	-1454.068580	-1454.067535
50	y	-1454.479173	-1453.983847	-1454.074163	-1454.068616	-1454.067613
60	y	-1454.479171	-1453.983831	-1454.074090	-1454.068559	-1454.067545
70	y	-1454.479174	-1453.983850	-1454.074236	-1454.068671	-1454.067736
80	y	-1454.479175	-1453.983840	-1454.074328	-1454.068705	-1454.067749
10	z	-1454.479175	-1453.983813	-1454.073989	-1454.068472	-1454.067440
20	z	-1454.479175	-1453.983818	-1454.073972	-1454.068463	-1454.067441
30	z	-1454.479176	-1453.983815	-1454.073946	-1454.068453	-1454.067454
40	z	-1454.479174	-1453.983870	-1454.074305	-1454.068723	-1454.067762
50	z	-1454.479175	-1453.983809	-1454.074020	-1454.068517	-1454.067537
60	z	-1454.479174	-1453.983865	-1454.074308	-1454.068716	-1454.067744
70	z	-1454.479173	-1453.983802	-1454.073945	-1454.068460	-1454.067461
80	z	-1454.479178	-1453.983781	-1454.073795	-1454.068337	-1454.067337

Absolute Energies, etc. for Reaction 3

Table S14. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for the reactant as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-541.718847	-541.47537	-541.527976	-541.526456	-541.526719
10	x	-541.718712	-541.475593	-541.5288265	-541.5269175	-541.5269885
20	x	-541.718936	-541.475292	-541.5275475	-541.5261865	-541.5264535
30	x	-541.718878	-541.47546	-541.5280095	-541.5264955	-541.5267605
40	x	-541.718891	-541.475511	-541.5283295	-541.5266535	-541.5268505
50	x	-541.718891	-541.475511	-541.5283295	-541.5266535	-541.5268505
60	x	-541.718878	-541.47546	-541.5280105	-541.5264955	-541.5267615
70	x	-541.718936	-541.475292	-541.5275475	-541.5261865	-541.5264535
80	x	-541.718712	-541.475593	-541.5288265	-541.5269175	-541.5269885
10	y	-541.718759	-541.475613	-541.5284015	-541.5267755	-541.5269965
20	y	-541.71887	-541.475476	-541.5287965	-541.5268045	-541.5268435
30	y	-541.718927	-541.475429	-541.5286305	-541.5266965	-541.5267625
40	y	-541.718744	-541.475562	-541.5283765	-541.5267455	-541.5269605
50	y	-541.718744	-541.475562	-541.5283765	-541.5267455	-541.5269605
60	y	-541.718953	-541.475477	-541.5282715	-541.5266095	-541.5268175
70	y	-541.71887	-541.475476	-541.5287975	-541.5268045	-541.5268435
80	y	-541.718759	-541.475613	-541.5284015	-541.5267755	-541.5269965
10	z	-541.71888	-541.475482	-541.527439	-541.526279	-541.526639
20	z	-541.718793				
30	z	-541.71887	-541.475346	-541.528265	-541.526481	-541.526634
40	z	-541.718652	-541.475573	-541.5285495	-541.5268105	-541.5269745
50	z	-541.71883	-541.475555	-541.5284205	-541.5266775	-541.5268505
60	z	-541.718806	-541.475301	-541.527951	-541.5264	-541.526649
70	z	-541.718858	-541.475686	-541.528624	-541.526907	-541.527083
80	z	-541.71881	-541.475617	-541.528793	-541.526893	-541.52699

Table S15. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for the reactant as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-541.718864	-541.475565	-541.529530	-541.527146	-541.526956
10	x	-541.718872	-541.475607	-541.530112	-541.527443	-541.527001
20	x	-541.718884	-541.475577	-541.530190	-541.527444	-541.526951
30	x	-541.718891	-541.475538	-541.528992	-541.526914	-541.526907
40	x	-541.718870	-541.475602	-541.530274	-541.527512	-541.526978
50	x	-541.718870	-541.475602	-541.530274	-541.527513	-541.526978
60	x	-541.718891	-541.475538	-541.528992	-541.526914	-541.526907
70	x	-541.718884	-541.475577	-541.530190	-541.527444	-541.526951
80	x	-541.718872	-541.475607	-541.530111	-541.527443	-541.527001
10	y	-541.718874	-541.475571	-541.530304	-541.527509	-541.526951
20	y	-541.718860	-541.475588	-541.529367	-541.527118	-541.526973
30	y	-541.718884	-541.475523	-541.528921	-541.526894	-541.526894
40	y	-541.718867	-541.475542	-541.529250	-541.527019	-541.526913
50	y	-541.718867	-541.475542	-541.529250	-541.527019	-541.526913
60	y	-541.718884	-541.475523	-541.528920	-541.526894	-541.526894
70	y	-541.718860	-541.475588	-541.529367	-541.527118	-541.526973
80	y	-541.718874	-541.475570	-541.530304	-541.527509	-541.526951
10	z	-541.718868	-541.475647	-541.530280	-541.527537	-541.527047
20	z	-541.718867	-541.475547	-541.529325	-541.527039	-541.526915
30	z	-541.718882	-541.475553	-541.528698	-541.526818	-541.526931
40	z	-541.718888	-541.475548	-541.529387	-541.527061	-541.526907
50	z	-541.718882	-541.475581	-541.530004	-541.527372	-541.526973
60	z	-541.718884	-541.475533	-541.529295	-541.527010	-541.526889
70	z	-541.718873	-541.475576	-541.529938	-541.527332	-541.526958
80	z	-541.718880	-541.475624	-541.530058	-541.527419	-541.527016

Table S16. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for the reactant as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-541.718871	-541.475593	-541.530320	-541.527523	-541.526984
10	x	-541.718874	-541.475591	-541.530332	-541.527528	-541.526981
20	x	-541.718873	-541.475575	-541.530191	-541.527450	-541.526959
30	x	-541.718873	-541.475561	-541.530285	-541.527488	-541.526944
40	x	-541.718870	-541.475566	-541.530285	-541.527491	-541.526949
50	x	-541.718870	-541.475566	-541.530285	-541.527491	-541.526949
60	x	-541.718873	-541.475561	-541.530285	-541.527488	-541.526944
70	x	-541.718873	-541.475575	-541.530191	-541.527450	-541.526959
80	x	-541.718874	-541.475591	-541.530332	-541.527528	-541.526981
10	y	-541.718878	-541.475536	-541.530059	-541.527366	-541.526908
20	y	-541.718873	-541.475566	-541.530084	-541.527395	-541.526949
30	y	-541.718877	-541.475573	-541.530424	-541.527563	-541.526953
40	y	-541.718874	-541.475559	-541.530166	-541.527430	-541.526940
50	y	-541.718874	-541.475559	-541.530166	-541.527430	-541.526940
60	y	-541.718877	-541.475573	-541.530424	-541.527563	-541.526953
70	y	-541.718873	-541.475566	-541.530084	-541.527395	-541.526949
80	y	-541.718878	-541.475536	-541.530059	-541.527366	-541.526908
10	z	-541.718878	-541.475542	-541.530193	-541.527433	-541.526915
20	z	-541.718873	-541.475574	-541.530087	-541.527400	-541.526958
30	z	-541.718874	-541.475579	-541.530596	-541.527649	-541.526965
40	z	-541.718873	-541.475547	-541.530189	-541.527433	-541.526923
50	z	-541.718875	-541.475545	-541.530220	-541.527446	-541.526920
60	z	-541.718874	-541.475579	-541.530136	-541.527428	-541.526964
70	z	-541.718873	-541.475566	-541.530237	-541.527467	-541.526948
80	z	-541.718878	-541.475552	-541.530363	-541.527520	-541.526926

Table S17. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for the reactant as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-541.718876	-541.475556	-541.530249	-541.527467	-541.526936
10	x	-541.718875	-541.475557	-541.530274	-541.527480	-541.526939
20	x	-541.718877	-541.475555	-541.530258	-541.527471	-541.526936
30	x	-541.718874	-541.475560	-541.530228	-541.527459	-541.526943
40	x	-541.718876	-541.475559	-541.530231	-541.527461	-541.526941
50	x	-541.718876	-541.475559	-541.530231	-541.527461	-541.526941
60	x	-541.718874	-541.475560	-541.530228	-541.527459	-541.526943
70	x	-541.718877	-541.475555	-541.530258	-541.527471	-541.526936
80	x	-541.718875	-541.475557	-541.530273	-541.527480	-541.526939
10	y	-541.718874	-541.475569	-541.530297	-541.527498	-541.526956
20	y	-541.718875	-541.475559	-541.530236	-541.527464	-541.526940
30	y	-541.718875	-541.475570	-541.530285	-541.527493	-541.526955
40	y	-541.718876	-541.475559	-541.530256	-541.527473	-541.526941
50	y	-541.718876	-541.475559	-541.530256	-541.527473	-541.526941
60	y	-541.718875	-541.475570	-541.530285	-541.527493	-541.526955
70	y	-541.718875	-541.475559	-541.530236	-541.527464	-541.526940
80	y	-541.718874	-541.475569	-541.530297	-541.527498	-541.526956
10	z	-541.718874	-541.475559	-541.530260	-541.527474	-541.526941
20	z	-541.718878	-541.475561	-541.530317	-541.527503	-541.526942
30	z	-541.718874	-541.475570	-541.530376	-541.527537	-541.526956
40	z	-541.718877	-541.475570	-541.530258	-541.527480	-541.526954
50	z	-541.718877	-541.475570	-541.530295	-541.527498	-541.526954
60	z	-541.718874	-541.475568	-541.530222	-541.527461	-541.526953
70	z	-541.718878	-541.475559	-541.530285	-541.527487	-541.526940
80	z	-541.718874	-541.475557	-541.530256	-541.527471	-541.526939

Table S18. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for the TS as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-541.715988	-541.473312	-541.523836	-541.522749	-541.522894
10	x	-541.71566	-541.473332	-541.5249405	-541.5232005	-541.5230525
20	x	-541.715586	-541.473423	-541.5242115	-541.5230235	-541.5231435
30	x	-541.715909	-541.473202	-541.5235335	-541.5225755	-541.5227955
40	x	-541.715676	-541.473272	-541.5237475	-541.5226995	-541.5228605
50	x	-541.715676	-541.473272	-541.5237475	-541.5226995	-541.5228605
60	x	-541.715897	-541.473222	-541.5235565	-541.5225955	-541.5228185
70	x	-541.715586	-541.473423	-541.5242115	-541.5230235	-541.5231435
80	x	-541.71566	-541.473332	-541.5249405	-541.5232005	-541.5230525
10	y	-541.715986	-541.473311	-541.5238425	-541.5227485	-541.5228895
20	y	-541.715722	-541.473278	-541.5238015	-541.5227565	-541.5229415
30	y	-541.715731	-541.473259	-541.5237475	-541.5227225	-541.5229165
40	y	-541.716123	-541.473101	-541.5241375	-541.5226645	-541.5226325
50	y	-541.716136	-541.473118	-541.5241135	-541.5226655	-541.5226485
60	y	-541.715731	-541.473259	-541.5237475	-541.5227225	-541.5229165
70	y	-541.715722	-541.473278	-541.5238015	-541.5227565	-541.5229415
80	y	-541.715987	-541.473311	-541.5238355	-541.5227455	-541.5228885
10	z	-541.715924	-541.473287	-541.523932	-541.522767	-541.5229
20	z	-541.715563	-541.473235	-541.5235565	-541.5226615	-541.5229295
30	z	-541.715735	-541.473429	-541.5244035	-541.5230565	-541.5230985
40	z	-541.715762	-541.473303	-541.523951	-541.522875	-541.52306
50	z	-541.715845	-541.47325	-541.5238565	-541.5227315	-541.5228795
60	z	-541.715708	-541.473293	-541.5246025	-541.5230085	-541.5229025
70	z	-541.715508	-541.473302	-541.524397	-541.523033	-541.523082
80	z	-541.715948	-541.473421	-541.524898	-541.523211	-541.523099

Table S19. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for the TS as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-541.715767	-541.473437	-541.526522	-541.523972	-541.523130
10	x	-541.715740	-541.473411	-541.525745	-541.523586	-541.523107
20	x	-541.715778	-541.473331	-541.524900	-541.523156	-541.522994
30	x	-541.715751	-541.473392	-541.525799	-541.523597	-541.523079
40	x	-541.715693	-541.473432	-541.525960	-541.523707	-541.523148
50	x	-541.715768	-541.473343	-541.525075	-541.523233	-541.523003
60	x	-541.715751	-541.473392	-541.525800	-541.523597	-541.523079
70	x	-541.715724	-541.473368	-541.525648	-541.523513	-541.523055
80	x	-541.715721	-541.473404	-541.525410	-541.523443	-541.523123
10	y	-541.715745	-541.473380	-541.525520	-541.523465	-541.523078
20	y	-541.715744	-541.473314	-541.524990	-541.523194	-541.523005
30	y	-541.715751	-541.473345	-541.525464	-541.523416	-541.523028
40	y	-541.715724	-541.473332	-541.524651	-541.523071	-541.523008
50	y	-541.715724	-541.473332	-541.524651	-541.523071	-541.523008
60	y	-541.715751	-541.473345	-541.525481	-541.523424	-541.523028
70	y	-541.715727	-541.473368	-541.525270	-541.523354	-541.523075
80	y	-541.715753	-541.473400	-541.525708	-541.523562	-541.523100
10	z	-541.715748	-541.473365	-541.527468	-541.524400	-541.523042
20	z	-541.715712	-541.473345	-541.527140	-541.524230	-541.523049
30	z	-541.715739	-541.473283	-541.524707	-541.523053	-541.522946
40	z	-541.715739				
50	z	-541.715726	-541.473386	-541.526063	-541.523731	-541.523107
60	z	-541.715753	-541.473255	-541.524869	-541.523078	-541.522876
70	z	-541.715707				
80	z	-541.715748	-541.473380	-541.525826	-541.523600	-541.523057

Table S20. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for the TS as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-541.715727	-541.473383	-541.526265	-541.523820	-541.523086
10	x	-541.715736	-541.473321	-541.526185	-541.523743	-541.523006
20	x	-541.715732	-541.473343	-541.525924	-541.523631	-541.523034
30	x	-541.715727	-541.473348	-541.525968	-541.523655	-541.523041
40	x	-541.715728	-541.473309	-541.525794	-541.523549	-541.522993
50	x	-541.715728	-541.473309	-541.525794	-541.523549	-541.522993
60	x	-541.715738	-541.473345	-541.525877	-541.523608	-541.523033
70	x	-541.715732	-541.473341	-541.525613	-541.523483	-541.523031
80	x	-541.715734	-541.473324	-541.526034	-541.523672	-541.523010
10	y	-541.715727	-541.473327	-541.525944	-541.523632	-541.523017
20	y	-541.715729	-541.473327	-541.525935	-541.523627	-541.523017
30	y	-541.715742	-541.473311	-541.526022	-541.523656	-541.522988
40	y	-541.715729	-541.473332	-541.525697	-541.523516	-541.523020
50	y	-541.715729	-541.473332	-541.525697	-541.523516	-541.523020
60	y	-541.715742	-541.473311	-541.526022	-541.523656	-541.522988
70	y	-541.715729	-541.473327	-541.525935	-541.523627	-541.523017
80	y	-541.715743	-541.473311	-541.526058	-541.523673	-541.522988
10	z	-541.715738	-541.473390	-541.526065	-541.523727	-541.523091
20	z	-541.715732	-541.473315	-541.526301	-541.523795	-541.522999
30	z	-541.715733	-541.473311	-541.525888	-541.523593	-541.522993
40	z	-541.715734	-541.473348	-541.526113	-541.523724	-541.523038
50	z	-541.715734	-541.473348	-541.525879	-541.523612	-541.523038
60	z	-541.715731	-541.473309	-541.526152	-541.523721	-541.522997
70	z	-541.715733	-541.473321	-541.525938	-541.523623	-541.523007
80	z	-541.715738	-541.473387	-541.525940	-541.523666	-541.523088

Table S21. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for the TS as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-541.715731	-541.473394	-541.526067	-541.523733	-541.523103
10	x	-541.715732	-541.473364	-541.525989	-541.523677	-541.523066
20	x	-541.715733	-541.473344	-541.525991	-541.523665	-541.523038
30	x	-541.715732	-541.473365	-541.525987	-541.523676	-541.523066
40	x	-541.715731	-541.473387	-541.526002	-541.523698	-541.523094
50	x	-541.715733	-541.473363	-541.526003	-541.523682	-541.523062
60	x	-541.715732	-541.473365	-541.525987	-541.523676	-541.523066
70	x	-541.715733	-541.473344	-541.525991	-541.523665	-541.523038
80	x	-541.715732	-541.473364	-541.525989	-541.523677	-541.523066
10	y	-541.715730	-541.473395	-541.526091	-541.523746	-541.523104
20	y	-541.715732	-541.473362	-541.526019	-541.523689	-541.523061
30	y	-541.715733	-541.473345	-541.526013	-541.523676	-541.523040
40	y	-541.715731	-541.473366	-541.526034	-541.523700	-541.523067
50	y	-541.715731	-541.473366	-541.526034	-541.523700	-541.523067
60	y	-541.715733	-541.473345	-541.526013	-541.523676	-541.523040
70	y	-541.715732	-541.473362	-541.526019	-541.523689	-541.523061
80	y	-541.715728	-541.473392	-541.526115	-541.523756	-541.523102
10	z	-541.715731	-541.473385	-541.526041	-541.523715	-541.523091
20	z	-541.715733	-541.473345	-541.526087	-541.523711	-541.523038
30	z	-541.715734	-541.473361	-541.526219	-541.523785	-541.523058
40	z	-541.715734	-541.473342	-541.526032	-541.523683	-541.523036
50	z	-541.715734	-541.473340	-541.525914	-541.523625	-541.523031
60	z	-541.715734	-541.473361	-541.526120	-541.523737	-541.523057
70	z	-541.715734	-541.473345	-541.525956	-541.523648	-541.523039
80	z	-541.715731	-541.473386	-541.526085	-541.523737	-541.523093

Absolute Energies, etc. for Reaction 4

Table S22. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS(R) as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-2702.675121	-2702.170499	-2702.267814	-2702.262796	-2702.262434
10	x	-2702.674927	-2702.170903	-2702.267745	-2702.262996	-2702.262740
20	x	-2702.675131	-2702.170601	-2702.267535	-2702.262586	-2702.262365
30	x	-2702.674975	-2702.170683	-2702.267825	-2702.262810	-2702.262354
40	x	-2702.675255	-2702.170955	-2702.267843	-2702.263039	-2702.262712
50	x	-2702.674847	-2702.170732	-2702.268514	-2702.263318	-2702.262850
60	x	-2702.675256	-2702.171171	-2702.269473	-2702.263993	-2702.263437
70	x	-2702.675273	-2702.171011	-2702.268486	-2702.263496	-2702.263252
80	x	-2702.675044	-2702.170844	-2702.269234	-2702.263734	-2702.263079
10	y	-2702.675210	-2702.170976	-2702.268246	-2702.263350	-2702.262989
20	y	-2702.674321	-2702.170382	-2702.268937	-2702.263501	-2702.263000
30	y	-2702.675638	-2702.171341	-2702.269129	-2702.263991	-2702.263711
40	y	-2702.675011	-2702.170850	-2702.269045	-2702.263685	-2702.263227
50	y	-2702.674965	-2702.171020	-2702.268722	-2702.263620	-2702.263381
60	y	-2702.675697	-2702.171161	-2702.267952	-2702.263223	-2702.263046
70	y	-2702.675439	-2702.170991	-2702.267297	-2702.262755	-2702.262589
80	y	-2702.674681	-2702.170796	-2702.268818	-2702.263524	-2702.262924
10	z	-2702.675089	-2702.170583	-2702.267786	-2702.262875	-2702.262577
20	z	-2702.675142	-2702.171281	-2702.268846	-2702.263697	-2702.263166
30	z	-2702.674946	-2702.170895	-2702.268394	-2702.263359	-2702.263119
40	z	-2702.675118	-2702.171052	-2702.268110	-2702.263270	-2702.262984
50	z	-2702.674982	-2702.170979	-2702.269491	-2702.263895	-2702.263022
60	z	-2702.675048	-2702.170482	-2702.267461	-2702.262493	-2702.262145
70	z	-2702.675550	-2702.171202	-2702.268098	-2702.263326	-2702.263132
80	z	-2702.674541	-2702.170613	-2702.268715	-2702.263305	-2702.262758

Table S23. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS(R) as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-2702.674952	-2702.170791	-2702.269745	-2702.264016	-2702.263471
10	x	-2702.674892	-2702.170931	-2702.269565	-2702.263981	-2702.263388
20	x	-2702.674985	-2702.170927	-2702.270054	-2702.264232	-2702.263705
30	x	-2702.674874	-2702.170957	-2702.270232	-2702.264346	-2702.263602
40	x	-2702.675032	-2702.170924	-2702.269925	-2702.264175	-2702.263688
50	x	-2702.674849	-2702.170831	-2702.270800	-2702.264518	-2702.263534
60	x	-2702.674907	-2702.170882	-2702.269817	-2702.264088	-2702.263528
70	x	-2702.674854	-2702.170809	-2702.270135	-2702.264230	-2702.263496
80	x	-2702.674804	-2702.170936	-2702.271131	-2702.264790	-2702.263916
10	y	-2702.674866	-2702.170913	-2702.270050	-2702.264259	-2702.263585
20	y	-2702.674981	-2702.170807	-2702.269495	-2702.263922	-2702.263507
30	y	-2702.674827	-2702.170924	-2702.270510	-2702.264424	-2702.263596
40	y	-2702.674972	-2702.170950	-2702.270083	-2702.264260	-2702.263584
50	y	-2702.674832	-2702.170939	-2702.270881	-2702.264636	-2702.263858
60	y	-2702.674990	-2702.170810	-2702.270294	-2702.264218	-2702.263258
70	y	-2702.674703	-2702.170793	-2702.270428	-2702.264398	-2702.263639
80	y	-2702.674893	-2702.170964	-2702.270582	-2702.264551	-2702.263866
10	z	-2702.674752	-2702.170825	-2702.270091	-2702.264176	-2702.263392
20	z	-2702.674933	-2702.170767	-2702.269396	-2702.263829	-2702.263285
30	z	-2702.674837	-2702.170896	-2702.270331	-2702.264371	-2702.263661
40	z	-2702.674856	-2702.170854	-2702.270205	-2702.264325	-2702.263628
50	z	-2702.674925	-2702.170941	-2702.269954	-2702.264184	-2702.263567
60	z	-2702.674852	-2702.170820	-2702.270095	-2702.264199	-2702.263512
70	z	-2702.674823	-2702.170801	-2702.270154	-2702.264212	-2702.263462
80	z	-2702.674896	-2702.170764	-2702.269251	-2702.263738	-2702.263217

Table S24. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS(R) as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-2702.674823	-2702.170875	-2702.270942	-2702.264637	-2702.263787
10	x	-2702.674865	-2702.170938	-2702.270766	-2702.264585	-2702.263728
20	x	-2702.674822	-2702.170887	-2702.270898	-2702.264631	-2702.263802
30	x	-2702.674842	-2702.170884	-2702.270622	-2702.264493	-2702.263694
40	x	-2702.674830	-2702.170913	-2702.270773	-2702.264599	-2702.263791
50	x	-2702.674852	-2702.170912	-2702.270877	-2702.264630	-2702.263767
60	x	-2702.674818	-2702.170910	-2702.270878	-2702.264639	-2702.263835
70	x	-2702.674846	-2702.170908	-2702.270615	-2702.264513	-2702.263749
80	x	-2702.674846	-2702.170927	-2702.270949	-2702.264684	-2702.263829
10	y	-2702.674842	-2702.170897	-2702.270744	-2702.264559	-2702.263718
20	y	-2702.674829	-2702.170929	-2702.271136	-2702.264768	-2702.263871
30	y	-2702.674854	-2702.170894	-2702.270725	-2702.264551	-2702.263781
40	y	-2702.674823	-2702.170877	-2702.270562	-2702.264476	-2702.263735
50	y	-2702.674848	-2702.170924	-2702.270815	-2702.264617	-2702.263841
60	y	-2702.674863	-2702.170935	-2702.271014	-2702.264708	-2702.263816
70	y	-2702.674799	-2702.170899	-2702.270879	-2702.264635	-2702.263853
80	y	-2702.674883	-2702.170904	-2702.270342	-2702.264364	-2702.263637
10	z	-2702.674859	-2702.170875	-2702.270762	-2702.264540	-2702.263781
20	z	-2702.674837	-2702.170927	-2702.270819	-2702.264624	-2702.263825
30	z	-2702.674842	-2702.170886	-2702.270732	-2702.264555	-2702.263755
40	z	-2702.674821	-2702.170921	-2702.270880	-2702.264650	-2702.263864
50	z	-2702.674864	-2702.170872	-2702.270465	-2702.264404	-2702.263668
60	z	-2702.674836	-2702.170899	-2702.270671	-2702.264524	-2702.263751
70	z	-2702.674825	-2702.170939	-2702.271377	-2702.264891	-2702.263889
80	z	-2702.674843	-2702.170873	-2702.270500	-2702.264441	-2702.263769

Table S25. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS(R) as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-2702.674843	-2702.170871	-2702.270711	-2702.264531	-2702.263727
10	x	-2702.674842	-2702.170884	-2702.270684	-2702.264536	-2702.263769
20	x	-2702.674842	-2702.170899	-2702.271064	-2702.264719	-2702.263857
30	x	-2702.674845	-2702.170913	-2702.270901	-2702.264647	-2702.263803
40	x	-2702.674837	-2702.170887	-2702.270803	-2702.264585	-2702.263754
50	x	-2702.674841	-2702.170900	-2702.270864	-2702.264624	-2702.263794
60	x	-2702.674844	-2702.170854	-2702.270643	-2702.264496	-2702.263734
70	x	-2702.674839	-2702.170895	-2702.270928	-2702.264655	-2702.263813
80	x	-2702.674841	-2702.170908	-2702.270976	-2702.264684	-2702.263817
10	y	-2702.674839	-2702.170931	-2702.270965	-2702.264693	-2702.263837
20	y	-2702.674838	-2702.170912	-2702.270899	-2702.264650	-2702.263813
30	y	-2702.674840	-2702.170895	-2702.270855	-2702.264617	-2702.263798
40	y	-2702.674839	-2702.170926	-2702.271090	-2702.264748	-2702.263851
50	y	-2702.674841	-2702.170928	-2702.271077	-2702.264744	-2702.263856
60	y	-2702.674835	-2702.170902	-2702.270971	-2702.264676	-2702.263829
70	y	-2702.674846	-2702.170905	-2702.270932	-2702.264658	-2702.263850
80	y	-2702.674844	-2702.170881	-2702.270731	-2702.264552	-2702.263761
10	z	-2702.674841	-2702.170899	-2702.270752	-2702.264564	-2702.263732
20	z	-2702.674846	-2702.170891	-2702.270834	-2702.264605	-2702.263781
30	z	-2702.674842	-2702.170889	-2702.270941	-2702.264654	-2702.263807
40	z	-2702.674839	-2702.170906	-2702.270894	-2702.264647	-2702.263826
50	z	-2702.674838	-2702.170890	-2702.270925	-2702.264647	-2702.263795
60	z	-2702.674841	-2702.170862	-2702.270679	-2702.264520	-2702.263764
70	z	-2702.674835	-2702.170917	-2702.270978	-2702.264693	-2702.263835
80	z	-2702.674845	-2702.170916	-2702.270908	-2702.264655	-2702.263834

Table S26. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS(S) as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-2702.674434	-2702.169918	-2702.266964	-2702.262173	-2702.262068
10	x	-2702.674045	-2702.169887	-2702.266927	-2702.262202	-2702.262058
20	x	-2702.674390	-2702.169962	-2702.266720	-2702.262032	-2702.261810
30	x	-2702.674315	-2702.169504	-2702.265270	-2702.260870	-2702.260869
40	x	-2702.674275	-2702.169568	-2702.266092	-2702.261371	-2702.261054
50	x	-2702.674013	-2702.169763	-2702.267286	-2702.262200	-2702.261800
60	x	-2702.674427	-2702.169698	-2702.265690	-2702.261337	-2702.261383
70	x	-2702.674264	-2702.169889	-2702.266105	-2702.261778	-2702.261769
80	x	-2702.673868	-2702.169648	-2702.266762	-2702.262025	-2702.261914
10	y	-2702.674502	-2702.169991	-2702.265815	-2702.261425	-2702.261322
20	y	-2702.673963	-2702.169537	-2702.266834	-2702.261967	-2702.261861
30	y	-2702.674033	-2702.169690	-2702.267365	-2702.262308	-2702.262157
40	y	-2702.673997	-2702.169633	-2702.267827	-2702.262515	-2702.262131
50	y	-2702.674000	-2702.169468	-2702.266419	-2702.261658	-2702.261424
60	y	-2702.674705	-2702.170241	-2702.269001	-2702.263311	-2702.262626
70	y	-2702.674215	-2702.169555	-2702.265887	-2702.261280	-2702.261021
80	y	-2702.674138	-2702.169966	-2702.267553	-2702.262568	-2702.262291
10	z	-2702.674453	-2702.170071	-2702.267462	-2702.262557	-2702.262335
20	z	-2702.673766	-2702.169791	-2702.267139	-2702.262292	-2702.262065
30	z	-2702.674236	-2702.169676	-2702.266534	-2702.261841	-2702.261760
40	z	-2702.673955	-2702.169663	-2702.266215	-2702.261697	-2702.261620
50	z	-2702.673964	-2702.169727	-2702.267353	-2702.262394	-2702.262152
60	z	-2702.674406	-2702.169792	-2702.266476	-2702.261862	-2702.261810
70	z	-2702.674251	-2702.169682	-2702.266543	-2702.261762	-2702.261577
80	z	-2702.674231	-2702.169755	-2702.266284	-2702.261715	-2702.261647

Table S27. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS(S) as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-2702.673939	-2702.169736	-2702.268130	-2702.262777	-2702.262463
10	x	-2702.673883	-2702.169618	-2702.267450	-2702.262369	-2702.262115
20	x	-2702.674028	-2702.169729	-2702.267367	-2702.262367	-2702.262169
30	x	-2702.673917	-2702.169600	-2702.267156	-2702.262134	-2702.261804
40	x	-2702.674024	-2702.169838	-2702.268617	-2702.263055	-2702.262440
50	x	-2702.673972	-2702.169781	-2702.268631	-2702.263015	-2702.262581
60	x	-2702.674073	-2702.169783	-2702.267236	-2702.262315	-2702.262144
70	x	-2702.673946	-2702.169828	-2702.268820	-2702.263194	-2702.262650
80	x	-2702.673794	-2702.169655	-2702.267889	-2702.262680	-2702.262404
10	y	-2702.674138	-2702.169718	-2702.266955	-2702.262158	-2702.262049
20	y	-2702.673925	-2702.169612	-2702.267679	-2702.262476	-2702.262200
30	y	-2702.674202	-2702.169845	-2702.267251	-2702.262405	-2702.262320
40	y	-2702.673934	-2702.169693	-2702.267952	-2702.262658	-2702.262266
50	y	-2702.674104	-2702.169831	-2702.267720	-2702.262602	-2702.262393
60	y	-2702.673905	-2702.169742	-2702.268741	-2702.263135	-2702.262515
70	y	-2702.674023	-2702.169741	-2702.267875	-2702.262606	-2702.262237
80	y	-2702.673967	-2702.169781	-2702.268272	-2702.262885	-2702.262491
10	z	-2702.674110	-2702.169777	-2702.267239	-2702.262357	-2702.262255
20	z	-2702.673948	-2702.169834	-2702.268300	-2702.262889	-2702.262508
30	z	-2702.673897	-2702.169716	-2702.268365	-2702.262872	-2702.262418
40	z	-2702.673941	-2702.169855	-2702.268361	-2702.262976	-2702.262678
50	z	-2702.674007	-2702.169688	-2702.267310	-2702.262268	-2702.261932
60	z	-2702.673999	-2702.169677	-2702.267670	-2702.262503	-2702.262258
70	z	-2702.673934	-2702.169616	-2702.267879	-2702.262528	-2702.262150
80	z	-2702.674059	-2702.169835	-2702.268609	-2702.263006	-2702.262509

Table S28. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS(S) as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-2702.674004	-2702.169807	-2702.268190	-2702.262848	-2702.262508
10	x	-2702.673988	-2702.169781	-2702.268521	-2702.262974	-2702.262509
20	x	-2702.673991	-2702.169847	-2702.268739	-2702.263130	-2702.262683
30	x	-2702.673974	-2702.169776	-2702.268415	-2702.262941	-2702.262485
40	x	-2702.674022	-2702.169805	-2702.268648	-2702.263030	-2702.262593
50	x	-2702.673986	-2702.169843	-2702.268780	-2702.263174	-2702.262677
60	x	-2702.673999	-2702.169775	-2702.268062	-2702.262773	-2702.262463
70	x	-2702.674003	-2702.169780	-2702.268368	-2702.262872	-2702.262415
80	x	-2702.673988	-2702.169829	-2702.269045	-2702.263261	-2702.262708
10	y	-2702.674010	-2702.169826	-2702.268228	-2702.262887	-2702.262555
20	y	-2702.673981	-2702.169788	-2702.268686	-2702.263057	-2702.262594
30	y	-2702.674016	-2702.169812	-2702.268819	-2702.263090	-2702.262497
40	y	-2702.673986	-2702.169817	-2702.268464	-2702.262997	-2702.262594
50	y	-2702.673995	-2702.169868	-2702.268768	-2702.263138	-2702.262678
60	y	-2702.674009	-2702.169782	-2702.268100	-2702.262795	-2702.262447
70	y	-2702.673986	-2702.169845	-2702.268857	-2702.263184	-2702.262682
80	y	-2702.673995	-2702.169814	-2702.268463	-2702.262972	-2702.262548
10	z	-2702.673996	-2702.169799	-2702.268458	-2702.262955	-2702.262542
20	z	-2702.673994	-2702.169818	-2702.268795	-2702.263130	-2702.262666
30	z	-2702.674001	-2702.169872	-2702.268711	-2702.263150	-2702.262726
40	z	-2702.674003	-2702.169797	-2702.268279	-2702.262880	-2702.262479
50	z	-2702.673978	-2702.169829	-2702.268724	-2702.263117	-2702.262658
60	z	-2702.673996	-2702.169813	-2702.268390	-2702.262955	-2702.262562
70	z	-2702.673988	-2702.169776	-2702.268247	-2702.262872	-2702.262514
80	z	-2702.673995	-2702.169794	-2702.268284	-2702.262873	-2702.262450

Table S29. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS(S) as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-2702.674002	-2702.169799	-2702.268354	-2702.262927	-2702.262536
10	x	-2702.673996	-2702.169845	-2702.269062	-2702.263286	-2702.262729
20	x	-2702.673998	-2702.169838	-2702.268832	-2702.263157	-2702.262630
30	x	-2702.674000	-2702.169789	-2702.268531	-2702.262984	-2702.262516
40	x	-2702.674001	-2702.169817	-2702.268736	-2702.263095	-2702.262586
50	x	-2702.673999	-2702.169804	-2702.268747	-2702.263080	-2702.262557
60	x	-2702.674000	-2702.169788	-2702.268408	-2702.262919	-2702.262480
70	x	-2702.674003	-2702.169765	-2702.268458	-2702.262905	-2702.262410
80	x	-2702.674003	-2702.169747	-2702.268278	-2702.262842	-2702.262397
10	y	-2702.674003	-2702.169766	-2702.268379	-2702.262894	-2702.262433
20	y	-2702.673999	-2702.169828	-2702.268760	-2702.263127	-2702.262651
30	y	-2702.673998	-2702.169795	-2702.268505	-2702.263000	-2702.262563
40	y	-2702.673998	-2702.169820	-2702.268783	-2702.263133	-2702.262644
50	y	-2702.674002	-2702.169799	-2702.268519	-2702.262999	-2702.262564
60	y	-2702.673999	-2702.169804	-2702.268646	-2702.263053	-2702.262576
70	y	-2702.674000	-2702.169802	-2702.268724	-2702.263075	-2702.262554
80	y	-2702.674001	-2702.169839	-2702.268835	-2702.263159	-2702.262677
10	z	-2702.673998	-2702.169812	-2702.268720	-2702.263108	-2702.262644
20	z	-2702.673999	-2702.169820	-2702.268676	-2702.263083	-2702.262633
30	z	-2702.673999	-2702.169815	-2702.268795	-2702.263124	-2702.262611
40	z	-2702.673997	-2702.169840	-2702.268820	-2702.263166	-2702.262664
50	z	-2702.674001	-2702.169802	-2702.268570	-2702.263015	-2702.262557
60	z	-2702.674004	-2702.169856	-2702.269002	-2702.263240	-2702.262703
70	z	-2702.674001	-2702.169823	-2702.268765	-2702.263122	-2702.262614
80	z	-2702.673999	-2702.169837	-2702.268715	-2702.263109	-2702.262620

Absolute Energies, etc. for Reaction 5

Table S30. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS1 as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1536.415188	-1535.965518	-1536.053551	-1536.049498	-1536.049008
5	x	-1536.414884	-1535.966056	-1536.055713	-1536.051395	-1536.050764
10	x	-1536.415573	-1535.965899	-1536.054318	-1536.050271	-1536.049855
15	x	-1536.415997	-1535.966974	-1536.056555	-1536.051965	-1536.051339
20	x	-1536.416134	-1535.965818	-1536.053951	-1536.049640	-1536.048956
25	x	-1536.416293	-1535.965573	-1536.053335	-1536.049289	-1536.048745
30	x	-1536.415615	-1535.965768	-1536.054708	-1536.050325	-1536.049822
35	x	-1536.415635	-1535.966134	-1536.054593	-1536.050460	-1536.050052
40	x	-1536.415995	-1535.966877	-1536.054737	-1536.050930	-1536.050597
45	x	-1536.415863	-1535.967269	-1536.055613	-1536.051791	-1536.051439
50	x	-1536.415868	-1535.967344	-1536.057094	-1536.052808	-1536.052224
55	x	-1536.415813	-1535.967023	-1536.055349	-1536.051649	-1536.051448
60	x	-1536.416006	-1535.967362	-1536.055806	-1536.051850	-1536.051450
65	x	-1536.415768	-1535.967584	-1536.057720	-1536.053049	-1536.052189
70	x	-1536.415840	-1535.967100	-1536.056168	-1536.051782	-1536.050911
75	x	-1536.415532	-1535.966094	-1536.054192	-1536.050207	-1536.049830
80	x	-1536.415534	-1535.966303	-1536.056287	-1536.051643	-1536.050794
85	x	-1536.415611	-1535.966766	-1536.054701	-1536.050926	-1536.050692
5	y	-1536.415421	-1535.966417	-1536.056000	-1536.051521	-1536.050854
10	y	-1536.415568	-1535.966780	-1536.054734	-1536.051117	-1536.050954
15	y	-1536.415536	-1535.965405	-1536.053313	-1536.049449	-1536.049232
20	y	-1536.415292	-1535.966502	-1536.055329	-1536.051108	-1536.050538
25	y	-1536.415316	-1535.966302	-1536.054697	-1536.050593	-1536.050057
30	y	-1536.415544	-1535.967016	-1536.055449	-1536.051576	-1536.051256
35	y	-1536.415493	-1535.967343	-1536.056853	-1536.052596	-1536.052174

40	y	-1536.415576	-1535.966744	-1536.055069	-1536.051035	-1536.050571
45	y	-1536.415861	-1535.966680	-1536.054975	-1536.051111	-1536.050750
50	y	-1536.415859	-1535.967157	-1536.055200	-1536.051421	-1536.051270
55	y	-1536.415228	-1535.965805	-1536.053601	-1536.049771	-1536.049430
60	y	-1536.415296	-1535.966147	-1536.054016	-1536.050349	-1536.050150
65	y	-1536.415614	-1535.966760	-1536.056467	-1536.052171	-1536.051674
70	y	-1536.415742	-1535.966616	-1536.056136	-1536.051864	-1536.051242
75	y	-1536.415207	-1535.967104	-1536.056756	-1536.052439	-1536.051891
80	y	-1536.414887	-1535.966526	-1536.055844	-1536.051586	-1536.051053
85	y	-1536.414990	-1535.965955	-1536.054685	-1536.050506	-1536.050061
5	z	-1536.415215	-1535.966247	-1536.054484	-1536.050496	-1536.050087
10	z	-1536.415259	-1535.966547	-1536.054901	-1536.050940	-1536.050615
15	z	-1536.415782	-1535.966575	-1536.055244	-1536.050808	-1536.049973
20	z	-1536.415499	-1535.966454	-1536.053611	-1536.050115	-1536.049951
25	z	-1536.415147	-1535.966712	-1536.055683	-1536.051678	-1536.051322
30	z	-1536.415010	-1535.966735	-1536.055117	-1536.051137	-1536.050782
35	z	-1536.415351	-1535.966915	-1536.056827	-1536.052371	-1536.051808
40	z	-1536.415129	-1535.966230	-1536.054192	-1536.050356	-1536.050144
45	z	-1536.415023	-1535.966388	-1536.055263	-1536.051046	-1536.050483
50	z	-1536.415171	-1535.966660	-1536.056088	-1536.051783	-1536.051291
55	z	-1536.415442	-1535.966519	-1536.055183	-1536.050849	-1536.050164
60	z	-1536.415433	-1535.966659	-1536.056251	-1536.051907	-1536.051383
65	z	-1536.415020	-1535.966205	-1536.055385	-1536.050985	-1536.050307
70	z	-1536.414888	-1535.966797	-1536.056448	-1536.052245	-1536.051825
75	z	-1536.415148	-1535.966641	-1536.055817	-1536.051650	-1536.051120
80	z	-1536.415057	-1535.966248	-1536.054914	-1536.050859	-1536.050406
85	z	-1536.415329	-1535.966122	-1536.054222	-1536.050182	-1536.049716

Table S31. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS1 as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1536.413447	-1535.965634	-1536.056763	-1536.052311	-1536.051673
5	x	-1536.413615	-1535.965644	-1536.056620	-1536.052254	-1536.051722
10	x	-1536.413534	-1535.965873	-1536.058189	-1536.053191	-1536.052240
15	x	-1536.413265	-1535.965813	-1536.059093	-1536.053787	-1536.052624
20	x	-1536.413490	-1535.965618	-1536.056975	-1536.052344	-1536.051500
25	x	-1536.413606	-1535.965827	-1536.057961	-1536.053055	-1536.052063
30	x	-1536.413704	-1535.965812	-1536.057342	-1536.052706	-1536.052025
35	x	-1536.413478	-1535.966423	-1536.059238	-1536.054506	-1536.053929
40	x	-1536.413508	-1535.965605	-1536.057277	-1536.052642	-1536.051917
45	x	-1536.413495	-1535.966186	-1536.058629	-1536.053756	-1536.052973
50	x	-1536.413472	-1535.965866	-1536.057230	-1536.052708	-1536.052095
55	x	-1536.413401	-1535.966365	-1536.060050	-1536.055006	-1536.054170
60	x	-1536.413435	-1535.965855	-1536.058223	-1536.053250	-1536.052380
65	x	-1536.413544	-1535.965476	-1536.057268	-1536.052296	-1536.051639
70	x	-1536.413668	-1535.965987	-1536.057417	-1536.052913	-1536.052424
75	x	-1536.413508	-1535.966010	-1536.058673	-1536.053791	-1536.053200
80	x	-1536.413440	-1535.966070	-1536.059377	-1536.054230	-1536.053513
85	x	-1536.413278	-1535.965647	-1536.057808	-1536.052960	-1536.052333
5	y	-1536.413396	-1535.966077	-1536.058357	-1536.053500	-1536.052809
10	y	-1536.413698	-1535.966011	-1536.057558	-1536.053095	-1536.052557
15	y	-1536.413527	-1535.965696	-1536.057323	-1536.052592	-1536.051829
20	y	-1536.413513	-1535.965593	-1536.057238	-1536.052430	-1536.051454
25	y	-1536.413350	-1535.965587	-1536.056827	-1536.052312	-1536.051625
30	y	-1536.413496	-1535.965850	-1536.057960	-1536.053226	-1536.052605
35	y	-1536.413465	-1535.965693	-1536.058201	-1536.053155	-1536.052254
40	y	-1536.413575	-1535.965474	-1536.057474	-1536.052609	-1536.051862
45	y	-1536.413523	-1535.965826	-1536.057194	-1536.052783	-1536.052196

50	y	-1536.413489	-1535.966165	-1536.058233	-1536.053486	-1536.052702
55	y	-1536.413604	-1535.966130	-1536.058125	-1536.053354	-1536.052422
60	y	-1536.413753	-1535.965985	-1536.057563	-1536.052975	-1536.052449
65	y	-1536.413582	-1535.965906	-1536.057947	-1536.053142	-1536.052271
70	y	-1536.413487	-1535.965855	-1536.058000	-1536.053189	-1536.052282
75	y	-1536.413510	-1535.965796	-1536.057422	-1536.052687	-1536.051848
80	y	-1536.413617	-1535.965878	-1536.057517	-1536.052837	-1536.051973
85	y	-1536.413391	-1535.965662	-1536.057137	-1536.052607	-1536.052005
5	z	-1536.413616	-1535.965955	-1536.057400	-1536.052881	-1536.052353
10	z	-1536.413524	-1535.966383	-1536.060388	-1536.054999	-1536.053919
15	z	-1536.413482	-1535.965675	-1536.057292	-1536.052614	-1536.051791
20	z	-1536.413329	-1535.965509	-1536.057569	-1536.052512	-1536.051329
25	z	-1536.413517	-1535.965463	-1536.056534	-1536.051986	-1536.051251
30	z	-1536.413679	-1535.965571	-1536.056401	-1536.052017	-1536.051517
35	z	-1536.413529	-1535.966127	-1536.058549	-1536.053671	-1536.052864
40	z	-1536.413433	-1535.965820	-1536.057744	-1536.052935	-1536.051999
45	z	-1536.413336	-1535.965905	-1536.058321	-1536.053568	-1536.052881
50	z	-1536.413533	-1535.965510	-1536.056646	-1536.052093	-1536.051418
55	z	-1536.413509	-1535.965909	-1536.057753	-1536.053215	-1536.052651
60	z	-1536.413466	-1535.965964	-1536.058880	-1536.053724	-1536.052716
65	z	-1536.413413	-1535.965987	-1536.059337	-1536.053997	-1536.052952
70	z	-1536.413331	-1535.966029	-1536.059294	-1536.054083	-1536.053126
75	z	-1536.413482	-1535.965957	-1536.057357	-1536.052965	-1536.052482
80	z	-1536.413664	-1535.965779	-1536.057455	-1536.052797	-1536.052234
85	z	-1536.413464	-1535.965846	-1536.058065	-1536.053415	-1536.052908

Table S32. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS1 as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1536.413414	-1535.966612	-1536.060872	-1536.055489	-1536.054542
5	x	-1536.413323	-1535.966543	-1536.061315	-1536.055725	-1536.054507
10	x	-1536.413383	-1535.966574	-1536.061608	-1536.055781	-1536.054604
15	x	-1536.413423	-1535.966544	-1536.060709	-1536.055326	-1536.054232
20	x	-1536.413367	-1535.966685	-1536.061463	-1536.055967	-1536.054981
25	x	-1536.413386	-1535.966547	-1536.060357	-1536.055197	-1536.054163
30	x	-1536.413383	-1535.966661	-1536.061001	-1536.055786	-1536.055075
35	x	-1536.413392	-1535.966668	-1536.061262	-1536.055843	-1536.055017
40	x	-1536.413400	-1535.966600	-1536.060970	-1536.055636	-1536.054809
45	x	-1536.413416	-1535.966552	-1536.060550	-1536.055355	-1536.054707
50	x	-1536.413383	-1535.966693	-1536.061718	-1536.056169	-1536.055109
55	x	-1536.413403	-1535.966584	-1536.061109	-1536.055709	-1536.054786
60	x	-1536.413374	-1535.966625	-1536.061218	-1536.055820	-1536.054975
65	x	-1536.413404	-1535.966511	-1536.060721	-1536.055370	-1536.054354
70	x	-1536.413387	-1535.966557	-1536.061009	-1536.055594	-1536.054568
75	x	-1536.413387	-1535.966684	-1536.061333	-1536.055911	-1536.055030
80	x	-1536.413392	-1535.966726	-1536.062491	-1536.056538	-1536.055329
85	x	-1536.413405	-1535.966612	-1536.061240	-1536.055759	-1536.054762
5	y	-1536.413409	-1535.966627	-1536.061207	-1536.055743	-1536.054763
10	y	-1536.413383	-1535.966544	-1536.060830	-1536.055480	-1536.054458
15	y	-1536.413400	-1535.966565	-1536.060971	-1536.055630	-1536.054601
20	y	-1536.413400	-1535.966682	-1536.061711	-1536.056100	-1536.055105
25	y	-1536.413396	-1535.966658	-1536.060604	-1536.055503	-1536.054799
30	y	-1536.413393	-1535.966624	-1536.060439	-1536.055346	-1536.054658
35	y	-1536.413414	-1535.966634	-1536.060541	-1536.055426	-1536.054517
40	y	-1536.413372	-1535.966563	-1536.060625	-1536.055336	-1536.054476
45	y	-1536.413400	-1535.966687	-1536.061175	-1536.055840	-1536.054964

50	y	-1536.413414	-1535.966621	-1536.061048	-1536.055726	-1536.054677
55	y	-1536.413386	-1535.966651	-1536.061558	-1536.055950	-1536.054807
60	y	-1536.413437	-1535.966613	-1536.060292	-1536.055274	-1536.054563
65	y	-1536.413379	-1535.966586	-1536.060892	-1536.055615	-1536.054585
70	y	-1536.413344	-1535.966654	-1536.061720	-1536.056179	-1536.055175
75	y	-1536.413391	-1535.966611	-1536.061556	-1536.055821	-1536.054583
80	y	-1536.413405	-1535.966602	-1536.061389	-1536.055867	-1536.054866
85	y	-1536.413390	-1535.966591	-1536.061339	-1536.055795	-1536.054852
5	z	-1536.413381	-1535.966557	-1536.062045	-1536.056042	-1536.054600
10	z	-1536.413391	-1535.966620	-1536.061850	-1536.056033	-1536.054508
15	z	-1536.413390	-1535.966653	-1536.061575	-1536.055981	-1536.054771
20	z	-1536.413381	-1535.966642	-1536.061805	-1536.056077	-1536.054808
25	z	-1536.413419	-1535.966636	-1536.061194	-1536.055701	-1536.054639
30	z	-1536.413368	-1535.966782	-1536.062423	-1536.056588	-1536.055513
35	z	-1536.413388	-1535.966677	-1536.060855	-1536.055717	-1536.054999
40	z	-1536.413407	-1535.966562	-1536.060863	-1536.055416	-1536.054476
45	z	-1536.413398	-1535.966527	-1536.061161	-1536.055505	-1536.054371
50	z	-1536.413382	-1535.966599	-1536.061658	-1536.055866	-1536.054663
55	z	-1536.413395	-1535.966639	-1536.061048	-1536.055717	-1536.054859
60	z	-1536.413402	-1535.966596	-1536.061242	-1536.055728	-1536.054643
65	z	-1536.413394	-1535.966597	-1536.061028	-1536.055629	-1536.054631
70	z	-1536.413388	-1535.966610	-1536.060979	-1536.055602	-1536.054557
75	z	-1536.413404	-1535.966660	-1536.061659	-1536.056003	-1536.054859
80	z	-1536.413335	-1535.966645	-1536.061592	-1536.056089	-1536.055031
85	z	-1536.413384	-1535.966639	-1536.061395	-1536.055836	-1536.054696

Table S33. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS1 as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1536.413370	-1535.966791	-1536.062401	-1536.056631	-1536.055519
5	x	-1536.413366	-1535.966771	-1536.062368	-1536.056588	-1536.055476
10	x	-1536.413366	-1535.966779	-1536.062476	-1536.056641	-1536.055432
15	x	-1536.413368	-1535.966804	-1536.062596	-1536.056735	-1536.055632
20	x	-1536.413362	-1535.966786	-1536.062256	-1536.056532	-1536.055476
25	x	-1536.413367	-1535.966795	-1536.062495	-1536.056685	-1536.055531
30	x	-1536.413366	-1535.966825	-1536.062901	-1536.056912	-1536.055749
35	x	-1536.413374	-1535.966786	-1536.062463	-1536.056642	-1536.055502
40	x	-1536.413367	-1535.966809	-1536.062496	-1536.056700	-1536.055653
45	x	-1536.413362	-1535.966805	-1536.062708	-1536.056808	-1536.055543
50	x	-1536.413369	-1535.966831	-1536.062836	-1536.056873	-1536.055710
55	x	-1536.413372	-1535.966756	-1536.062068	-1536.056380	-1536.055267
60	x	-1536.413366	-1535.966805	-1536.062685	-1536.056747	-1536.055574
65	x	-1536.413366	-1535.966816	-1536.062734	-1536.056824	-1536.055628
70	x	-1536.413369	-1535.966802	-1536.062303	-1536.056587	-1536.055511
75	x	-1536.413371	-1535.966797	-1536.062510	-1536.056677	-1536.055567
80	x	-1536.413368	-1535.966777	-1536.062343	-1536.056588	-1536.055500
85	x	-1536.413371	-1535.966794	-1536.062523	-1536.056683	-1536.055585
5	y	-1536.413362	-1535.966777	-1536.062277	-1536.056543	-1536.055471
10	y	-1536.413368	-1535.966815	-1536.062456	-1536.056686	-1536.055605
15	y	-1536.413370	-1535.966795	-1536.062711	-1536.056787	-1536.055543
20	y	-1536.413369	-1535.966773	-1536.062434	-1536.056606	-1536.055501
25	y	-1536.413370	-1535.966819	-1536.062485	-1536.056701	-1536.055646
30	y	-1536.413368	-1535.966785	-1536.062597	-1536.056728	-1536.055565
35	y	-1536.413367	-1535.966808	-1536.062515	-1536.056693	-1536.055569
40	y	-1536.413364	-1535.966785	-1536.062700	-1536.056747	-1536.055524
45	y	-1536.413368	-1535.966818	-1536.062644	-1536.056778	-1536.055565

50	y	-1536.413372	-1535.966785	-1536.062181	-1536.056502	-1536.055499
55	y	-1536.413371	-1535.966757	-1536.062186	-1536.056443	-1536.055292
60	y	-1536.413364	-1535.966784	-1536.062709	-1536.056753	-1536.055538
65	y	-1536.413368	-1535.966803	-1536.062430	-1536.056648	-1536.055485
70	y	-1536.413358	-1535.966795	-1536.062491	-1536.056664	-1536.055566
75	y	-1536.413374	-1535.966765	-1536.062375	-1536.056570	-1536.055489
80	y	-1536.413370	-1535.966787	-1536.062529	-1536.056690	-1536.055522
85	y	-1536.413372	-1535.966792	-1536.062624	-1536.056737	-1536.055595
5	z	-1536.413365	-1535.966799	-1536.062609	-1536.056723	-1536.055569
10	z	-1536.413365	-1535.966812	-1536.062540	-1536.056720	-1536.055580
15	z	-1536.413363	-1535.966787	-1536.062458	-1536.056653	-1536.055534
20	z	-1536.413372	-1535.966779	-1536.062375	-1536.056589	-1536.055444
25	z	-1536.413365	-1535.966820	-1536.062701	-1536.056808	-1536.055676
30	z	-1536.413368	-1535.966815	-1536.062727	-1536.056805	-1536.055640
35	z	-1536.413365	-1535.966794	-1536.062527	-1536.056675	-1536.055559
40	z	-1536.413374	-1535.966806	-1536.062351	-1536.056606	-1536.055574
45	z	-1536.413363	-1535.966790	-1536.062584	-1536.056700	-1536.055506
50	z	-1536.413367	-1535.966818	-1536.062764	-1536.056871	-1536.055690
55	z	-1536.413370	-1535.966792	-1536.062406	-1536.056629	-1536.055553
60	z	-1536.413367	-1535.966764	-1536.062232	-1536.056479	-1536.055359
65	z	-1536.413372	-1535.966806	-1536.062606	-1536.056739	-1536.055578
70	z	-1536.413367	-1535.966796	-1536.062542	-1536.056707	-1536.055550
75	z	-1536.413368	-1535.966786	-1536.062475	-1536.056647	-1536.055518
80	z	-1536.413382	-1535.966789	-1536.062246	-1536.056551	-1536.055545
85	z	-1536.413366	-1535.966810	-1536.062581	-1536.056747	-1536.055627

Table S34. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS2 as a function of rotations around the Cartesian axes from the standard orientation using the SG1 grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1536.413929	-1535.963345	-1536.049029	-1536.045678	-1536.045624
5	x	-1536.413813	-1535.964620	-1536.051417	-1536.048254	-1536.048343
10	x	-1536.413598	-1535.964413	-1536.052167	-1536.048770	-1536.048696
15	x	-1536.413496	-1535.964597	-1536.053000	-1536.049120	-1536.048845
20	x	-1536.413581	-1535.963539	-1536.050647	-1536.046937	-1536.046684
25	x	-1536.413235	-1535.964764	-1536.054411	-1536.050082	-1536.049458
30	x	-1536.413794	-1535.964620	-1536.051692	-1536.048097	-1536.047821
35	x	-1536.413835	-1535.964909	-1536.052486	-1536.048760	-1536.048560
40	x	-1536.414171	-1535.964990	-1536.052587	-1536.048812	-1536.048590
45	x	-1536.413703	-1535.964524	-1536.052423	-1536.048585	-1536.048432
50	x	-1536.413715	-1535.964435	-1536.051456	-1536.047795	-1536.047625
55	x	-1536.413044	-1535.964434	-1536.053099	-1536.049196	-1536.048917
60	x	-1536.413208	-1535.965182	-1536.052864	-1536.049539	-1536.049640
65	x	-1536.413493	-1535.963841	-1536.051737	-1536.047968	-1536.047687
70	x	-1536.414075	-1535.963777	-1536.050884	-1536.047385	-1536.047223
75	x	-1536.413632	-1535.964348	-1536.050723	-1536.047621	-1536.047668
80	x	-1536.413146	-1535.964187	-1536.052533	-1536.048600	-1536.048307
85	x	-1536.413833	-1535.962979	-1536.048743	-1536.045398	-1536.045310
5	y	-1536.414506	-1535.963519	-1536.048961	-1536.045862	-1536.045923
10	y	-1536.413519	-1535.963179	-1536.049913	-1536.046082	-1536.045847
15	y	-1536.413747	-1535.964043	-1536.050945	-1536.047431	-1536.047316
20	y	-1536.413190	-1535.963554	-1536.050160	-1536.046748	-1536.046616
25	y	-1536.413847	-1535.964068	-1536.051330	-1536.047919	-1536.047851
30	y	-1536.414238	-1535.964809	-1536.052605	-1536.049039	-1536.048838
35	y	-1536.413678	-1535.964398	-1536.054313	-1536.049797	-1536.049143
40	y	-1536.413374	-1535.963887	-1536.051988	-1536.048120	-1536.047768
45	y	-1536.413414	-1535.964569	-1536.053701	-1536.049666	-1536.049229

50	y	-1536.413821	-1535.964366	-1536.051048	-1536.047711	-1536.047555
55	y	-1536.413412	-1535.964212	-1536.051723	-1536.048170	-1536.048093
60	y	-1536.413489	-1535.963973	-1536.052148	-1536.048337	-1536.048236
65	y	-1536.413077	-1535.964347	-1536.052631	-1536.048756	-1536.048383
70	y	-1536.413632	-1535.963932	-1536.051145	-1536.047500	-1536.047378
75	y	-1536.413976	-1535.963922	-1536.051671	-1536.047753	-1536.047412
80	y	-1536.413317	-1535.962786	-1536.049578	-1536.046004	-1536.045828
85	y	-1536.414046	-1535.963324	-1536.049088	-1536.045854	-1536.045773
5	z	-1536.413720	-1535.963265	-1536.049623	-1536.046019	-1536.045740
10	z	-1536.413826	-1535.964394	-1536.051665	-1536.048116	-1536.047922
15	z	-1536.414071	-1535.964172	-1536.050903	-1536.047552	-1536.047440
20	z	-1536.413767	-1535.964108	-1536.050815	-1536.047522	-1536.047502
25	z	-1536.413617	-1535.963566	-1536.051138	-1536.047293	-1536.046963
30	z	-1536.413552	-1535.964001	-1536.051312	-1536.047769	-1536.047630
35	z	-1536.414015	-1535.963045	-1536.048764	-1536.045656	-1536.045806
40	z	-1536.413596	-1535.964425	-1536.052518	-1536.048897	-1536.048717
45	z	-1536.413969	-1535.963888	-1536.050567	-1536.046879	-1536.046563
50	z	-1536.414346	-1535.963482	-1536.049676	-1536.046172	-1536.046052
55	z	-1536.414244	-1535.963571	-1536.049569	-1536.046007	-1536.045810
60	z	-1536.414674	-1535.964219	-1536.050750	-1536.047086	-1536.046870
65	z	-1536.414725	-1535.964194	-1536.051929	-1536.047877	-1536.047345
70	z	-1536.413903	-1535.964122	-1536.052669	-1536.048402	-1536.047776
75	z	-1536.413970	-1535.963859	-1536.051348	-1536.047462	-1536.047053
80	z	-1536.414109	-1535.964574	-1536.051592	-1536.047984	-1536.047730
85	z	-1536.414771	-1535.962878	-1536.047808	-1536.044635	-1536.044664

Table S35. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS2 as a function of rotations around the Cartesian axes from the standard orientation using the (75,302) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1536.411530	-1535.963348	-1536.053675	-1536.049313	-1536.048688
5	x	-1536.411534	-1535.963489	-1536.054031	-1536.049660	-1536.049038
10	x	-1536.411625	-1535.963324	-1536.053694	-1536.049209	-1536.048502
15	x	-1536.411240	-1535.964120	-1536.058203	-1536.052537	-1536.051352
20	x	-1536.411382	-1535.963996	-1536.056612	-1536.051688	-1536.050963
25	x	-1536.411562	-1535.963148	-1536.052578	-1536.048613	-1536.048373
30	x	-1536.411653	-1535.963187	-1536.052203	-1536.048404	-1536.048115
35	x	-1536.411470	-1535.963931	-1536.054747	-1536.050724	-1536.050479
40	x	-1536.411525	-1535.964059	-1536.056086	-1536.051557	-1536.051122
45	x	-1536.411445	-1535.963519	-1536.053515	-1536.049369	-1536.048933
50	x	-1536.411727	-1535.963033	-1536.052107	-1536.048217	-1536.047923
55	x	-1536.411667	-1535.963463	-1536.053426	-1536.049304	-1536.048883
60	x	-1536.411297	-1535.963519	-1536.056271	-1536.051288	-1536.050594
65	x	-1536.411264	-1535.963595	-1536.054179	-1536.049946	-1536.049392
70	x	-1536.411494	-1535.963304	-1536.053457	-1536.049242	-1536.048755
75	x	-1536.411562	-1535.963467	-1536.052993	-1536.049041	-1536.048710
80	x	-1536.411620	-1535.963074	-1536.052823	-1536.048588	-1536.047996
85	x	-1536.411457	-1535.963704	-1536.054437	-1536.050196	-1536.049874
5	y	-1536.411359	-1535.963349	-1536.053689	-1536.049469	-1536.048950
10	y	-1536.411388	-1535.963174	-1536.055142	-1536.050091	-1536.049051
15	y	-1536.411313	-1535.963641	-1536.054690	-1536.050319	-1536.049723
20	y	-1536.411462	-1535.963627	-1536.054308	-1536.049999	-1536.049405
25	y	-1536.411441	-1535.963806	-1536.054640	-1536.050354	-1536.049788
30	y	-1536.411549	-1535.963871	-1536.055085	-1536.050612	-1536.049888
35	y	-1536.411509	-1535.963537	-1536.054300	-1536.049843	-1536.049067
40	y	-1536.411563	-1535.963601	-1536.054229	-1536.050064	-1536.049724
45	y	-1536.411749	-1535.963346	-1536.053181	-1536.048977	-1536.048420

50	y	-1536.411659	-1535.963402	-1536.054107	-1536.049667	-1536.049203
55	y	-1536.411428	-1535.963469	-1536.053623	-1536.049611	-1536.049257
60	y	-1536.411284	-1535.964038	-1536.056046	-1536.051440	-1536.050785
65	y	-1536.411640	-1535.963855	-1536.053684	-1536.049798	-1536.049497
70	y	-1536.411611	-1535.963793	-1536.053896	-1536.049827	-1536.049398
75	y	-1536.411499	-1535.963460	-1536.053895	-1536.049592	-1536.048985
80	y	-1536.411798	-1535.963175	-1536.052848	-1536.048672	-1536.048239
85	y	-1536.411453	-1535.963513	-1536.053781	-1536.049562	-1536.049156
5	z	-1536.411562	-1535.963663	-1536.053882	-1536.049575	-1536.049179
10	z	-1536.411710	-1535.963676	-1536.054566	-1536.050189	-1536.049719
15	z	-1536.411546	-1535.963453	-1536.053980	-1536.049636	-1536.049156
20	z	-1536.411594	-1535.963403	-1536.052662	-1536.048850	-1536.048660
25	z	-1536.411546	-1535.963373	-1536.053126	-1536.048962	-1536.048596
30	z	-1536.411696	-1535.963432	-1536.052624	-1536.048710	-1536.048419
35	z	-1536.411648	-1535.963369	-1536.052756	-1536.048796	-1536.048550
40	z	-1536.411363	-1535.963348	-1536.053859	-1536.049483	-1536.048882
45	z	-1536.411581	-1535.963092	-1536.053612	-1536.048994	-1536.048179
50	z	-1536.411471	-1535.963741	-1536.054751	-1536.050345	-1536.049706
55	z	-1536.411404	-1535.963654	-1536.054514	-1536.050151	-1536.049619
60	z	-1536.411577	-1535.963250	-1536.053224	-1536.049076	-1536.048771
65	z	-1536.411348	-1535.963744	-1536.054988	-1536.050472	-1536.050078
70	z	-1536.411641	-1535.963604	-1536.054269	-1536.049881	-1536.049415
75	z	-1536.411454	-1535.963270	-1536.053632	-1536.049356	-1536.048780
80	z	-1536.411534	-1535.963481	-1536.054951	-1536.050240	-1536.049811
85	z	-1536.411437	-1535.963878	-1536.055488	-1536.051035	-1536.050755

Table S36. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS2 as a function of rotations around the Cartesian axes from the standard orientation using the (99,590) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1536.411353	-1535.964483	-1536.057814	-1536.052772	-1536.052110
5	x	-1536.411346	-1535.964539	-1536.058189	-1536.053026	-1536.052372
10	x	-1536.411307	-1535.964442	-1536.058407	-1536.053036	-1536.052062
15	x	-1536.411317	-1535.964421	-1536.058647	-1536.052995	-1536.052107
20	x	-1536.411326	-1535.964347	-1536.057727	-1536.052537	-1536.051856
25	x	-1536.411311	-1535.964775	-1536.059466	-1536.053957	-1536.053176
30	x	-1536.411370	-1535.964551	-1536.057932	-1536.052917	-1536.052354
35	x	-1536.411307	-1535.964332	-1536.057644	-1536.052559	-1536.051801
40	x	-1536.411300	-1535.964681	-1536.058929	-1536.053619	-1536.052976
45	x	-1536.411319	-1535.964573	-1536.058151	-1536.052988	-1536.052330
50	x	-1536.411362	-1535.964405	-1536.057495	-1536.052654	-1536.052220
55	x	-1536.411327	-1535.964563	-1536.058681	-1536.053203	-1536.052403
60	x	-1536.411334	-1535.964621	-1536.058480	-1536.053304	-1536.052648
65	x	-1536.411344	-1535.964449	-1536.058004	-1536.052887	-1536.052263
70	x	-1536.411286	-1535.964595	-1536.058395	-1536.053227	-1536.052514
75	x	-1536.411296	-1535.964530	-1536.058011	-1536.052967	-1536.052264
80	x	-1536.411318	-1535.964596	-1536.058611	-1536.053336	-1536.052588
85	x	-1536.411330	-1535.964569	-1536.058185	-1536.053091	-1536.052482
5	y	-1536.411327	-1535.964380	-1536.057726	-1536.052575	-1536.051948
10	y	-1536.411322	-1535.964362	-1536.057618	-1536.052522	-1536.051810
15	y	-1536.411324	-1535.964561	-1536.058043	-1536.052976	-1536.052439
20	y	-1536.411344	-1535.964676	-1536.058883	-1536.053576	-1536.052822
25	y	-1536.411307	-1535.964553	-1536.058497	-1536.053192	-1536.052580
30	y	-1536.411304	-1535.964470	-1536.057726	-1536.052765	-1536.052158
35	y	-1536.411319	-1535.964436	-1536.057447	-1536.052661	-1536.052155
40	y	-1536.411321	-1535.964664	-1536.057976	-1536.053057	-1536.052635
45	y	-1536.411359	-1535.964562	-1536.057763	-1536.052852	-1536.052409

50	y	-1536.411357	-1535.964371	-1536.056898	-1536.052209	-1536.051858
55	y	-1536.411313	-1535.964432	-1536.057667	-1536.052598	-1536.052057
60	y	-1536.411321	-1535.964522	-1536.057476	-1536.052685	-1536.052153
65	y	-1536.411314	-1535.964629	-1536.058645	-1536.053359	-1536.052713
70	y	-1536.411298	-1535.964549	-1536.059183	-1536.053510	-1536.052599
75	y	-1536.411324	-1535.964512	-1536.058448	-1536.053131	-1536.052373
80	y	-1536.411299	-1535.964671	-1536.059703	-1536.053919	-1536.052940
85	y	-1536.411338	-1535.964531	-1536.057951	-1536.052957	-1536.052243
5	z	-1536.411330	-1535.964574	-1536.058800	-1536.053484	-1536.052683
10	z	-1536.411315	-1535.964439	-1536.057862	-1536.052820	-1536.052042
15	z	-1536.411334	-1535.964453	-1536.057620	-1536.052619	-1536.051982
20	z	-1536.411313	-1535.964570	-1536.058310	-1536.053166	-1536.052381
25	z	-1536.411370	-1535.964626	-1536.058603	-1536.053320	-1536.052590
30	z	-1536.411338	-1535.964317	-1536.057912	-1536.052646	-1536.051881
35	z	-1536.411306	-1535.964405	-1536.057358	-1536.052456	-1536.051954
40	z	-1536.411317	-1535.964613	-1536.059381	-1536.053696	-1536.052629
45	z	-1536.411332	-1535.964528	-1536.058194	-1536.052976	-1536.052296
50	z	-1536.411275	-1535.964560	-1536.058993	-1536.053337	-1536.052306
55	z	-1536.411342	-1535.964436	-1536.058008	-1536.052839	-1536.052025
60	z	-1536.411328	-1535.964482	-1536.057680	-1536.052743	-1536.052217
65	z	-1536.411309	-1535.964537	-1536.057998	-1536.052891	-1536.052251
70	z	-1536.411364	-1535.964399	-1536.057735	-1536.052568	-1536.051960
75	z	-1536.411330	-1535.964622	-1536.059081	-1536.053503	-1536.052645
80	z	-1536.411305	-1535.964585	-1536.058222	-1536.053174	-1536.052540
85	z	-1536.411300	-1535.964468	-1536.058413	-1536.053053	-1536.052203

Table S37. Values of the energy (E, in hartree), 298K enthalpy (H, in hartree), free energy using the RRHO, quasi-RRHO, and quasi-harmonic approximations (in hartree) for TS2 as a function of rotations around the Cartesian axes from the standard orientation using the (175,974) grid.

Angle	Axis	E	H	G(RRHO)	G(quasi-RRHO)	G(quasi-harmonic)
0	x	-1536.411275	-1535.964805	-1536.060600	-1536.054774	-1536.053690
5	x	-1536.411282	-1535.964842	-1536.060818	-1536.054910	-1536.053812
10	x	-1536.411292	-1535.964765	-1536.060131	-1536.054459	-1536.053443
15	x	-1536.411278	-1535.964782	-1536.060179	-1536.054503	-1536.053517
20	x	-1536.411278	-1535.964794	-1536.060478	-1536.054658	-1536.053576
25	x	-1536.411291	-1535.964822	-1536.060495	-1536.054745	-1536.053714
30	x	-1536.411276	-1535.964856	-1536.061191	-1536.055125	-1536.053893
35	x	-1536.411285	-1535.964783	-1536.060231	-1536.054546	-1536.053518
40	x	-1536.411291	-1535.964829	-1536.060507	-1536.054711	-1536.053698
45	x	-1536.411275	-1535.964844	-1536.060928	-1536.055020	-1536.053900
50	x	-1536.411284	-1535.964809	-1536.060408	-1536.054671	-1536.053628
55	x	-1536.411285	-1535.964807	-1536.060479	-1536.054705	-1536.053693
60	x	-1536.411290	-1535.964806	-1536.060348	-1536.054644	-1536.053636
65	x	-1536.411275	-1535.964833	-1536.060622	-1536.054804	-1536.053714
70	x	-1536.411279	-1535.964818	-1536.060433	-1536.054693	-1536.053682
75	x	-1536.411283	-1535.964810	-1536.060602	-1536.054808	-1536.053760
80	x	-1536.411290	-1535.964806	-1536.060330	-1536.054628	-1536.053622
85	x	-1536.411285	-1535.964779	-1536.060195	-1536.054525	-1536.053512
5	y	-1536.411288	-1535.964795	-1536.060346	-1536.054644	-1536.053606
10	y	-1536.411284	-1535.964804	-1536.060523	-1536.054729	-1536.053636
15	y	-1536.411280	-1535.964782	-1536.060343	-1536.054620	-1536.053627
20	y	-1536.411285	-1535.964819	-1536.060325	-1536.054666	-1536.053689
25	y	-1536.411282	-1535.964822	-1536.060689	-1536.054814	-1536.053684
30	y	-1536.411276	-1535.964845	-1536.060976	-1536.055010	-1536.053831
35	y	-1536.411280	-1535.964846	-1536.060962	-1536.054998	-1536.053814
40	y	-1536.411284	-1535.964807	-1536.060370	-1536.054659	-1536.053621
45	y	-1536.411284	-1535.964792	-1536.060535	-1536.054700	-1536.053598

50	y	-1536.411284	-1535.964802	-1536.060296	-1536.054574	-1536.053584
55	y	-1536.411278	-1535.964840	-1536.060784	-1536.054885	-1536.053811
60	y	-1536.411283	-1535.964821	-1536.060478	-1536.054728	-1536.053739
65	y	-1536.411289	-1535.964789	-1536.060269	-1536.054570	-1536.053526
70	y	-1536.411280	-1535.964771	-1536.060450	-1536.054661	-1536.053585
75	y	-1536.411279	-1535.964871	-1536.060940	-1536.055022	-1536.053978
80	y	-1536.411286	-1535.964816	-1536.060432	-1536.054727	-1536.053777
85	y	-1536.411285	-1535.964815	-1536.060540	-1536.054704	-1536.053608
5	z	-1536.411289	-1535.964788	-1536.060294	-1536.054536	-1536.053501
10	z	-1536.411287	-1535.964791	-1536.060320	-1536.054607	-1536.053542
15	z	-1536.411283	-1535.964822	-1536.060716	-1536.054812	-1536.053705
20	z	-1536.411281	-1535.964820	-1536.060768	-1536.054871	-1536.053729
25	z	-1536.411283	-1535.964825	-1536.060454	-1536.054759	-1536.053758
30	z	-1536.411281	-1535.964819	-1536.060838	-1536.054864	-1536.053681
35	z	-1536.411278	-1535.964785	-1536.060236	-1536.054555	-1536.053543
40	z	-1536.411282	-1535.964825	-1536.060745	-1536.054900	-1536.053836
45	z	-1536.411282	-1535.964785	-1536.060325	-1536.054575	-1536.053536
50	z	-1536.411287	-1535.964820	-1536.060703	-1536.054818	-1536.053662
55	z	-1536.411282	-1535.964787	-1536.060405	-1536.054648	-1536.053617
60	z	-1536.411283	-1535.964789	-1536.060249	-1536.054555	-1536.053541
65	z	-1536.411278	-1535.964825	-1536.060683	-1536.054833	-1536.053722
70	z	-1536.411284	-1535.964812	-1536.060584	-1536.054711	-1536.053541
75	z	-1536.411284	-1535.964817	-1536.060480	-1536.054751	-1536.053748
80	z	-1536.411285	-1535.964784	-1536.060455	-1536.054641	-1536.053534
85	z	-1536.411286	-1535.964846	-1536.060652	-1536.054887	-1536.053890

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