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I am submitting herewith a thesis written by Mohamad Hadi Kassaee entitled "Theoretical Techniques for Determining Precise Thermophysical Properties." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

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Original signatures are on file with official student records)

# Theoretical Techniques for Determining Precise Thermophysical Properties

A Thesis
Presented for the
Master of Science Degree
The University of Tennessee, Knoxville

Mohamad Hadi Kassaee
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# Dedication

I dedicate this thesis to my dear parents, Ameneh Mahrou Kassaee, and Dr. Mohamad Z. Kassaee, for their constant support and encouragement. It is also dedicated to my brother Ali, my sisters Maryam and Lili, my brother in Law Dr. Saeed Talebzadeh, my cousin Mohamad Hadi, and my dear nephew Daniel.

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# Abstract

Quantum mechanics (QM) calculations, coupled with statistical mechanics (SM), provide a means to obtain thermophysical properties from first principles. Because of the limitations in modern computational resources, many of these properties are obtained for isolated molecules. Despite this limitation, QM is still very useful for thermophysical property generation in an ideal gas reference state where the molecules are isolated.

In this thesis, a combination of quantum mechanics and statistical mechanics calculations is used to generate entropies of aromatic compounds in the ideal gas reference state. This information is necessary for practical calculations such as the determination of the free energy of a reaction involving these compounds and the equilibrium distribution between isomers.

The QM and SM calculation procedure is used to generate entropies of simple aromatic compounds—benzene, toluene, *p*-xylene, *m*-xylene and *o*-xylene— in the ideal gas state from 250 K to 540 K. Having accurate experimental frequencies and entropies for these compounds from literature, we systematically examine how the choice of the QM level of theory impacts the agreement between theory and experiment. The calculated entropies fall within 0.5% of experimentally determined values for these compounds. We acknowledge that given the state of the art of computational quantum mechanics today, all levels of theory require an empirical scaling factor for vibrational frequencies. This empirical scaling factor largely eliminates the advantage in accuracy of more sophisticated levels of theory. Thus we see that our "purely computational"

estimates of the entropy still have a fundamental connection to experiment through this single empirical scaling factor.

We then apply the same QM/SM procedure to generate the entropies of thirteen other aromatic compounds—naphthalene, two methylnaphthalene isomers (MN), and ten Dimethylnaphthalene isomers (DMN)—in the ideal gas state. The calculated entropies are compared to accurate experimental entropies available for four of these compounds: naphthalene, 1-MN, 2-MN, and 2,7-DMN. The calculated entropies match the experiment very well, with the percentage errors close to the experimental uncertainty, less than 0.4%. Finally, the equilibrium distribution of DMN isomers in the mixture is predicted using the calculated entropies and energies from QM and SM calculations in the 300-740 K temperature range.

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# PART 1

# Introduction

## 1.1 Motivation

Knowledge of the free energy of chemical compounds in the ideal gas state is useful for a variety of reasons. For reactive systems in general, the thermodynamic distribution of products and reactants is governed by an equilibrium coefficient, which is a function of the relative free energies. In systems where a set of isomers can exist, these free energies provide the equilibrium distribution of isomers, at least in the ideal gas reference state. In a reactor, in order to optimize the production of a certain compound in a reaction, it is necessary to know the distribution of compounds across the operating temperature range.

The Gibbs free energy has an energetic component in the enthalpy and an entropic component. Various group-theory methods provide relatively reliable ways of estimating the enthalpy of polyatomic organic molecules in the ideal gas reference state. Unlike the enthalpy, the entropy component of the free energy is more difficult to estimate. Furthermore, the entropy is difficult and expensive to measure through experiment.

Our motivation in this work is a desire to determine, given the state of computational chemistry today, if experimental measurements of entropy can be replaced by computational tools. Moreover, we want to establish a clear procedure for the calculation of the entropy, using a combination of quantum mechanics (QM) and statistical mechanics (SM). Finally, we want to compare these computational results to precise experimental determination of entropies in order to quantify the accuracy of the computational method.

In this work, we specifically examine aromatics due to their importance in the energy and chemical industry. They make ideal subjects for this study because for simple aromatics—benzene, toluene, and the xylene isomers—as well as some larger aromatics—napthalene, methyl naphthalenes, and some dimethylnaphthalene isomers—very precise experimentally determined entropies are available.

## 1.2 Background

Quantum mechanics (QM) calculations, coupled with statistical mechanics (SM), provide a means to obtain thermophysical properties from first principles. Because of the limitations in modern computational resources, many of these properties are obtained for isolated molecules. Despite this limitation, QM is still very useful for thermophysical property generation in an ideal gas reference state where the molecules are isolated.

Such generation of thermophysical properties requires a combination of quantum mechanics and statistical mechanics. The QM calculations provide the equilibrium configuration from which one can directly calculate (i) the moments of inertia of the entire molecule, required for the rotational contribution to the thermodynamic properties (ii) the moments of inertia for internal rotors, required for the internal rotational contribution, (iii) the normal vibrational frequencies, required for the vibrational contribution, and (iv) the energetic barrier to internal rotation, required for the internal rotational contribution.

A SM analysis takes this QM-generated information as input into a model and predicts thermodynamic properties. The SM model makes various approximations in

order to provide a tractable model. For example, the SM model assumes that the vibrational modes can be modeled as harmonic oscillators, that the rotational modes can be modeled as rigid rotors, and that there is no coupling between translational, rotational and vibrational modes.

In calculating entropy as an important thermophysical property, we need to get all of its contributions such as translational, rotational, vibrational and internal rotational contributions. The different QM approximation methods are called levels of theory. The state of the art of computational QM today is that, regardless of the QM level of theory, all calculated frequencies require an empirical scaling factor to correct the vibrational contribution to the entropy. The empirical scale factor can either be calculated from direct comparison of frequencies with experiment, or be taken from averaged scale factors over many compounds available in a NIST database. In this work, we calculate the scaling factor for all of the compounds at several levels of theory for small aromatic molecules since the experimental frequencies are available. For larger aromatics, we use a single averaged scale factor determined from the simple aromatics for correcting the frequencies. Thus we see that our "purely computational" estimates of the entropy still have a fundamental connection to experiment through this single empirical scaling factor.

The equilibrium distribution of isomers can be calculated from the relative Gibbs free energy of the compounds. Calculating the entropy and enthalpy in the QM/SM procedure results in the Gibbs free energy as a function of temperature, and eventually gives the equilibrium distribution of the compounds across the temperature range.

## 1.3 Synopsis

In this thesis, we are interested in using a combination of quantum mechanics (QM) and statistical mechanics (SM) to generate entropies of aromatic compounds in the ideal gas reference state. This information is necessary for practical calculations such as the determination of the free energy of a reaction involving these compounds and the equilibrium distribution between isomers.

In Part 2, "A Comparison between Entropies of Aromatic Compounds from Quantum Mechanical Calculations and Experiment," we are particularly interested in using a combination of QM and SM to generate entropies of simple aromatic compounds—benzene, toluene, *p*-xylene, *m*-xylene and *o*-xylene— in the ideal gas state. Having accurate experimental frequencies and entropies for these compounds from literature, we systematically examine how the choice of the QM level of theory impacts the agreement between theory and experiment.

Similarly, in Part 3, "Theoretical Calculation of Thermodynamic Properties of Naphthalene, Methylnaphthalenes and Dimethylnaphthalenes," we use a combination of QM and SM to generate the entropy of thirteen aromatic compounds—naphthalene, two methylnaphthalene isomers, and ten dimethylnaphthalene isomers—in the ideal gas state. We compare the calculated entropies to accurate experimental entropies available for four of these compounds: naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, and 2,7-dimethylnaphthalene. The equilibrium distribution of dimethylnaphthalene isomers in the mixture is predicted using the calculated entropies and energies from QM and SM calculations in the 300-740 K temperature range.

# PART 2

# A Comparison between Entropies of Aromatic Compounds from Quantum Mechanical Calculations and Experiment

## Abstract

In this work, we perform a set of quantum mechanical and statistical mechanical calculations to generate the entropy of five simple aromatic compounds—benzene, toluene, *p*-xylene, *m*-xylene and *o*-xylene—in the ideal gas state. We systematically examine how the choice of quantum mechanical level of theory and size of basis set impact the agreement between theory and experiment. Regardless of level of theory and basis set, all calculations require an empirical scaling factor to correct the vibrational contribution to the entropy. Once this scaling factor is applied, there is at most nominal advantage in more sophisticated levels of theory or increased basis set size, while a heavy computational penalty is paid for the more advanced theory. We find that the variation in scaling factor across these aromatic compounds is on average 0.3%. Across a range from 250 K to 540 K, the difference in the entropies obtained from all quantum mechanical calculations and from experiment is less than half a percent.

## 2.1. Introduction

Quantum mechanical (QM) calculations, coupled with statistical mechanics (SM), provide a means to obtain thermophysical properties from first principles. Owing to the limitations of modern computational resources, many of these properties are obtained for isolated molecules. This limitation does not eliminate the usefulness of QM in thermophysical property generation because many times one is interested in an ideal gas reference state, in which the molecules are essentially isolated.

Quantum mechanics must be coupled with statistical mechanics in order to generate thermophysical properties. For example, we can obtain a set of normal vibrational spectra for an isolated molecule from QM, but it requires SM to take the spectra as input and output the vibrational contributions to thermophysical properties. In this work, we are particularly interested in using a combination of QM and SM to generate entropies of five simple aromatic compounds—benzene, toluene, *p*-xylene, *m*-xylene and *o*-xylene—in the ideal gas reference state. This information is necessary for such practical calculations as the determination of the free energy of a reaction involving these compounds.

The use of QM and SM to generate entropies is not new. Barret and Meier [1] used the semiempirical AM1 method to calculate entropy for a series of organic molecules. East and Radom [2] carried out an extensive study of small molecules at different levels of QM molecular orbital theory and different methods for calculating entropies and showed that entropies could be calculated to within 1 (J/K)/mol. Notably, they used high levels of theory (ranging from MP2/6-31G(d) to MP2/6-311+G(2df,p)). Subsequently,

Vansteenkiste *et al.* calculated entropies of linear alkanes with an emphasis on considering more elaborate treatments of low vibrational modes [3]. Wang et al. [4] used *ab initio* calculations to determine thermodynamic functions like entropy for dibenzo-p-dioxin (DD) and 75 polychlorinated dibenzo-dioxions (PCDDs) at B3LYP/6-311G** level of theory.

In all of these cases, it is well known that there is a systematic problem with the calculation of normal vibrational modes via QM [5]. Tables of empirical scaling factors exist to correct these vibrational modes [6]. In general, the scaling factors are tabulated as functions of method and size of basis set, but are not functions of the individual compounds of interest. To date, these scaling factors are still required to calculate reasonable thermodynamic properties. Since these scaling factors are defined by comparison with experiment, we still have a need for experiment. Where experimental results are not available, we must assume that the variation in the scaling factor from one molecule to another similar molecule is relatively small.

This work is distinguished from previous work in the area of thermophysical property generation via QM and SM in several ways. First, we focus very carefully on comparing our entropies to excellent experimental data. This provides an objective measure by which we can evaluate the relative merits of the various levels of theory and basis sets for specific compounds. Second, the statistical mechanical analysis is done in a way in which the effect of individual contributions—vibration, rotation, internal rotation—can be separately examined. Third, by performing the analysis for benzene, toluene and three xylenes, we are able to evaluate the QM and SM procedures on a

material set, which in itself is of industrial importance and which provides a sound basis for extending the conclusions of this work to larger aromatic molecules. This set of materials will also allow us to examine how the vibrational scaling factors vary from one component to the next, which directly impacts the ability of this QM/SM procedure to be used to reliably generate entropies for larger aromatic molecules.

## 2.2 Computational Methods

We first perform the necessary QM calculations to generate the equilibrium configuration of the five aromatic compounds. In the energy minimization of the structures, the known symmetry is enforced for each molecule. This calculation is done for both the Hartree-Fock (HF) and B3LYP methods. Furthermore, for each method, three basis sets are used, 6-31G(d), 6-31++G(d,p) and 6-311++G(3df,2pd), resulting in six calculations for each of the five compound, or a total of thirty calculations. Previous studies have examined broader sets of molecules[4, 7] , but in this work we specifically restrict ourselves to aromatic compounds.

Once we have the equilibrium structure, we can obtain the moment of inertia for the equilibrium structure, required for the rotational partition function. We can also perform a QM normal mode analysis to obtain the vibrational frequencies, required for the vibrational partition function. As is well known, there is a systematic error in the evaluation of normal vibrational frequencies from QM. Therefore, at this point in time, it is necessary to use an empirical scaling factor. Traditionally, a single scaling factor is used for the entire set of frequencies. This scaling factor is obtained by minimizing the

average of the absolute percentage error between the vibrational frequencies obtained from QM and the experimental values. The experimental values of the frequencies for benzene and toluene are taken from Draeger [8] . The experimental values of the xylene isomers are taken from Chirico *et al.* [9-12]. It is necessary to make a one-to-one correspondence between the QM and experimental frequencies. There is not an obvious assignment owing to the different values of the frequencies between the two methods. One cannot simply make the assignment based upon some simple formula, such as increasing magnitude of frequency. Because we enforced the symmetry in the QM calculations, we were able to make one-to-one assignments between QM and experimental vibrational frequencies relying both on magnitude and symmetry number [13]. In Table one, we present an example for benzene, which illustrates how we matched the HF/6-31G(d) frequencies with the experimental values. One can see that the assignment does not strictly obey increasing order of magnitude. A FORTRAN program was written to make the assignments taking into account both magnitude of the frequency and symmetry number. This was then applied to all 30 calculations. Once the one-to-one assignment was made for each calculation, a scaling factor was determined for each calculation and compound, by minimizing the average absolute error.

There is one more piece of information required before we can input this information into the SM calculations, namely the barrier for internal rotation. In this work, the barrier for internal rotation of the methyl group is taken to be zero for toluene, *p*-xylene and *m*-xylene. This assumption has been experimentally validated [14]. It has been shown experimentally that *o*-xylene has a non-negligible barrier to internal rotation

of the methyl groups. We examined obtaining this barrier from both QM calculations and from experiment[14, 15]. We ultimately used internal rotation barriers from the QM calculations, where we systematically varied the torsion angle of one of the methyl groups.

With the scaled vibrational frequencies, moments of inertia, and barriers in hand, we can now proceed with the calculation of the entropy using SM [1-6]. One can approximate the entropy of a molecule by making the assumption that the various degrees of freedom within the molecule contribute to the entropy independently [1]. In this work, we assume that the electronic and nuclear degrees of freedom do not contribute to the entropy and we neglect cross terms. Neglecting the electronic degrees of freedom is not an issue since the ultimate purpose of these entropies is to serve as a reference state for a molecule in an ideal gas in its ground electronic state.

$$S = S_{tran} + S_{rot} + S_{vib} + S_{\mathrm{int}-rot} \quad (1)$$

The translational contribution is well known, given the molecular weight of the molecule. We assume a rigid-rotor approximation for the rotational degrees of freedom, which requires only the moment of inertia around the principle axes obtained from QM and the symmetry number. Given the normal vibrational modes, we compute the vibrational contribution to the entropy using the harmonic oscillator approximation. Finally, for the internal rotation, we can use the rigid rotor approximation and assume there is no energy barrier for the methyl groups of toluene, *m*-xylene, and *p*-xylene. For *o*-xylene, in which hindered rotation is present, we require either the energy barriers or

the energy levels associated with internal rotation. We have examined both of these approaches, using the energy landscape from QM and the energy levels from experiment.

For each of the QM calculations, entropy is calculated at 250K, 298.15K and from 260K to 540K in 20K increments. This temperature range is chosen based upon the availability of experimental data [10-12].

In terms of software, we used Gaussian98 for the QM calculations [15] and Therpoly for the SM calculations [16].

## 2.3 Results and Discussion

In Table 1, we compare the QM and experimental vibrational frequencies for benzene. Such a comparison was made for all five compounds. Analogous tables for the other compounds are found in the supplementary material. The percent difference between the QM and experimental frequencies both before scaling (direct QM results) and after scaling are shown in Table 2. As we can see the relative error for the HF method directly from QM averaged over all molecules and basis sets is about 10.4% as compared to 3.3% for B3LYP. The difference between methods drops substantially after the application of the scaling factor, which is now 2.0% for HF and 1.5% for B3LYP.

In Table 3, we present the values of the scale factors. This information is useful to analyze because it shows the variability of the scale factor among the five components. For the various combinations of method and basis set, the standard deviation of the scaling factor ranges from 0.1% to 0.5%, meaning that an averaged scaling factor is meaningful to, at best, the third significant digit. The available NIST reported scale

factors are also shown [6]. The NIST data are averaged over many compounds and are not specific to the aromatic compounds studied here. The difference between the NIST scaling factors and the average scaling factors reported here for the same method and basis set are approximately 0.4%.

In the supplementary material, we present the relative CPU time required for each of the calculations. One of the points to be made here is that the B3LYP/6-311++G(3df,2pd) required 168 times as much CPU resources as HF/6-31G(d) and resulted in a reduction of the error in the scaled vibrational frequencies of 0.6%. One must also take into account that the scale factors themselves have a variability from compound to compounds which is as large as 0.5% even among these very similar aromatic compounds. This information is useful in providing a perspective when making a decision on the relative trade-off between computational resources and resulting accuracy. For some applications, the less sophisticated method and basis set may be equally satisfactory.

In Table 4, we report the entropies as a function of temperature for benzene. We plot the relative error of the entropies in Figure 1. All of the errors for all of the combinations of method and basis set fall within 0.5% relative to the experimental result, which has been reported to be accurate in the range of 0.09% to 0.26% [9]. As noted with the vibrational frequencies, the B3LYP method is slightly more accurate than the HF method. However, there is no monotonic trend for basis set size.

We can immediately see in Figure 1 that there is a systematic error in the calculations, in which the entropy is underestimated at the low temperature and over-

estimated at higher temperatures. Curiously, for the most accurate methods, the temperature at which the theory best agrees with experiment is at 298.15 K. All of the QM results, normal vibrational frequencies and moments of inertia, are independent of temperature. Therefore, this systematic error in the temperature dependence comes from either (i) errors in the QM properties at 0 K or (ii) the SM mechanical approximation of independence of the various degrees of freedom.

Tables analogous to Table 4 and figures analogous to Figure 1 for the other compounds are found in the supplementary material. The results for toluene, *p*-xylene and *m*-xylene are very similar to benzene and the above discussion for benzene applies equally to them. The errors for the entropy averaged over all temperatures are shown in Table 5. For benzene, toluene, *p*-xylene and *m*-xylene all of the entropy errors are less than 0.5% for all combinations of basis set and method.

We reserve a separate discussion for *o*-xylene since it (uniquely among the compounds examined) here has a non negligible energy barrier to internal rotation of the methyl groups. In order to calculate *o*-xylene entropy we need to take into account the effect of this internal rotational barrier. In order to get the rotational barrier, one can use QM calculation to calculate the molecule's energy as a function of methyl orientation. We find two rotational barrier energies; the larger barrier is $V_3$ and the smaller one is $V_6$ energy barrier [14]. Because the V6 barrier is relatively very small ($V_6$ = 14.3 $cm^{-1}$ vs. $V_3$ = 573.5 $cm^{-1}$ for HF/6-31G(d)), we neglect it. By fitting a potential function to $V_3$, one can solve the Hamiltonian and get the rotational barrier effect on the calculated entropies.

In the SM model, we include two restricted rotors, each with the same rotational barrier, representing the two methyl groups.

In Figure 2, we plot the percentage error between the calculated and experimental entropies for *o*-xylene. As was the case for all of the combinations of method and basis set for the other four compounds, the maximum error for o-xylene at any temperature is less than 0.5%. Thus, the addition of restricted internal rotation does not introduce significant additional error to the overall entropy, when internal rotation is properly accounted for. Treating the internal rotation as barrier-free, results in an additional error of up to 2%.

## 2.4 Conclusion

Entropies of a set of simple aromatic molecules—benzene, toluene, *p*-xylene, *m*-xylene and *o*-xylene—were calculated using quantum mechanics and statistical mechanics across the range of 250 K to 540 K. The calculated entropies were compared with the experimental entropies in the same temperature interval. All of the input for the statistical mechanical evaluation of the entropy, including vibrational frequencies, moments of inertia, and barriers to internal rotation, was generated via quantum mechanical calculations. The vibrational frequencies were scaled based upon comparison with experimentally determined frequencies. We examined the effect of different levels of theory on agreement with experimentally determined entropies.

We find that we are able to use a combination of quantum mechanical calculations and statistical mechanics to generate entropies across a temperature range of

250 K to 540 K within 0.5% of experimentally determined values for all compounds studied. We also acknowledge that, given the current state of quantum mechanical computations, an empirical scaling factor for the vibration frequencies is still required. This empirical factor largely eliminates the advantage in accuracy of increased basis set size. However, the empirical factor does not eliminate the advantage in accuracy of B3LYP over Hartree-Fock. Therefore, we recommend that B3LYP with a relatively small basis set is sufficient for accurate entropy calculations, so long as one scales the vibrational frequencies with an appropriate empirical factor. Finally, we find that the variation between scaling factors from one compound to the next is on average 0.3%, rendering the reported scaling factors meaningful to at most the third significant digit.

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# Appendices

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Table 1:Benzene experimental, computed and corrected frequencies ($cm^{-1}$)

| | HF | | | | | | B3LYP | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Benzene | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | Symmetry | Pitzer Number |
| Experimental Freq. | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Symbol | Symbol |
| 3062 | 3390 | 3064 | 3374 | 3062 | 3347 | 3063 | 3212 | 3108 | 3208 | 3135 | 3194 | 3123 | $A_{1G}$ | 2 |
| 3053 | 3378 | 3053 | 3363 | 3052 | 3336 | 3053 | 3201 | 3098 | 3198 | 3126 | 3184 | 3113 | $E_{1U}$ | 20b |
| 3053 | 3378 | 3053 | 3363 | 3052 | 3336 | 3053 | 3201 | 3098 | 3198 | 3126 | 3184 | 3113 | $E_{1U}$ | 20a |
| 3048 | 3360 | 3036 | 3345 | 3036 | 3317 | 3036 | 3185 | 3083 | 3182 | 3110 | 3168 | 3098 | $E_{2G}$ | 7b |
| 3048 | 3360 | 3036 | 3345 | 3036 | 3317 | 3036 | 3185 | 3083 | 3182 | 3110 | 3168 | 3098 | $E_{2G}$ | 7a |
| 3048 | 3349 | 3026 | 3334 | 3025 | 3300 | 3020 | 3175 | 3073 | 3172 | 3101 | 3154 | 3084 | $B_{1U}$ | 13 |
| 1599 | 1797 | 1625 | 1782 | 1617 | 1768 | 1618 | 1656 | 1603 | 1642 | 1605 | 1632 | 1596 | $E_{2G}$ | 8b |
| 1599 | 1797 | 1625 | 1782 | 1617 | 1768 | 1618 | 1656 | 1603 | 1642 | 1604 | 1632 | 1596 | $E_{2G}$ | 8a |
| 1482 | 1652 | 1493 | 1637 | 1486 | 1632 | 1493 | 1531 | 1482 | 1515 | 1481 | 1516 | 1482 | $E_{1U}$ | 19b |
| 1482 | 1652 | 1493 | 1637 | 1486 | 1632 | 1493 | 1531 | 1482 | 1515 | 1481 | 1515 | 1482 | $E_{1U}$ | 19a |
| 1350 | 1508 | 1363 | 1498 | 1360 | 1495 | 1368 | 1387 | 1342 | 1378 | 1347 | 1386 | 1355 | $A_{2G}$ | 3 |
| 1309 | 1352 | 1222 | 1351 | 1226 | 1336 | 1222 | 1357 | 1313 | 1353 | 1322 | 1333 | 1304 | $B_{2U}$ | 14 |
| 1178 | 1294 | 1170 | 1285 | 1166 | 1280 | 1172 | 1208 | 1169 | 1199 | 1172 | 1199 | 1173 | $E_{2G}$ | 9b |
| 1178 | 1294 | 1170 | 1284 | 1166 | 1280 | 1172 | 1208 | 1169 | 1198 | 1171 | 1199 | 1173 | $E_{2G}$ | 9a |
| 1146 | 1197 | 1082 | 1195 | 1084 | 1170 | 1071 | 1186 | 1147 | 1177 | 1150 | 1176 | 1150 | $B_{2U}$ | 15 |
| 1037 | 1142 | 1032 | 1133 | 1028 | 1127 | 1032 | 1069 | 1035 | 1061 | 1037 | 1060 | 1037 | $E_{1U}$ | 18b |
| 1037 | 1142 | 1032 | 1133 | 1028 | 1127 | 1032 | 1069 | 1035 | 1061 | 1037 | 1060 | 1037 | $E_{1U}$ | 18a |
| 1010 | 1097 | 991 | 1096 | 994 | 974 | 892 | 1020 | 987 | 1018 | 995 | 933 | 912 | $B_{1U}$ | 12 |
| 993 | 1084 | 980 | 1074 | 975 | 1070 | 979 | 1021 | 988 | 1013 | 990 | 1013 | 991 | $A_{1G}$ | 1 |
| 990 | 1137 | 1027 | 1146 | 1040 | 1112 | 1018 | 1012 | 979 | 1010 | 987 | 996 | 974 | $B_{2G}$ | 5 |
| 967 | 1100 | 995 | 1107 | 1004 | 1093 | 1000 | 970 | 939 | 985 | 963 | 988 | 966 | $E_{2U}$ | 17b |
| 967 | 1100 | 995 | 1107 | 1004 | 1093 | 1000 | 970 | 939 | 984 | 962 | 987 | 965 | $E_{2U}$ | 17a |
| 846 | 962 | 869 | 958 | 870 | 953 | 872 | 866 | 838 | 865 | 845 | 868 | 848 | $E_{1G}$ | 10b |
| 846 | 962 | 869 | 958 | 870 | 953 | 872 | 866 | 838 | 863 | 843 | 865 | 846 | $E_{1G}$ | 10a |
| 707 | 777 | 702 | 785 | 713 | 744 | 680 | 718 | 695 | 710 | 694 | 688 | 673 | $B_{2G}$ | 4 |
| 673 | 765 | 691 | 759 | 688 | 757 | 692 | 696 | 673 | 689 | 673 | 690 | 675 | $A_{2U}$ | 11 |
| 606 | 666 | 601 | 663 | 602 | 657 | 601 | 622 | 602 | 619 | 605 | 620 | 606 | $E_{2G}$ | 6b |
| 606 | 666 | 601 | 663 | 602 | 657 | 601 | 622 | 602 | 619 | 605 | 620 | 606 | $E_{2G}$ | 6a |
| 398 | 453 | 410 | 452 | 410 | 447 | 409 | 416 | 402 | 412 | 403 | 411 | 402 | $E_{2U}$ | 16b |
| 398 | 453 | 410 | 452 | 410 | 447 | 409 | 416 | 402 | 411 | 402 | 411 | 401 | $E_{2U}$ | 16a |

Table 2: Average % errors of frequencies, before and after applying the scale factors

| **Molecule** | HF | | | | | | B3LYP | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | |
| | QM | scaled | QM | Scaled | QM | scaled | QM | scaled | QM | scaled | QM | scaled |
| Benzene | 10.93% | 1.69% | 10.52% | 1.76% | 9.30% | 2.16% | 3.09% | 0.93% | 2.66% | 0.81% | 2.79% | 1.07% |
| Toluene | 10.91% | 1.78% | 10.44% | 2.24% | 9.56% | 2.43% | 3.99% | 2.08% | 3.56% | 1.94% | 2.82% | 1.22% |
| *m*-xylene | 11.07% | 1.76% | 10.45% | 1.83% | 9.74% | 1.89% | 3.55% | 1.39% | 3.03% | 1.28% | 2.80% | 1.18% |
| *p*-xylene | 11.18% | 2.33% | 10.53% | 2.17% | 9.88% | 2.28% | 4.05% | 2.00% | 3.39% | 1.89% | 3.33% | 1.79% |
| *o*-xylene | 10.95% | 1.97% | 10.34% | 1.96% | 9.42% | 2.06% | 3.81% | 1.59% | 3.20% | 1.58% | 2.97% | 1.48% |
| Average | 11.01% | 1.91% | 10.46% | 1.99% | 9.58% | 2.16% | 3.70% | 1.60% | 3.17% | 1.50% | 2.94% | 1.35% |

Table 3: Scale Factors based on comparing with Draeger's experimental frequencies

| **Molecule** | HF | | | B3LYP | | |
|---|---|---|---|---|---|---|
| | 6-31G(d) | 6-31++G(d,p) | 6-311++G(3df,2pd) | 6-31G(d) | 6-31++G(d,p) | 6-311++G(3df,2pd) |
| Benzene | 0.9038 | 0.9074 | 0.9151 | 0.9678 | 0.9774 | 0.9779 |
| Toluene | 0.8994 | 0.9028 | 0.9137 | 0.9680 | 0.9757 | 0.9766 |
| *m*-xylene | 0.8978 | 0.9138 | 0.9214 | 0.9623 | 0.9742 | 0.9757 |
| *p*-xylene | 0.8969 | 0.9030 | 0.9099 | 0.9634 | 0.9751 | 0.9740 |
| *o*-xylene | 0.8967 | 0.9036 | 0.9079 | 0.9656 | 0.9745 | 0.9762 |
| **Average scale factor** | 0.8989 | 0.9061 | 0.9136 | 0.9654 | 0.9754 | 0.9761 |
| NIST recommended | 0.8953 | | | 0.9614 | | |
| % error (vs. NIST) | 0.40% | | | 0.42% | | |

Table 4: Benzene experimental and calculated entropies over 250 K to 540 K (Cal/mol/K)

| Temp. (K) | Experiment | HF/ 6-31G(d) | HF/ 6-31G++(d,p) | HF/ 6-311G++(3df,2pd) | B3LYP/ 6-31G(d) | B3LYP/ 6-31G++(d,p) | B3LYP/ 6-311G++(3df,2pd) |
|---|---|---|---|---|---|---|---|
| 250 | 61.3 | 61.1 | 61.1 | 61.1 | 61.2 | 61.2 | 61.2 |
| 260 | 62.0 | 61.7 | 61.7 | 61.8 | 61.9 | 61.9 | 61.9 |
| 280 | 63.2 | 63.0 | 63.0 | 63.1 | 63.2 | 63.2 | 63.2 |
| 298.15 | 64.4 | 64.2 | 64.2 | 64.3 | 64.4 | 64.4 | 64.4 |
| 300 | 64.5 | 64.3 | 64.3 | 64.4 | 64.5 | 64.5 | 64.5 |
| 320 | 65.9 | 65.6 | 65.6 | 65.7 | 65.9 | 65.8 | 65.9 |
| 340 | 67.2 | 67.0 | 67.0 | 67.0 | 67.2 | 67.1 | 67.2 |
| 360 | 68.5 | 68.3 | 68.3 | 68.4 | 68.6 | 68.5 | 68.6 |
| 380 | 69.9 | 69.6 | 69.6 | 69.7 | 69.9 | 69.8 | 69.9 |
| 400 | 71.2 | 71.0 | 71.0 | 71.1 | 71.3 | 71.2 | 71.3 |
| 420 | 72.5 | 72.3 | 72.3 | 72.5 | 72.6 | 72.5 | 72.6 |
| 440 | 73.9 | 73.7 | 73.7 | 73.8 | 74.0 | 73.9 | 74.0 |
| 460 | 75.2 | 75.0 | 75.0 | 75.2 | 75.3 | 75.2 | 75.3 |
| 480 | 76.5 | 76.4 | 76.3 | 76.5 | 76.7 | 76.6 | 76.7 |
| 500 | 77.8 | 77.7 | 77.7 | 77.8 | 78.0 | 77.9 | 78.0 |
| 520 | 79.2 | 79.0 | 79.0 | 79.2 | 79.4 | 79.2 | 79.3 |
| 540 | 80.5 | 80.3 | 80.3 | 80.5 | 80.7 | 80.5 | 80.7 |

Table 5: Average percentage error for entropies over the 250-540K temperature range

| **Molecule** | HF | | | B3LYP | | |
|---|---|---|---|---|---|---|
| | 6-31G(d) | 6-31G++(d,p) | 6-311G++(3df,2pd) | 6-31G(d) | 6-31G++(d,p) | 6-311G++(3df,2pd) |
| Benzene | -0.30% | -0.32% | -0.16% | 0.08% | -0.03% | 0.06% |
| Toluene | -0.19% | -0.17% | -0.30% | 0.02% | -0.07% | -0.12% |
| *p*-xylene | -0.03% | -0.11% | -0.19% | 0.21% | 0.00% | -0.02% |
| *m*-xylene | -0.01% | -0.15% | -0.18% | 0.26% | 0.02% | -0.04% |
| *o*-xylene | -0.25% | -0.35% | -0.20% | 0.08% | -0.03% | 0.00% |

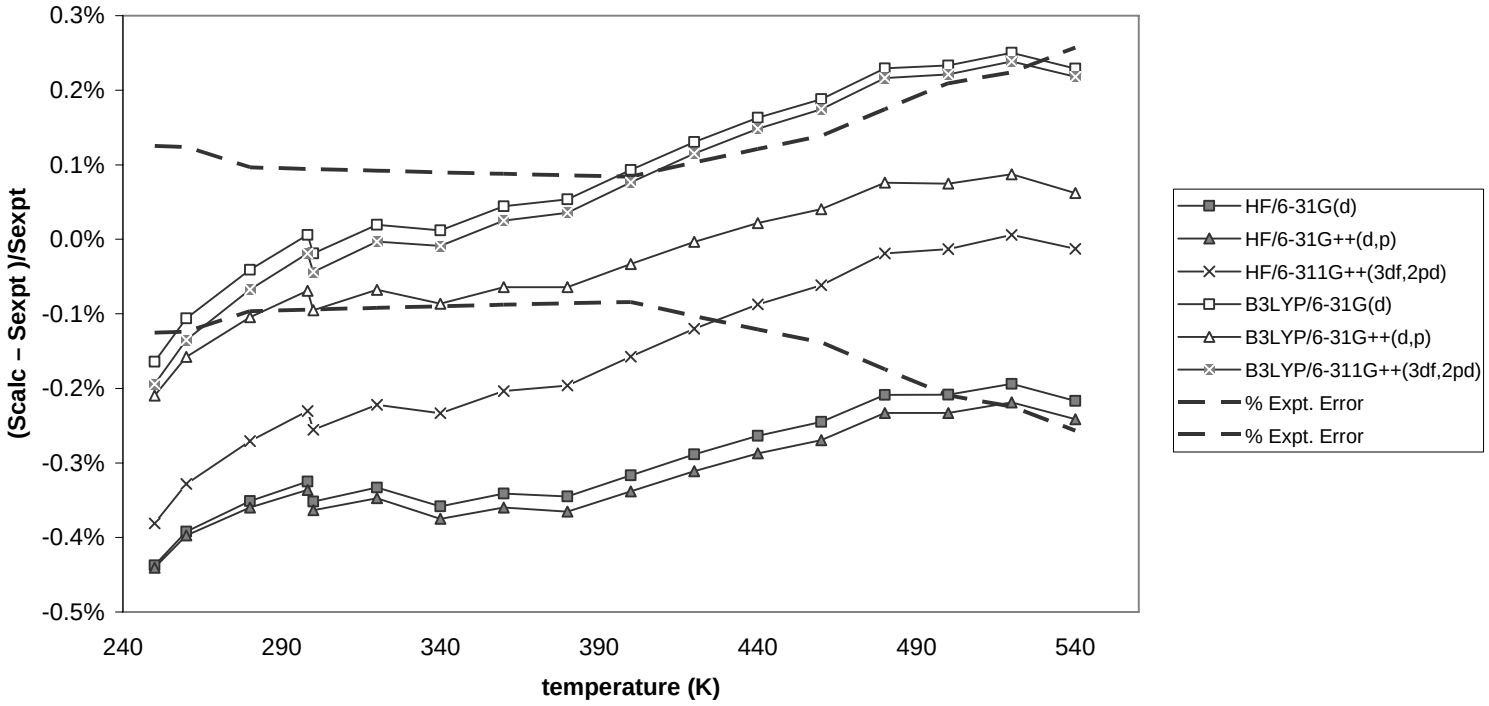


Figure 1 – Percentage error of the calculated benzene entropy in the temperature range of 250K-540K.

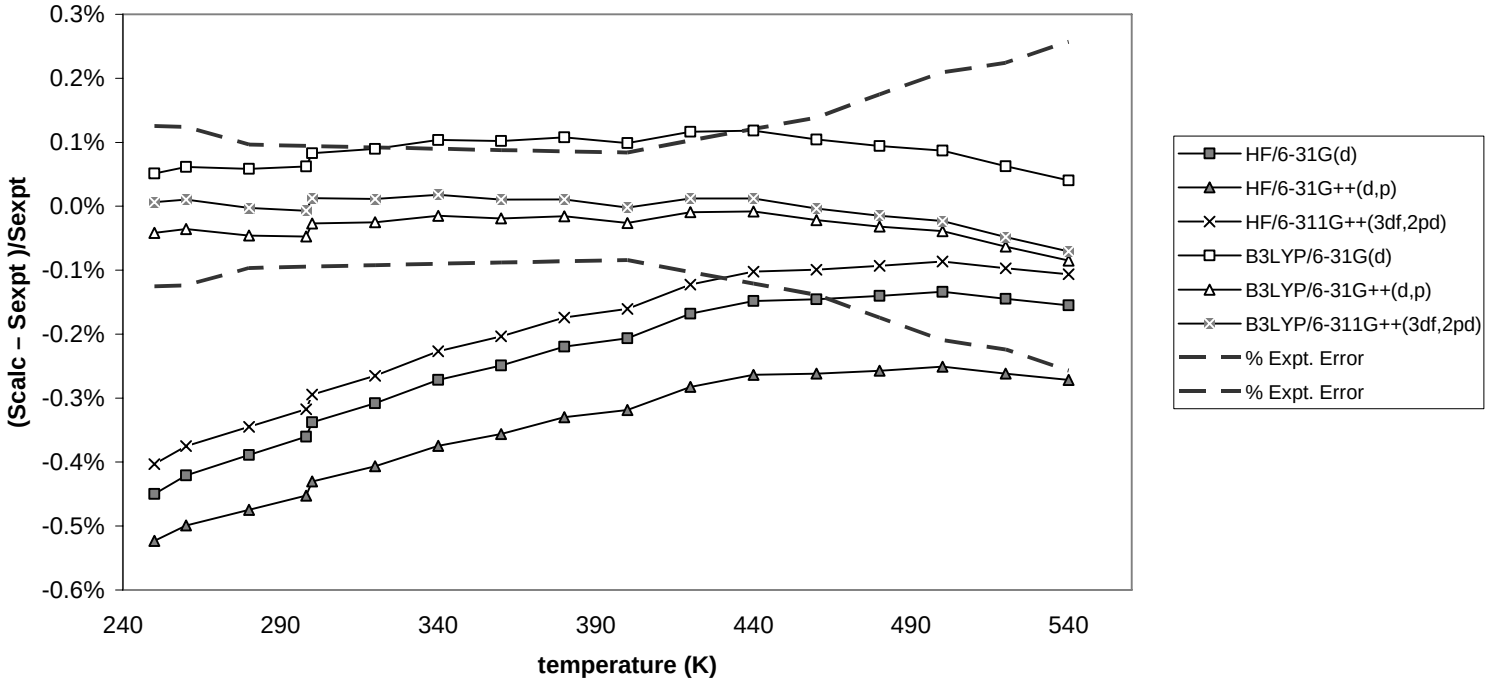


Figure 2– Percentage error of the calculated *o*-xylene entropy vs. experiment in the temperature range of 250K-540K.

**II. Supplementary Tables and Figures**

Table 1: Toluene experimental and calculated entropies over 250 K to 540 K (Cal/mol/K)

| Temp. (K) | Experiment | HF/ 6-31G(d) | HF/ 6-31G++(d,p) | HF/ 6-311G++(3df,2pd) | B3LYP/ 6-31G(d) | B3LYP/ 6-31G++(d,p) | B3LYP/ 6-311G++(3df,2pd) |
|---|---|---|---|---|---|---|---|
| 250 | **72.9** | 72.6 | 72.6 | 72.6 | 72.8 | 72.7 | 72.7 |
| 260 | **73.7** | 73.5 | 73.5 | 73.4 | 73.6 | 73.5 | 73.5 |
| 280 | **75.3** | 75.1 | 75.1 | 75.0 | 75.3 | 75.2 | 75.2 |
| 298.15 | **76.8** | 76.6 | 76.6 | 76.5 | 76.8 | 76.7 | 76.7 |
| 300 | **76.9** | 76.8 | 76.8 | 76.7 | 76.9 | 76.9 | 76.8 |
| 320 | **78.6** | 78.5 | 78.5 | 78.4 | 78.6 | 78.6 | 78.5 |
| 340 | **80.2** | 80.1 | 80.1 | 80.0 | 80.3 | 80.2 | 80.2 |
| 360 | **81.9** | 81.8 | 81.8 | 81.7 | 82.0 | 81.9 | 81.9 |
| 380 | **83.6** | 83.5 | 83.5 | 83.4 | 83.7 | 83.6 | 83.5 |
| 400 | **85.3** | 85.2 | 85.2 | 85.1 | 85.3 | 85.3 | 85.2 |
| 420 | **87.0** | 86.8 | 86.8 | 86.7 | 87.0 | 86.9 | 86.9 |
| 440 | **88.6** | 88.5 | 88.5 | 88.4 | 88.7 | 88.6 | 88.6 |
| 460 | **90.3** | 90.2 | 90.2 | 90.0 | 90.4 | 90.3 | 90.2 |
| 480 | **92.0** | 91.8 | 91.8 | 91.7 | 92.0 | 91.9 | 91.9 |
| 500 | **93.6** | 93.4 | 93.5 | 93.3 | 93.6 | 93.5 | 93.5 |
| 520 | **95.3** | 95.1 | 95.1 | 95.0 | 95.3 | 95.2 | 95.1 |
| 540 | **96.9** | 96.7 | 96.7 | 96.6 | 96.9 | 96.8 | 96.8 |

Table 2: *p*-xylene experimental and calculated entropies over 250 K to 540 K (Cal/mol/K)

| Temp. (K) | Experiment | HF/ 6-31G(d) | HF/ 6-31G++(d,p) | HF/ 6-311G++(3df,2pd) | B3LYP/ 6-31G(d) | B3LYP/ 6-31G++(d,p) | B3LYP/ 6-311G++(3df,2pd) |
|---|---|---|---|---|---|---|---|
| 250 | **79.2** | 79.3 | 79.2 | 79.2 | 79.4 | 79.3 | 79.3 |
| 260 | **80.2** | 80.3 | 80.2 | 80.2 | 80.5 | 80.3 | 80.3 |
| 280 | **82.3** | 82.3 | 82.2 | 82.2 | 82.5 | 82.3 | 82.3 |
| 298.15 | **84.1** | 84.1 | 84.1 | 84.0 | 84.3 | 84.2 | 84.2 |
| 300 | **84.3** | 84.3 | 84.3 | 84.2 | 84.5 | 84.4 | 84.3 |
| 320 | **86.3** | 86.4 | 86.3 | 86.2 | 86.5 | 86.4 | 86.4 |
| 340 | **88.4** | 88.4 | 88.3 | 88.2 | 88.6 | 88.4 | 88.4 |
| 360 | **90.4** | 90.4 | 90.3 | 90.2 | 90.6 | 90.4 | 90.4 |
| 380 | **92.4** | 92.4 | 92.3 | 92.2 | 92.6 | 92.4 | 92.4 |
| 400 | **94.4** | 94.4 | 94.3 | 94.2 | 94.6 | 94.4 | 94.4 |
| 420 | **96.4** | 96.4 | 96.3 | 96.2 | 96.6 | 96.4 | 96.4 |
| 440 | **98.4** | 98.4 | 98.3 | 98.2 | 98.6 | 98.4 | 98.4 |
| 460 | **100.4** | 100.3 | 100.3 | 100.2 | 100.6 | 100.4 | 100.4 |
| 480 | **102.4** | 102.3 | 102.2 | 102.1 | 102.6 | 102.3 | 102.3 |
| 500 | **104.4** | 104.3 | 104.2 | 104.1 | 104.5 | 104.3 | 104.3 |
| 520 | **106.3** | 106.2 | 106.1 | 106.0 | 106.5 | 106.2 | 106.2 |
| 540 | **108.2** | 108.1 | 108.0 | 107.9 | 108.4 | 108.1 | 108.1 |

Table 3 : *m*-xylene experimental and calculated entropies over 250 K to 540 K (Cal/mol/K)

| Temp. (K) | Experiment | HF/ 6-31G(d) | HF/ 6-31G++(d,p) | HF/ 6-311G++(3df,2pd) | B3LYP/ 6-31G(d) | B3LYP/ 6-31G++(d,p) | B3LYP/ 6-311G++(3df,2pd) |
|---|---|---|---|---|---|---|---|
| 250 | **80.6** | 80.6 | 80.5 | 80.4 | 80.7 | 80.6 | 80.5 |
| 260 | **81.6** | 81.6 | 81.5 | 81.5 | 81.8 | 81.6 | 81.6 |
| 280 | **83.6** | 83.6 | 83.5 | 83.5 | 83.8 | 83.6 | 83.6 |
| 298.15 | **85.5** | 85.4 | 85.3 | 85.3 | 85.7 | 85.5 | 85.4 |
| 300 | **85.7** | 85.6 | 85.5 | 85.5 | 85.8 | 85.7 | 85.6 |
| 320 | **87.7** | 87.6 | 87.5 | 87.5 | 87.9 | 87.7 | 87.6 |
| 340 | **89.7** | 89.7 | 89.5 | 89.5 | 89.9 | 89.7 | 89.6 |
| 360 | **91.7** | 91.7 | 91.5 | 91.5 | 91.9 | 91.7 | 91.6 |
| 380 | **93.7** | 93.7 | 93.5 | 93.5 | 93.9 | 93.7 | 93.6 |
| 400 | **95.7** | 95.7 | 95.5 | 95.5 | 96.0 | 95.7 | 95.6 |
| 420 | **97.7** | 97.7 | 97.5 | 97.5 | 98.0 | 97.7 | 97.6 |
| 440 | **99.7** | 99.7 | 99.5 | 99.5 | 100.0 | 99.7 | 99.6 |
| 460 | **101.6** | 101.6 | 101.5 | 101.5 | 101.9 | 101.7 | 101.6 |
| 480 | **103.6** | 103.6 | 103.4 | 103.4 | 103.9 | 103.6 | 103.6 |
| 500 | **105.5** | 105.5 | 105.4 | 105.4 | 105.9 | 105.6 | 105.5 |
| 520 | **107.5** | 107.5 | 107.3 | 107.3 | 107.8 | 107.5 | 107.4 |
| 540 | **109.4** | 109.4 | 109.2 | 109.2 | 109.7 | 109.4 | 109.4 |

Table 4: *o*-xylene experimental and calculated entropies over 250 K to 540 K (Cal/mol/K)

| Temp. (K) | Experiment | HF/ 6-31G(d) | HF/ 6-31G++(d,p) | HF/ 6-311G++(3df,2pd) | B3LYP/ 6-31G(d) | B3LYP/ 6-31G++(d,p) | B3LYP/ 6-311G++(3df,2pd) |
|---|---|---|---|---|---|---|---|
| 250 | **78.9** | 78.6 | 78.5 | 78.6 | 79.0 | 78.9 | 78.9 |
| 260 | **80.0** | 79.7 | 79.6 | 79.7 | 80.0 | 80.0 | 80.0 |
| 280 | **82.1** | 81.8 | 81.7 | 81.9 | 82.2 | 82.1 | 82.1 |
| 298.15 | **84.1** | 83.8 | 83.7 | 83.8 | 84.1 | 84.0 | 84.1 |
| 300 | **84.2** | 84.0 | 83.9 | 84.0 | 84.3 | 84.2 | 84.3 |
| 320 | **86.3** | 86.1 | 86.0 | 86.1 | 86.4 | 86.3 | 86.4 |
| 340 | **88.4** | 88.2 | 88.1 | 88.2 | 88.5 | 88.4 | 88.4 |
| 360 | **90.5** | 90.3 | 90.2 | 90.3 | 90.6 | 90.5 | 90.5 |
| 380 | **92.6** | 92.4 | 92.3 | 92.4 | 92.7 | 92.6 | 92.6 |
| 400 | **94.6** | 94.5 | 94.3 | 94.5 | 94.7 | 94.6 | 94.6 |
| 420 | **96.7** | 96.5 | 96.4 | 96.6 | 96.8 | 96.7 | 96.7 |
| 440 | **98.7** | 98.6 | 98.4 | 98.6 | 98.8 | 98.7 | 98.7 |
| 460 | **100.7** | 100.6 | 100.5 | 100.6 | 100.8 | 100.7 | 100.7 |
| 480 | **102.7** | 102.6 | 102.5 | 102.6 | 102.8 | 102.7 | 102.7 |
| 500 | **104.7** | 104.6 | 104.5 | 104.6 | 104.8 | 104.7 | 104.7 |
| 520 | **106.7** | 106.5 | 106.4 | 106.6 | 106.8 | 106.6 | 106.7 |
| 540 | **108.7** | 108.5 | 108.4 | 108.6 | 108.7 | 108.6 | 108.6 |

Table 5: Toluene experimental, computed and corrected frequencies ($cm^{-1}$)

| | HF | | | | | | B3LYP | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Toluene | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | Symmetry | Pitzer Number |
| Experimental Freq. | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Symbol | Symbol |
| 3067 | 3385 | 3044 | 3370 | 3042 | 3343 | 3054 | 3208 | 3105 | 3204 | 3126 | 3190 | 3116 | A1 | 20a |
| 3056 | 3362 | 3023 | 3348 | 3022 | 3320 | 3033 | 3186 | 3084 | 3183 | 3106 | 3169 | 3095 | A1 | 2 |
| 3056 | 3371 | 3032 | 3357 | 3030 | 3329 | 3042 | 3195 | 3092 | 3191 | 3114 | 3178 | 3103 | B2 | 20b |
| 3039 | 3349 | 3012 | 3335 | 3011 | 3307 | 3022 | 3174 | 3072 | 3170 | 3093 | 3157 | 3083 | B2 | 7b |
| 3039 | 3346 | 3009 | 3332 | 3008 | 3302 | 3017 | 3172 | 3071 | 3169 | 3092 | 3154 | 3080 | A1 | 13 |
| 2933 | 3279 | 2949 | 3261 | 2944 | 3233 | 2954 | 3123 | 3023 | 3116 | 3040 | 3101 | 3029 | B2 | M2 |
| 2933 | 3257 | 2929 | 3239 | 2924 | 3210 | 2933 | 3097 | 2997 | 3089 | 3014 | 3075 | 3003 | B1 | M2 |
| 2921 | 3201 | 2879 | 3181 | 2872 | 3158 | 2886 | 3040 | 2942 | 3030 | 2957 | 3022 | 2951 | A1 | M1 |
| 1611 | 1813 | 1630 | 1799 | 1624 | 1786 | 1631 | 1668 | 1614 | 1654 | 1614 | 1645 | 1607 | A1 | 8a |
| 1585 | 1786 | 1606 | 1772 | 1600 | 1758 | 1606 | 1646 | 1593 | 1632 | 1592 | 1623 | 1585 | B2 | 8b |
| 1500 | 1672 | 1504 | 1659 | 1497 | 1653 | 1510 | 1549 | 1499 | 1533 | 1496 | 1533 | 1497 | A1 | 19a |
| 1463 | 1645 | 1479 | 1624 | 1467 | 1620 | 1480 | 1529 | 1480 | 1506 | 1469 | 1505 | 1470 | B2 | M4 |
| 1453 | 1636 | 1471 | 1613 | 1456 | 1608 | 1469 | 1518 | 1470 | 1493 | 1457 | 1492 | 1457 | B1 | M4 |
| 1436 | 1480 | 1331 | 1470 | 1327 | 1468 | 1342 | 1368 | 1324 | 1359 | 1326 | 1362 | 1330 | B2 | 14 |
| 1384 | 1567 | 1409 | 1546 | 1396 | 1540 | 1407 | 1443 | 1396 | 1420 | 1386 | 1416 | 1383 | A1 | M3 |
| 1330 | 1609 | 1447 | 1592 | 1437 | 1587 | 1450 | 1491 | 1443 | 1473 | 1437 | 1472 | 1438 | B2 | 19b |
| 1278 | 1342 | 1207 | 1340 | 1209 | 1326 | 1211 | 1349 | 1306 | 1343 | 1310 | 1327 | 1296 | B2 | 3 |
| 1212 | 1325 | 1192 | 1318 | 1190 | 1306 | 1193 | 1239 | 1199 | 1231 | 1201 | 1225 | 1196 | A1 | 7a |
| 1178 | 1302 | 1171 | 1165 | 1052 | 1161 | 1060 | 1076 | 1042 | 1063 | 1037 | 1206 | 1178 | A1 | 9a |
| 1155 | 1234 | 1110 | 1228 | 1108 | 1215 | 1110 | 1192 | 1154 | 1183 | 1154 | 1183 | 1155 | B2 | 9b |
| 1083 | 1184 | 1065 | 1178 | 1063 | 1164 | 1063 | 1122 | 1086 | 1113 | 1086 | 1113 | 1087 | B2 | 15 |
| 1043 | 1173 | 1055 | 1293 | 1167 | 1288 | 1177 | 1215 | 1176 | 1205 | 1176 | 1065 | 1040 | B1 | M6 |
| 1030 | 1132 | 1018 | 1126 | 1016 | 1115 | 1019 | 1060 | 1026 | 1052 | 1027 | 1050 | 1026 | A1 | 18a |
| 1004 | 1121 | 1008 | 1124 | 1015 | 1102 | 1007 | 1018 | 986 | 1014 | 990 | 1000 | 976 | A1 | 1 |
| 980 | 1090 | 980 | 1086 | 980 | 1055 | 964 | 992 | 961 | 999 | 975 | 998 | 975 | B1 | 5 |
| 980 | 1085 | 976 | 1104 | 997 | 1099 | 1004 | 1012 | 980 | 1002 | 978 | 1002 | 978 | B2 | M6 |
| 964 | 1097 | 987 | 1077 | 972 | 1070 | 978 | 964 | 933 | 980 | 956 | 990 | 967 | A2 | 17a |
| 894 | 1017 | 915 | 1014 | 915 | 1010 | 922 | 911 | 882 | 912 | 890 | 918 | 896 | B1 | 17b |
| 843 | 956 | 860 | 952 | 859 | 949 | 867 | 860 | 832 | 856 | 836 | 860 | 840 | A2 | 10a |
| 786 | 852 | 766 | 849 | 766 | 837 | 764 | 802 | 776 | 798 | 779 | 794 | 775 | A1 | 12 |
| 730 | 824 | 741 | 819 | 740 | 813 | 743 | 748 | 724 | 743 | 725 | 743 | 725 | B1 | 10b |
| 695 | 773 | 695 | 773 | 698 | 744 | 679 | 711 | 689 | 707 | 690 | 698 | 682 | B1 | 4 |
| 623 | 682 | 614 | 680 | 613 | 675 | 617 | 637 | 617 | 635 | 619 | 636 | 621 | B2 | 6b |
| 521 | 563 | 506 | 561 | 507 | 560 | 511 | 529 | 512 | 527 | 514 | 529 | 517 | A1 | 6a |
| 462 | 520 | 467 | 519 | 468 | 516 | 471 | 478 | 462 | 475 | 463 | 476 | 465 | B1 | 16b |
| 405 | 456 | 410 | 454 | 410 | 452 | 413 | 417 | 404 | 415 | 405 | 415 | 405 | A2 | 16a |
| 341 | 367 | 330 | 367 | 331 | 366 | 335 | 342 | 331 | 343 | 335 | 344 | 336 | B2 | 18b |
| 205 | 229 | 206 | 228 | 205 | 227 | 207 | 211 | 204 | 210 | 204 | 209 | 204 | B1 | 11 |
| 15 | Internal Rotation | | | | | | | | | | | | A2 | i-rot |

Table 6: *p*-xylene experimental, computed and corrected frequencies ($cm^{-1}$)

| | HF | | | | | | B3LYP | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *p* -xylene | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | Symmetry | Pitzer Number |
| Experimental Freq. | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Symbol | Symbol |
| 3059 | 3365 | 3018 | 3349 | 3025 | 3322 | 3023 | 3188 | 3071 | 3183 | 3104 | 3169 | 3087 | A1g | 2 |
| 3056 | 3361 | 3015 | 3346 | 3022 | 3319 | 3020 | 3184 | 3067 | 3180 | 3101 | 3166 | 3084 | B2u | 20b |
| 3045 | 3342 | 2997 | 3327 | 3004 | 3299 | 3002 | 3168 | 3052 | 3163 | 3085 | 3149 | 3067 | B1u | 13 |
| 3042 | 3342 | 2998 | 3327 | 3005 | 3300 | 3003 | 3168 | 3052 | 3163 | 3085 | 3150 | 3068 | B3g | 7b |
| 2939 | 3277 | 2939 | 3258 | 2942 | 3230 | 2939 | 3122 | 3007 | 3115 | 3038 | 3099 | 3019 | B3g | M2 |
| 2939 | 3277 | 2939 | 3258 | 2942 | 3230 | 2939 | 3122 | 3007 | 3115 | 3038 | 3099 | 3019 | B2u | M2 |
| 2938 | 3254 | 2919 | 3235 | 2922 | 3207 | 2918 | 3095 | 2981 | 3088 | 3011 | 3072 | 2992 | B2g | M2 |
| 2938 | 3255 | 2919 | 3236 | 2922 | 3207 | 2918 | 3095 | 2981 | 3088 | 3011 | 3072 | 2992 | B3u | M2 |
| 2927 | 3200 | 2870 | 3179 | 2871 | 3156 | 2872 | 3038 | 2927 | 3030 | 2955 | 3020 | 2941 | A1g | M1 |
| 2927 | 3199 | 2869 | 3179 | 2870 | 3156 | 2872 | 3038 | 2927 | 3030 | 2954 | 3020 | 2941 | B1u | M1 |
| 1616 | 1827 | 1638 | 1814 | 1638 | 1801 | 1639 | 1678 | 1616 | 1664 | 1623 | 1656 | 1613 | A1g | 8a |
| 1578 | 1773 | 1590 | 1760 | 1589 | 1747 | 1589 | 1633 | 1574 | 1620 | 1580 | 1612 | 1570 | B3g | 8b |
| 1520 | 1696 | 1521 | 1683 | 1520 | 1677 | 1526 | 1568 | 1511 | 1553 | 1514 | 1552 | 1511 | B1u | 19a |
| 1458 | 1644 | 1475 | 1622 | 1465 | 1617 | 1471 | 1529 | 1473 | 1504 | 1466 | 1503 | 1463 | B2u | 14 |
| 1458 | 1635 | 1467 | 1612 | 1456 | 1608 | 1463 | 1518 | 1462 | 1492 | 1455 | 1491 | 1452 | B2g | M4 |
| 1458 | 1636 | 1467 | 1613 | 1457 | 1608 | 1463 | 1518 | 1463 | 1493 | 1456 | 1492 | 1453 | B3u | M4 |
| 1446 | 1634 | 1465 | 1611 | 1455 | 1606 | 1461 | 1517 | 1462 | 1491 | 1454 | 1489 | 1451 | B3g | M4 |
| 1400 | 1317 | 1181 | 1314 | 1187 | 1298 | 1181 | 1346 | 1297 | 1339 | 1306 | 1320 | 1286 | B2u | 19b |
| 1385 | 1566 | 1405 | 1545 | 1396 | 1539 | 1400 | 1442 | 1389 | 1419 | 1384 | 1416 | 1379 | B1u | M3 |
| 1378 | 1568 | 1406 | 1547 | 1397 | 1541 | 1402 | 1443 | 1390 | 1420 | 1384 | 1417 | 1380 | A1g | M3 |
| 1320 | 1569 | 1407 | 1554 | 1403 | 1548 | 1409 | 1456 | 1403 | 1441 | 1405 | 1439 | 1402 | B2u | M4 |
| 1313 | 1467 | 1315 | 1456 | 1315 | 1455 | 1324 | 1353 | 1304 | 1341 | 1308 | 1348 | 1313 | B3g | 3 |
| 1225 | 1338 | 1200 | 1332 | 1203 | 1322 | 1203 | 1247 | 1201 | 1238 | 1208 | 1236 | 1204 | B1u | 20a |
| 1203 | 1313 | 1178 | 1304 | 1178 | 1299 | 1182 | 1235 | 1190 | 1226 | 1195 | 1222 | 1190 | A1g | 7a |
| 1183 | 1311 | 1176 | 1301 | 1175 | 1296 | 1179 | 1220 | 1176 | 1210 | 1180 | 1211 | 1179 | A1g | 9a |
| 1099 | 1093 | 981 | 1101 | 994 | 1100 | 1000 | 1000 | 964 | 990 | 965 | 990 | 964 | B2u | 15 |
| 1032 | 1172 | 1051 | 1165 | 1052 | 1157 | 1053 | 1074 | 1035 | 1060 | 1034 | 1061 | 1034 | B2g | M6 |
| 1032 | 1174 | 1053 | 1165 | 1052 | 1164 | 1059 | 1077 | 1038 | 1064 | 1038 | 1067 | 1040 | B3u | M6 |
| 1026 | 1118 | 1002 | 1113 | 1005 | 1100 | 1001 | 1042 | 1004 | 1036 | 1011 | 1034 | 1007 | B1u | 18a |
| 1001 | 1122 | 1007 | 1113 | 1005 | 1111 | 1011 | 1037 | 999 | 1024 | 999 | 1026 | 999 | B3g | M6 |
| 972 | 1065 | 955 | 1059 | 956 | 1050 | 955 | 959 | 924 | 975 | 950 | 988 | 962 | A1u | 17a |
| 972 | 1197 | 1073 | 1191 | 1075 | 1173 | 1068 | 1153 | 1110 | 1143 | 1115 | 1143 | 1113 | B2u | M6 |
| 930 | 1070 | 959 | 1065 | 962 | 1055 | 960 | 957 | 922 | 954 | 930 | 958 | 933 | B2g | 5 |
| 832 | 952 | 854 | 946 | 855 | 945 | 860 | 856 | 825 | 850 | 829 | 854 | 832 | B1g | 10a |
| 830 | 893 | 801 | 889 | 803 | 886 | 806 | 841 | 810 | 836 | 815 | 838 | 816 | A1g | 1 |
| 795 | 902 | 809 | 899 | 812 | 899 | 818 | 814 | 784 | 810 | 790 | 816 | 795 | B3u | 17b |
| 700 | 780 | 700 | 785 | 709 | 753 | 685 | 718 | 692 | 714 | 696 | 705 | 686 | B2g | 4 |
| 694 | 773 | 693 | 771 | 696 | 765 | 696 | 731 | 704 | 728 | 710 | 727 | 708 | B1u | 12 |
| 643 | 707 | 634 | 704 | 636 | 700 | 637 | 660 | 636 | 657 | 641 | 658 | 641 | B3g | 6b |
| 481 | 544 | 488 | 542 | 490 | 541 | 492 | 500 | 481 | 495 | 483 | 497 | 484 | B3u | 16b |
| 454 | 494 | 443 | 492 | 445 | 492 | 447 | 464 | 447 | 463 | 451 | 465 | 453 | A1g | 6a |
| 410 | 458 | 410 | 457 | 413 | 455 | 414 | 418 | 403 | 418 | 407 | 417 | 406 | A1u | 16a |
| 389 | 413 | 371 | 414 | 374 | 413 | 376 | 385 | 371 | 386 | 376 | 387 | 377 | B3g | 9b |
| 312 | 335 | 301 | 335 | 302 | 332 | 303 | 309 | 298 | 309 | 301 | 308 | 300 | B2g | 10b |
| 285 | 305 | 274 | 305 | 276 | 305 | 277 | 285 | 275 | 286 | 279 | 287 | 279 | B2u | 18b |
| 132 | 149 | 133 | 148 | 133 | 147 | 134 | 137 | 132 | 136 | 133 | 136 | 132 | B3u | 11 |
| Ir = 5.09 | Internal Rotation | | | | | | | | | | | | B1g | i-rot |
| Ir = 5.09 | Internal Rotation | | | | | | | | | | | | A1u | i-rot |

Table 7: *m*-xylene experimental, computed and corrected frequencies ($cm^{-1}$)

| | HF | | | | | | B3LYP | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *m* -xylene | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | Symmetry | Pitzer Number |
| Experimental Freq. | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Symbol | Symbol |
| 3060 | 3376 | 3031 | 3361 | 3045 | 3332 | 3035 | 3200 | 3079 | 3198 | 3121 | 3182 | 3105 | A1 | 2 |
| 3052 | 3347 | 3005 | 3333 | 3019 | 3307 | 3013 | 3174 | 3054 | 3173 | 3096 | 3156 | 3079 | A1 | 7a |
| 3052 | 3359 | 3015 | 3345 | 3030 | 3311 | 3016 | 3182 | 3062 | 3182 | 3105 | 3165 | 3088 | B1 | 20b |
| 3032 | 3332 | 2991 | 3317 | 3005 | 3300 | 3006 | 3159 | 3040 | 3157 | 3081 | 3142 | 3065 | A1 | 13 |
| 2953 | 3279 | 2943 | 3260 | 2954 | 3159 | 2878 | 3124 | 3006 | 3121 | 3046 | 3102 | 3027 | B1 | M2 |
| 2953 | 3254 | 2921 | 3235 | 2931 | 3207 | 2921 | 3094 | 2977 | 3092 | 3018 | 3072 | 2997 | B2 | M2 |
| 2953 | 3253 | 2921 | 3235 | 2931 | 3206 | 2921 | 3093 | 2977 | 3092 | 3017 | 3072 | 2997 | A2 | M2 |
| 2939 | 3279 | 2944 | 3261 | 2954 | 3160 | 2879 | 3124 | 3006 | 3121 | 3046 | 3102 | 3027 | A1 | M1 |
| 2923 | 3202 | 2874 | 3181 | 2882 | 3233 | 2945 | 3042 | 2927 | 3037 | 2964 | 3025 | 2951 | B1 | M1 |
| 2923 | 3202 | 2875 | 3182 | 2882 | 3233 | 2945 | 3043 | 2928 | 3038 | 2964 | 3025 | 2952 | A1 | M2 |
| 1613 | 1815 | 1629 | 1802 | 1632 | 1789 | 1630 | 1667 | 1604 | 1654 | 1614 | 1646 | 1606 | B1 | 14 |
| 1604 | 1792 | 1609 | 1778 | 1610 | 1764 | 1607 | 1650 | 1588 | 1637 | 1597 | 1628 | 1588 | A1 | 8a |
| 1492 | 1669 | 1498 | 1654 | 1498 | 1649 | 1502 | 1546 | 1488 | 1529 | 1492 | 1528 | 1491 | B1 | 8b |
| 1458 | 1635 | 1468 | 1613 | 1461 | 1607 | 1464 | 1518 | 1461 | 1493 | 1457 | 1492 | 1456 | B1 | 19b |
| 1458 | 1588 | 1426 | 1572 | 1424 | 1566 | 1427 | 1471 | 1415 | 1453 | 1418 | 1451 | 1416 | A1 | M3 |
| 1458 | 1633 | 1466 | 1609 | 1458 | 1605 | 1462 | 1516 | 1459 | 1490 | 1454 | 1489 | 1452 | B2 | M4 |
| 1458 | 1650 | 1481 | 1630 | 1476 | 1626 | 1481 | 1533 | 1475 | 1509 | 1473 | 1509 | 1472 | A1 | M4 |
| 1458 | 1633 | 1466 | 1609 | 1458 | 1605 | 1462 | 1516 | 1459 | 1490 | 1454 | 1489 | 1453 | A2 | M4 |
| 1382 | 1567 | 1407 | 1546 | 1401 | 1540 | 1403 | 1443 | 1389 | 1418 | 1384 | 1416 | 1382 | A1 | 19a |
| 1382 | 1566 | 1406 | 1545 | 1399 | 1539 | 1402 | 1441 | 1387 | 1416 | 1382 | 1415 | 1381 | B1 | M4 |
| 1326 | 1465 | 1316 | 1455 | 1318 | 1455 | 1326 | 1360 | 1309 | 1353 | 1320 | 1349 | 1316 | B1 | M3 |
| 1265 | 1335 | 1198 | 1331 | 1205 | 1315 | 1198 | 1340 | 1290 | 1329 | 1297 | 1320 | 1288 | B1 | 3 |
| 1265 | 1373 | 1233 | 1366 | 1238 | 1353 | 1233 | 1284 | 1235 | 1273 | 1243 | 1271 | 1240 | A1 | 20a |
| 1172 | 1288 | 1156 | 1279 | 1159 | 1275 | 1162 | 1209 | 1164 | 1199 | 1170 | 1199 | 1170 | B1 | 15 |
| 1157 | 1239 | 1112 | 1234 | 1118 | 1228 | 1119 | 1186 | 1141 | 1175 | 1147 | 1175 | 1147 | B1 | 9b |
| 1095 | 1215 | 1091 | 1205 | 1092 | 1197 | 1090 | 1135 | 1092 | 1125 | 1098 | 1125 | 1097 | A1 | 9a |
| 1036 | 1174 | 1054 | 1165 | 1056 | 1159 | 1056 | 1077 | 1036 | 1062 | 1037 | 1065 | 1039 | B2 | M6 |
| 1036 | 1171 | 1051 | 1161 | 1052 | 1161 | 1057 | 1074 | 1034 | 1061 | 1035 | 1063 | 1037 | A2 | M6 |
| 1001 | 1099 | 987 | 1092 | 989 | 1084 | 988 | 1023 | 984 | 1017 | 992 | 1014 | 990 | A1 | M6 |
| 990 | 1105 | 992 | 1099 | 996 | 1074 | 979 | 1049 | 1010 | 1037 | 1012 | 1038 | 1013 | B1 | M6 |
| 965 | 1082 | 971 | 1076 | 974 | 1067 | 972 | 1005 | 967 | 995 | 971 | 996 | 972 | A1 | 1 |
| 965 | 1106 | 993 | 1111 | 1006 | 1101 | 1003 | 973 | 936 | 984 | 961 | 993 | 969 | B2 | 5 |
| 906 | 979 | 879 | 974 | 882 | 980 | 893 | 920 | 886 | 914 | 892 | 914 | 892 | B1 | 7b |
| 892 | 1010 | 907 | 1008 | 913 | 1008 | 918 | 903 | 869 | 903 | 881 | 910 | 888 | A2 | 17a |
| 887 | 1003 | 900 | 998 | 904 | 987 | 899 | 903 | 869 | 899 | 877 | 907 | 885 | B2 | 17b |
| 770 | 871 | 782 | 866 | 784 | 865 | 788 | 787 | 758 | 781 | 762 | 784 | 765 | B2 | 10b |
| 712 | 787 | 706 | 784 | 710 | 775 | 706 | 740 | 712 | 736 | 718 | 735 | 717 | A1 | 12 |
| 692 | 771 | 692 | 768 | 696 | 746 | 679 | 710 | 683 | 704 | 687 | 698 | 681 | B2 | 4 |
| 537 | 579 | 520 | 577 | 523 | 573 | 522 | 543 | 523 | 541 | 528 | 543 | 530 | A1 | 6a |
| 515 | 557 | 500 | 556 | 503 | 555 | 505 | 523 | 503 | 522 | 509 | 524 | 511 | B1 | 6b |
| 484 | 580 | 521 | 583 | 528 | 571 | 521 | 531 | 511 | 532 | 520 | 530 | 517 | A2 | 16a |
| 431 | 483 | 433 | 482 | 437 | 484 | 441 | 442 | 425 | 441 | 430 | 442 | 432 | B2 | 16b |
| 402 | 431 | 387 | 431 | 391 | 432 | 394 | 402 | 387 | 403 | 393 | 405 | 395 | B1 | 18b |
| 274 | 291 | 261 | 292 | 264 | 292 | 266 | 274 | 264 | 274 | 267 | 275 | 268 | A1 | 18a |
| 213 | 250 | 224 | 248 | 225 | 236 | 215 | 231 | 222 | 228 | 222 | 227 | 221 | A2 | 10a |
| 189 | 211 | 189 | 210 | 190 | 219 | 199 | 194 | 187 | 194 | 189 | 193 | 188 | B2 | 11 |
| Ir = 5.23 | Internal Rotation | | | | | | | | | | | | A2 | i-rot |
| Ir = 5.23 | Internal Rotation | | | | | | | | | | | | B2 | i-rot |

Table 8: *o*-xylene experimental, computed and corrected frequencies ($cm^{-1}$)

| | HF | | | | | | B3LYP | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *o*-xylene | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | 6-31G(d) | | 6-31++G(d,p) | | 6-311++G(3df,2pd) | | Symmetry | Pitzer Number |
| Experimental Freq. | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Computed | Corrected | Symbol | Symbol |
| 3076 | 3382 | 3032 | 3369 | 3044 | 3340 | 3032 | 3205 | 3095 | 3202 | 3120 | 3188 | 3112 | A1 | 20b |
| 3052 | 3366 | 3018 | 3354 | 3031 | 3325 | 3018 | 3190 | 3081 | 3187 | 3106 | 3173 | 3098 | B1 | 20a |
| 3045 | 3352 | 3006 | 3340 | 3018 | 3311 | 3006 | 3176 | 3067 | 3173 | 3092 | 3159 | 3084 | A1 | 2 |
| 3041 | 3346 | 3000 | 3334 | 3012 | 3302 | 2998 | 3172 | 3063 | 3168 | 3087 | 3153 | 3078 | B1 | 13 |
| 2936 | 3201 | 2870 | 3182 | 2875 | 3159 | 2868 | 3036 | 2932 | 3029 | 2951 | 3019 | 2948 | A1 | M1 |
| 2936 | 3197 | 2867 | 3179 | 2872 | 3155 | 2865 | 3035 | 2931 | 3028 | 2951 | 3019 | 2947 | B1 | M2 |
| 2936 | 3249 | 2913 | 3231 | 2920 | 3202 | 2907 | 3081 | 2975 | 3075 | 2997 | 3060 | 2987 | B2 | M2 |
| 2936 | 3246 | 2911 | 3229 | 2918 | 3199 | 2905 | 3083 | 2977 | 3078 | 2999 | 3062 | 2989 | A2 | M2 |
| 2927 | 3279 | 2940 | 3262 | 2948 | 3234 | 2936 | 3123 | 3016 | 3117 | 3037 | 3103 | 3029 | B1 | M1 |
| 2927 | 3281 | 2942 | 3265 | 2950 | 3236 | 2938 | 3125 | 3017 | 3118 | 3038 | 3104 | 3030 | A1 | M2 |
| 1608 | 1813 | 1626 | 1800 | 1626 | 1786 | 1622 | 1668 | 1610 | 1654 | 1612 | 1645 | 1606 | B1 | 8b |
| 1587 | 1780 | 1596 | 1767 | 1596 | 1754 | 1593 | 1638 | 1581 | 1624 | 1583 | 1616 | 1578 | A1 | 14 |
| 1496 | 1668 | 1496 | 1655 | 1495 | 1649 | 1497 | 1543 | 1490 | 1527 | 1488 | 1526 | 1490 | A1 | 8a |
| 1461 | 1609 | 1443 | 1592 | 1439 | 1587 | 1441 | 1488 | 1437 | 1470 | 1432 | 1470 | 1435 | B1 | 19a |
| 1461 | 1640 | 1471 | 1619 | 1463 | 1614 | 1465 | 1523 | 1471 | 1499 | 1461 | 1497 | 1461 | A1 | 19b |
| 1461 | 1641 | 1471 | 1618 | 1462 | 1614 | 1465 | 1524 | 1472 | 1499 | 1461 | 1496 | 1461 | B2 | M4 |
| 1461 | 1626 | 1458 | 1603 | 1449 | 1599 | 1452 | 1508 | 1457 | 1483 | 1445 | 1482 | 1447 | A2 | M4 |
| 1448 | 1645 | 1475 | 1625 | 1468 | 1619 | 1470 | 1528 | 1476 | 1505 | 1467 | 1505 | 1469 | B1 | M4 |
| 1390 | 1564 | 1402 | 1543 | 1394 | 1536 | 1394 | 1442 | 1393 | 1419 | 1382 | 1416 | 1382 | B1 | M3 |
| 1390 | 1575 | 1412 | 1554 | 1404 | 1547 | 1405 | 1454 | 1404 | 1430 | 1393 | 1426 | 1392 | A1 | M4 |
| 1293 | 1342 | 1203 | 1336 | 1207 | 1327 | 1204 | 1349 | 1303 | 1343 | 1309 | 1324 | 1293 | A1 | M3 |
| 1290 | 1439 | 1290 | 1428 | 1290 | 1426 | 1294 | 1328 | 1282 | 1316 | 1282 | 1321 | 1289 | B1 | 7b |
| 1220 | 1295 | 1161 | 1290 | 1165 | 1275 | 1157 | 1211 | 1169 | 1203 | 1173 | 1197 | 1169 | B1 | 3 |
| 1181 | 1340 | 1201 | 1333 | 1205 | 1324 | 1202 | 1255 | 1212 | 1245 | 1213 | 1242 | 1213 | A1 | 7a |
| 1164 | 1236 | 1108 | 1231 | 1112 | 1214 | 1102 | 1196 | 1155 | 1186 | 1156 | 1186 | 1158 | A1 | 15 |
| 1120 | 1236 | 1108 | 1228 | 1110 | 1218 | 1106 | 1151 | 1112 | 1143 | 1114 | 1140 | 1112 | B1 | M6 |
| 1056 | 1182 | 1060 | 1176 | 1062 | 1164 | 1056 | 1086 | 1049 | 1074 | 1047 | 1070 | 1045 | A2 | M6 |
| 1054 | 1150 | 1031 | 1143 | 1032 | 1134 | 1030 | 1084 | 1046 | 1075 | 1048 | 1074 | 1049 | A1 | 9a |
| 1020 | 1156 | 1036 | 1146 | 1036 | 1146 | 1040 | 1061 | 1024 | 1048 | 1021 | 1049 | 1025 | B2 | M6 |
| 989 | 1101 | 987 | 1092 | 987 | 1082 | 983 | 1021 | 986 | 1011 | 985 | 1008 | 984 | B1 | 9b |
| 982 | 1113 | 998 | 1118 | 1010 | 1100 | 998 | 981 | 948 | 991 | 965 | 995 | 972 | A2 | 5 |
| 966 | 1081 | 970 | 1074 | 970 | 1066 | 967 | 1017 | 983 | 1006 | 981 | 1005 | 982 | A1 | M6 |
| 929 | 1057 | 948 | 1059 | 957 | 1056 | 959 | 937 | 905 | 948 | 923 | 958 | 935 | B2 | 17b |
| 862 | 981 | 879 | 975 | 881 | 971 | 881 | 880 | 850 | 878 | 855 | 882 | 861 | A2 | 17a |
| 826 | 892 | 800 | 889 | 804 | 869 | 789 | 837 | 808 | 834 | 812 | 824 | 805 | B1 | 12 |
| 740 | 843 | 756 | 836 | 755 | 834 | 757 | 762 | 736 | 757 | 738 | 759 | 741 | B2 | 10a |
| 738 | 796 | 714 | 792 | 716 | 788 | 715 | 750 | 725 | 746 | 727 | 746 | 729 | A1 | 1 |
| 702 | 789 | 708 | 802 | 725 | 739 | 671 | 727 | 702 | 728 | 709 | 699 | 682 | A2 | 4 |
| 581 | 630 | 565 | 628 | 568 | 626 | 568 | 592 | 571 | 590 | 574 | 591 | 577 | A1 | 6a |
| 503 | 543 | 487 | 542 | 489 | 540 | 490 | 511 | 493 | 509 | 496 | 511 | 499 | B1 | 6b |
| 482 | 566 | 507 | 569 | 514 | 558 | 506 | 522 | 504 | 522 | 509 | 519 | 507 | A2 | 16a |
| 434 | 489 | 439 | 489 | 441 | 487 | 442 | 452 | 436 | 450 | 439 | 449 | 439 | B2 | 11 |
| 405 | 440 | 395 | 440 | 397 | 439 | 398 | 412 | 398 | 411 | 400 | 412 | 402 | B1 | 18a |
| 323 | 325 | 292 | 325 | 294 | 324 | 295 | 300 | 290 | 301 | 293 | 300 | 293 | A1 | 18b |
| 246 | 281 | 252 | 279 | 252 | 279 | 253 | 260 | 251 | 259 | 252 | 258 | 252 | B2 | 16b |
| 163 | 188 | 169 | 186 | 168 | 185 | 168 | 178 | 172 | 176 | 171 | 174 | 170 | A2 | 10b |
| Ir = 517 | Internal Rotation | | | | | | | | | | | | A2 | i-rot |
| Ir = 517 | Internal Rotation | | | | | | | | | | | | B2 | i-rot |

Table 9: Relative CPU time required to calculate molecules frequencies

| Level of Theory | Benzene | Toluene | *p*-xylene | *o*-xylene | *m*-xylene |
|---|---|---|---|---|---|
| HF/6-31G(d) | 1.0 | 5.4 | 5.7 | 9.1 | 8.8 |
| HF/6-31G++(d,p) | 6.0 | 23.1 | 27.5 | 44.2 | 39.1 |
| HF/6-311G++(3df,2pd) | 162.5 | 675.8 | 879.0 | 1229.1 | 1292.7 |
| B3LYP/6-31G(d) | 1.4 | 11.5 | 10.0 | 11.9 | 11.6 |
| B3LYP/6-31G++(d,p) | 6.0 | 44.1 | 44.0 | 52.6 | 46.7 |
| B3LYP/6-311G++(3df,2pd) | 167.7 | 769.9 | 1541.1 | 1404.6 | 1857.5 |

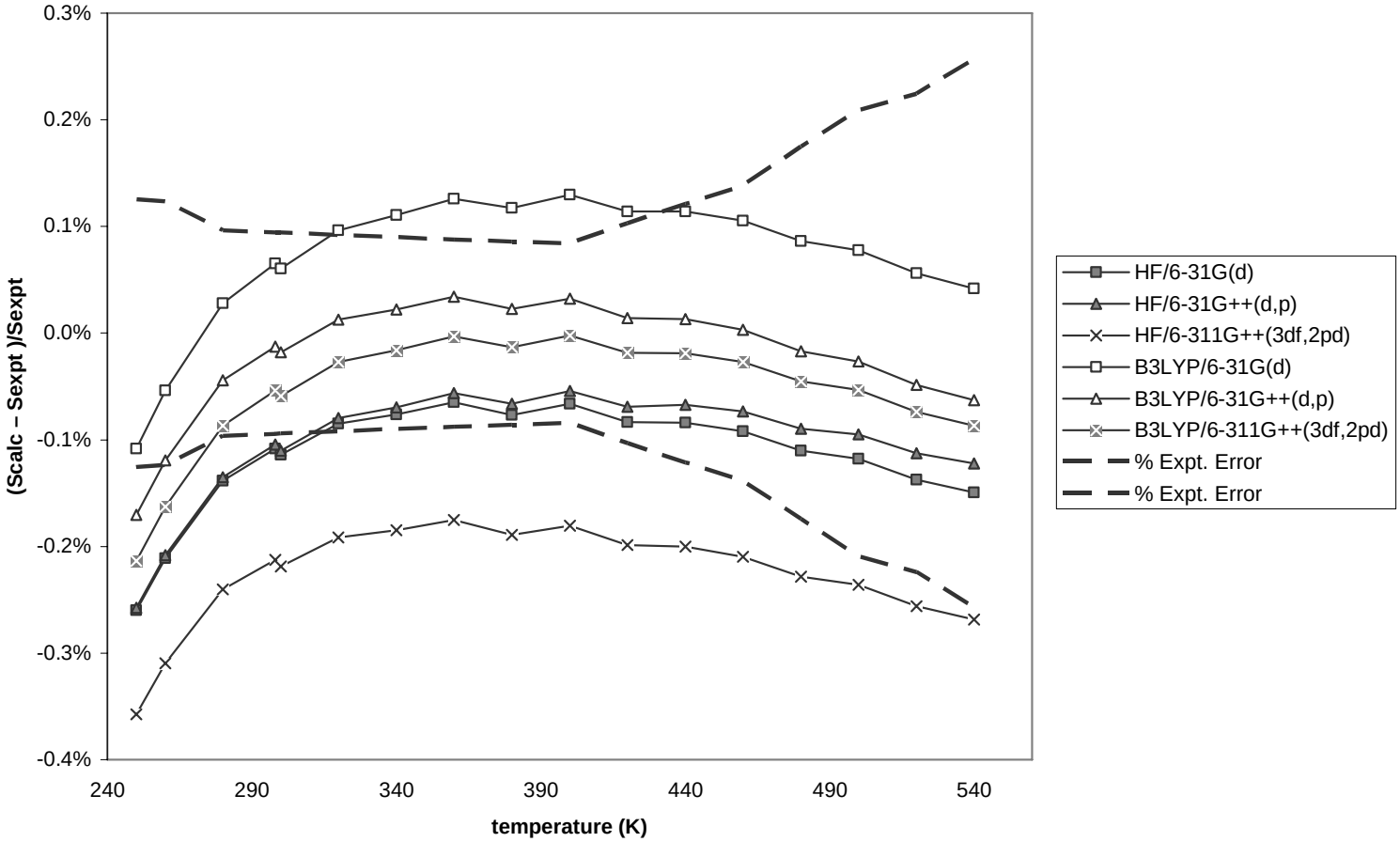


Figure 1 – Percentage error of the calculated toluene entropy vs. experiment in the temperature range of 250K-540K

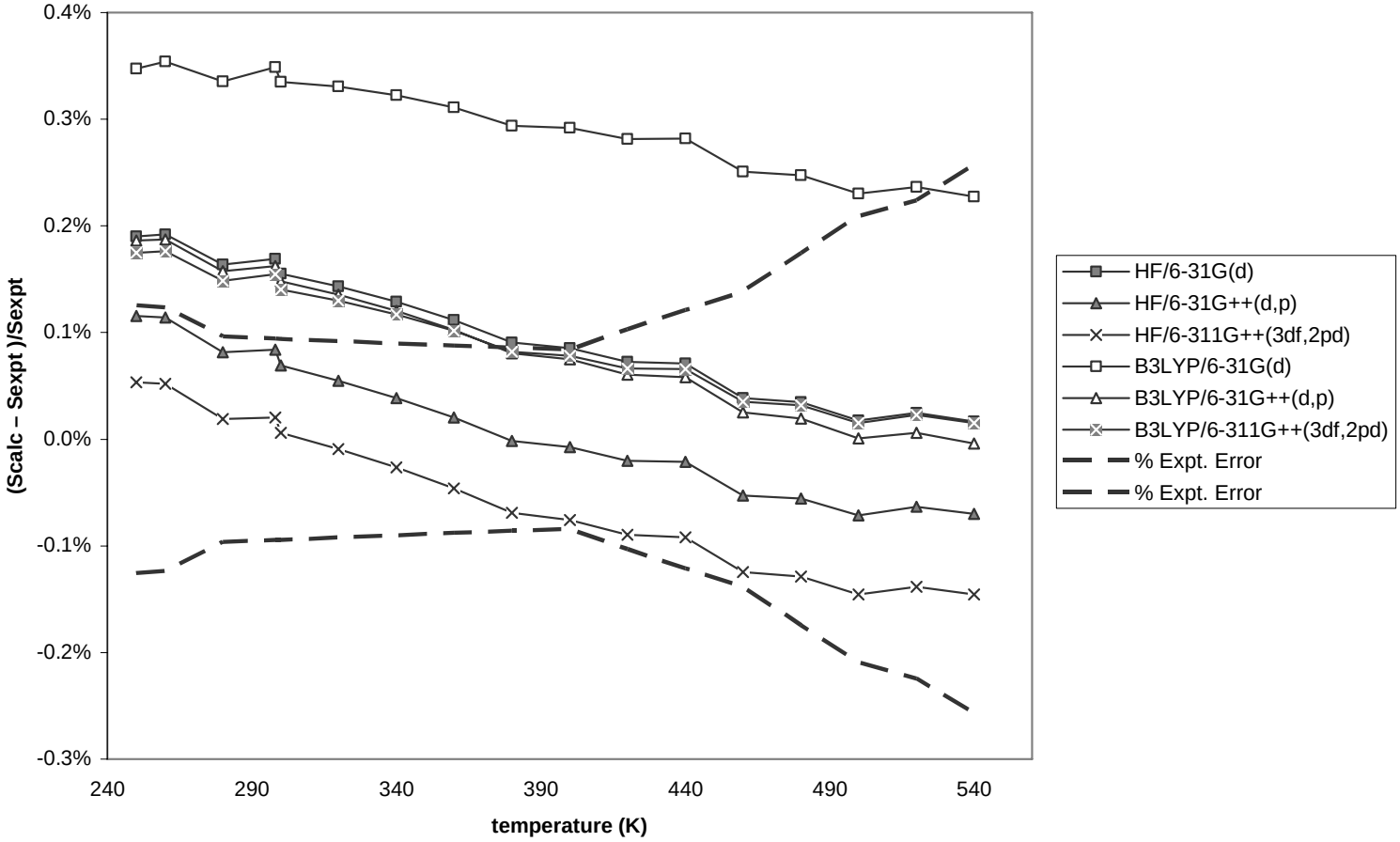


Figure 2 – Percentage error of the calculated *p*-xylene entropy vs. experiment in the temperature range of 250K-540K

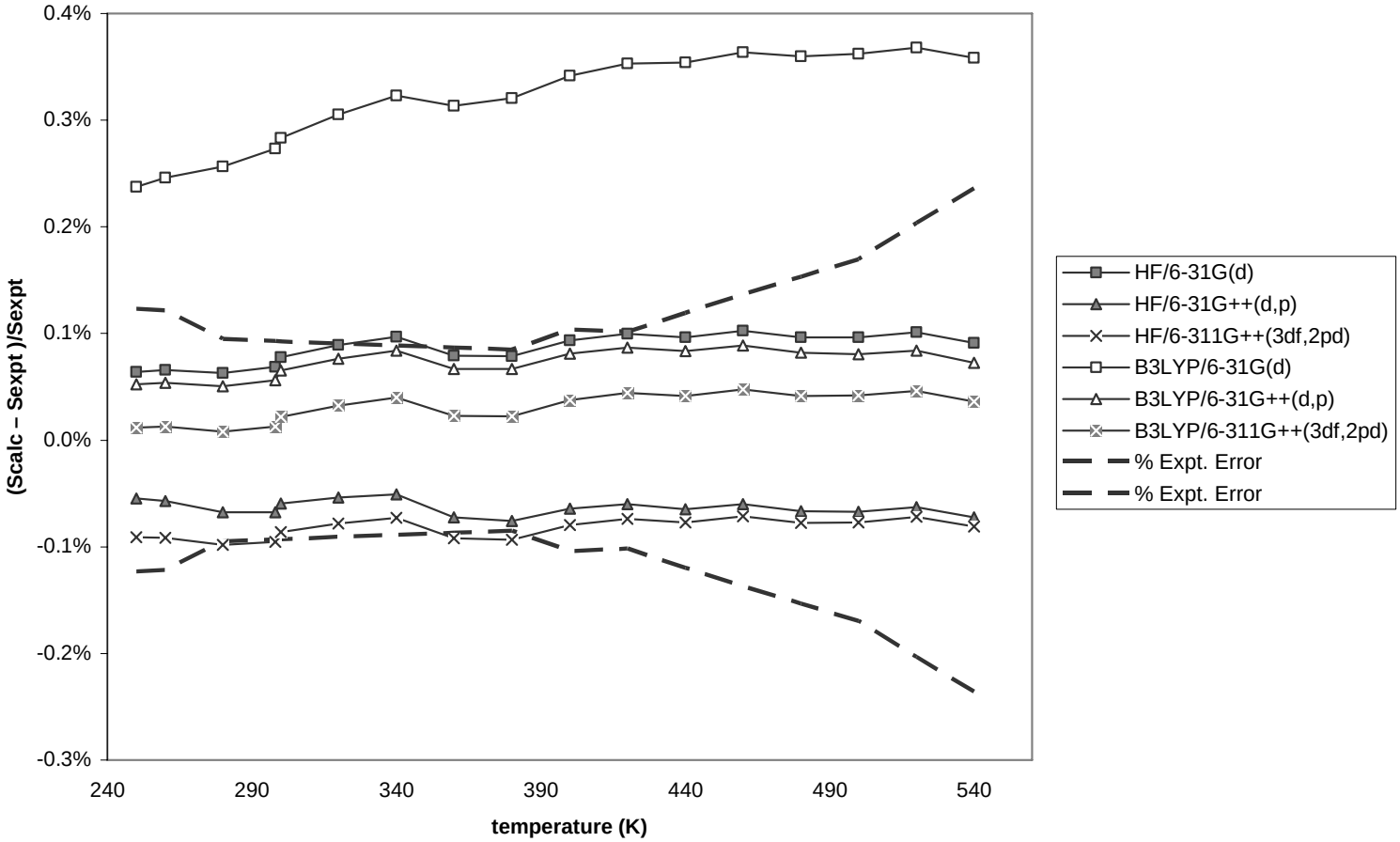


Figure 3 – Percentage error of the calculated *m*-xylene entropy vs. experiment in the temperature range of 250K-540K

# PART 3

# Theoretical Calculation of Thermodynamic Properties of Naphthalene, Methylnaphthalenes and Dimethylnaphthalenes

## Abstract

In this work, we perform a set of quantum mechanical and statistical mechanical calculations to generate the entropy of thirteen aromatic compounds—naphthalene, two methylnaphthalene isomers, and ten dimethylnaphthalene isomers—in the ideal gas state. Using density functional theory (DFT), we have calculated the equilibrium structure and performed a full normal mode analysis. The DFT level of theory used in this paper is B3LYP/6-31G(d,p). We have also used DFT to determine barriers for the internal rotation contribution to the entropy. For four compounds where experimental data is available, we have compared the calculated entropies to the experimental values. The calculated entropies match experiment very well, with the percentage errors close to the experimental uncertainty, less than 0.4%. The equilibrium distribution of dimethylnaphthalene isomers in the mixture is predicted using the calculated entropies and energies from QM and SM calculations in the 300-740 K temperature range.

## 3.1 Introduction

Thermophysical properties can be obtained from first principles with coupling of quantum mechanics (QM) and statistical mechanics (SM) calculations. The quantum mechanics calculations provide the required information for statistical mechanics models that predict thermophysical properties. Specifically, the QM calculations provide the equilibrium configuration from which one can directly calculate (i) the moments of inertia of the entire molecule, required for the rotational contribution to the thermodynamic properties (ii) the moments of inertia for internal rotors, required for the internal rotational contribution, (iii) the normal vibrational frequencies, required for the vibrational contribution, and the (iv) barrier to internal rotation, required for the internal rotational contribution. A SM analysis takes this QM-generated information as input and predicts thermophysical properties. In this work, we are interested in generating properties in the ideal gas reference state and thus limit ourselves to isolated molecules.

We have previously followed this QM/SM procedure in Part 2 to generate the entropies of benzene, toluene and the three xylene isomers with excellent agreement with precise experimental values [1]. In this work, we generate and report entropies of thirteen aromatic compounds—naphthalene, two methylnaphthalene (MN) isomers, and ten dimethylnaphthalene (DMN) isomers—in the ideal gas state. The MN isomers are 1-MN and 2-MN. The DMN isomers are 1,2-DMN, 1,3-DMN, 1,4-DMN, 1,5-DMN, 1,6-DMN, 1,7-DMN, 1,8-DMN, 2,3-DMN, 2,6-DMN, and 2,7-DMN. These compounds represent all possible MN and DMN isomers. In Part 3, we attempt to follow the QM/SM procedure established in Part 2, as much as possible; however, certain differences in the

complexity of internal rotation in MN and DMN compounds require some additional steps, which are detailed below. Additionally, we report the equilibrium distribution of DMN isomers across a temperature range (300-740 K), based on the free energies composed of the QM energies and the QM/SM entropies.

The use of QM and SM to generate entropies is not new. We have previously reviewed this body of work in Part 2. Here we provide a synopsis. Barret and Meier [2] used the semiempirical AM1 method to calculate entropy for a series of organic molecules. East and Radom [3] carried out an extensive study of small molecules at different levels of QM molecular orbital theory and different methods for calculating entropies and showed that entropies could be calculated to within 1 J/K/mol. Subsequently, Vansteenkiste *et al.* [4] calculated entropies of linear alkanes with an emphasis on considering more elaborate treatments of low vibrational modes. Wang *et al.* [5] used *ab initio* calculations to determine thermodynamic functions like entropy for dibenzo-p-dioxin (DD) and 75 polychlorinated dibenzo-dioxions (PCDDs) at B3LYP/6-311G** level of theory. Kassaee *et al.* used QM and SM calculations to generate entropy for five aromatic compounds in the ideal gas state and systematically examined how the choice of QM level of theory and size of basis set impact the agreement between theory and experiment [1]. Notably Kassaee *et al.* reports less than half a percent error between calculated entropies and experiment in the 250-540 K temperature range, when using an empirical scaling factor for the vibrational frequencies.

We now turn special attention to the matter of internal rotation. Ayala *et al.* [6] outlined a procedure that systematically identifies internal rotation modes and rotating

groups during normal mode analysis. In this work, we have generated "movies" representing the eigenvectors (or vibrational modes) associated with every frequency of every compound. These movies are available for viewing on the web [7]. One can view these movies in order to distinguish between normal modes that will be treated as vibrational modes and those that will be treated as internal rotation. The identification is not always obvious. With the DMN compounds, there were typically several possible low wavelength modes that could potentially be identified as internal rotation.

Additionally, one must determine rotational barriers. The traditional way to estimate rotational barriers via quantum mechanical calculations has been to first determine the equilibrium structure, then rotate the internal rotor and perform a single point energy calculation. This procedure assumes that the energy of the rest of the molecule is completely independent of the energy associated with the internal rotor. For some compounds, the assumption of independence between the rotor and the rest of the molecule is not true. Various alternative approaches have been proposed. Specifically, Sancho-Garcia *et al.* [8] performed a detailed study of the torsional potential of nitrobenzene by using state–of-the-art *ab initio* methods, including density functional theory (DFT) methods. In their procedure, one begins by understanding that there are 3N degrees of freedom in the atomic coordinates of a nonlinear molecule containing N atoms. Three of these degrees of freedom are associated with center-of-mass translation and three more with center-of-mass rotation, leaving 3N-6 modes. One of these modes is the dihedral torsion angle governing the rotation of the internal rotor, which we must specify in order to generate energy as a function of torsion angle. Therefore, there are

3N-7 remaining modes. In determining the activation barrier for internal rotation of the nitro group, Sancho-Garcia *et al.* [8] allowed for 3N-7 degrees of freedom to relax. This procedure allows for redistribution of the electrons in the rest of the molecule based upon the orientation of the rotor. If these modes are coupled, such redistribution is essential. The traditional single point energy will provide an unrealistically high rotation barrier that does not represent the correlated relaxation associated with internal rotation.

Other investigators have also computed relaxed rotational barriers. Goodman and his coworkers [9] reported on the nature of internal rotation in acetaldehyde. They divide the formation of internal rotation barrier in Acetaldehyde into three conceptual steps: (1) Rigid rotation, (2) the C-C bond lengthening to relieve repulsive π-nuclear virial, and (3) other skeletal and methyl flexings, necessary to achieve the fully relaxed barrier height. Sinha *et al.* have used the relaxed rotational barrier for 4-methylstyrene [10]. In this work, we follow the procedure of Sancho-Garcia *et al.* [8] in relaxing 3N-7 modes for MN isomers, which have one rotor. For DMN isomers, which have two rotors, we naturally extend the procedure to relax only 3N-8 modes. We report on the substantial difference between single-point and relaxed rotational barriers for MN and DMN.

This work is distinguished from previous work in the area of thermophysical property generation via QM and SM in several ways. First, we focus very carefully on comparing our entropies to excellent, experimental data where available. Second, the statistical mechanical analysis is done in a way in which the effect of individual contributions—vibration, rotation, internal rotation—can be separately examined. Third, by performing the analysis for naphthalene, MN, and DMN compounds, we are able to

evaluate the QM and SM procedures on a material set, which is of industrial importance and which provides a sound basis for extending the conclusions of this work to larger aromatic molecules. Fourth, we have generated the equilibrium distribution of dimethylnaphthalene compounds in the mixture with calculated entropies and energies from QM and SM calculations in the 300-740 K temperature range.

## 3.2 Computational Methods

We perform QM calculations to generate the equilibrium structure of the thirteen compounds studied here. We use the B3LYP method, an efficient and widely used density functional theory (DFT) method, and a mid sized 6-31G(d,p) split-valence basis set. Our choice of method and mid-sized basis set comes from the conclusions of I, in which we showed the effectiveness of B3LYP method and the fact that the advantage in accuracy of larger basis sizes is largely lost once the empirical scaling factor is applied to the vibrational frequencies. Once a suitable vibrational scaling factor is applied, there is not a remarkable difference between using different basis sets, while the larger basis sets have huge computational disadvantage.

The QM calculations provide the equilibrium configuration from which one can directly calculate (i) the moments of inertia of the entire molecule, required for the rotational contribution to the thermodynamic properties (ii) the moments of inertia for internal rotors, required for the internal rotational contribution, (iii) the normal vibrational frequencies, required for the vibrational contribution, and the (iv) barrier to internal rotation, required for the internal rotational contribution.

There are known systematic errors in calculating frequencies at different levels of theory in QM. The consequence is that one must use an empirical scaling factor for the vibrational frequencies. This factor is a function of the choice of basis set and method. This factor also varies to some degree from one compound to another [1]. Tables compiling compound-averaged scaling factors as a function of method and basis set are available from NIST [11]. In this work we use a single factor for all compounds and all frequencies. We determined this factor ourselves using the procedure in I. We chose the scaling factor that minimize the error between vibrational frequencies from theory (B3LYP/6-31G(d,p)) and experiment for the three xylene isomers. The accurate experimental frequencies for xylene isomers are taken from Draeger's paper [12]. For *o*-xylene, we have used the Draeger's corrected frequencies by Chirico *et al.* [13]. The average scaling factor for xylenes by B3LYP/6-31G(d,p) and the scale factor we used in this paper is 0.970.

As noted above, to identify internal rotation modes, we created movies of all of the eigenvectors for every compound. The internal rotation modes were recognized for their large components of the methyl dihedral angles [6]. Also as noted above, in determining rotational barriers, we followed the procedure of Sancho-Garcia *et al.* [8] in relaxing 3N-7 modes for MN isomers, which have one rotor. For DMN isomers, which have two rotors, we naturally extended the procedure to relax only 3N-8 modes.

With the internal rotation barriers, scaled vibrational frequencies, and moments of inertia, we calculated the entropy using SM. One can approximate the entropy of a molecule by making the assumption that the various degrees of freedom within the

molecule contribute to the entropy independently [2]. In this work, we do not consider any electronic or nuclear contribution to the entropy, since we are interested in the ground state. Furthermore, we neglect coupling between translational, rotational and vibrational modes.

$$S = S_{tran} + S_{rot} + S_{vib} + S_{\text{int}-rot} \tag{1}$$

We used the Therpoly software for the SM calculations to get the translational, rotational, vibrational, and internal rotation contributions to entropy [14]. The translational contribution is easily calculated given the molecular weight of the molecule. The molecular weights were taken from the NIST web reference [11]. For the rotational degrees of freedom, we assume a rigid-rotor approximation, which requires the moment of inertia of the equilibrium configuration around the principal axes obtained from QM and also the molecule's symmetry number. With the scaled normal vibrational frequencies, we computed the vibrational contribution to the entropy using the harmonic oscillator approximation. All of the compounds in this work except naphthalene have internal rotation contribution to entropy, which requires the energy barrier, moment of inertia and symmetry number of the rotor. We used QM calculation to determine the relaxed energy barrier and used the symmetry number of 3 for the methyl group rotor.

For each compound, entropy is calculated at 298.15 K and from 300 to 740 K in 10 K increments. This temperature range was chosen because it covers the whole range of temperatures for which the experimental entropies are available. The experimental entropies are available for four compounds: naphthalene [15], 2,7-dimethylnaphthalene [15], 1-methylnaphthalene [16], and 2-methylnaphthelene [16].

We can calculate the equilibrium distribution of each dimethylnaphthalene compound in the mixture, based on its equilibrium constant:

$$K_{eq} = \frac{N_1}{N_2} = \exp(-\frac{\Delta G}{RT}) \tag{2}$$

where $\Delta G$ is the difference in Gibbs free energy between each isomer. In this work, the enthalpy change equals the change in the internal energy ($\Delta H = \Delta U$), because the material is in the ideal gas state, in which the pressure and molar volume are constant across isomers. We calculate $\Delta U$ from the optimized energy of each compound in QM. The $\Delta U$ or $\Delta H$ is calculated at 0 K in the QM calculation output. In order to have $\Delta H$ as a function of temperature, we need to have an enthalpy in a range in which we can use experimental tables such as JANAF [17] to interpolate the results. We can get the enthalpy at the 298.15 K from Gaussian software using the procedure demonstrated by Ochterski [18] that is published by Gaussian Inc. . By performing the full frequency calculation on the equilibrium structures in Gaussian [19], we get the correction needed to calculate $\Delta H$ at 298.15 K. In the "Thermochemistry" section of the Gaussian output, we can get the corrected enthalpy for DMN isomers in 298.15 K by subtracting the zero-point energy correction ($\varepsilon_{ZPE}$) from the thermal correction to the enthalpy ($H_{corr}$) and adding it to the energy at 0 K [17]. Then, by calculating the entropy difference between compounds at each temperature, $\Delta S$, we arrive at the free energy, the equilibrium constant, and the equilibrium distribution of isomers.

In terms of software, we used Gaussian 98 [19] for the QM calculations and Therpoly [14] for the SM calculations.

## 3.3 Results and Discussion

In Figure 1, we show a schematic of naphthalene, in which the methyl locations are numbered. Positions 1, 4, 5, and 8 (hereafter called the 1 position) are equivalent and positions 2, 3, 6, and 7 (hereafter called the 2 position) are equivalent. It is known that placing a methyl group at the 1 position results in a higher energy state than the 2 position. The image in Figure 1 shows this difference between 1-MN and 2-MN. This energetic difference can explain the differences in energy for the DMN in which the methyl groups do not occupy adjacent positions. Therefore, 2,6-DMN and 2,7-DMN have the lowest energy, because they have two methyl groups in 2 positions. Isomers, including 1,3-DMN, 1,6-DMN, and 1,7 DMN, that have one methyl group in the 1 position and one in the 2 position, have a higher energy. Isomers, including 1,4-DMN and 1,5-DMN, that have 2 methyl groups in the 1 position have yet higher energies. Isomers that have adjacent methyl groups, including 2,3-DMN, 1,2-DMN, and 1,8-DMN, have energies that are higher than an isomer with methyl groups in the same type of position but located further away from each other, *i.e.* 2,3-DMN is higher than 2,6-DMN; 1,2-DMN is higher than 1,3-DMN; and 1,8-DMN is higher than 1,4-DMN. The relative energy for the DMN and MN compounds is shown in Figure 2.

The energetic barrier to internal rotation for all MN and DMN compounds is shown in Figure 3. In each case we compute the barrier calculated via a single-point energy procedure and that based on the relaxed rotational barrier procedure. Starting with the MN, we see that even in the case of a single rotor, there is a barrier to rotation present due to the naphthalene portion of the molecule. This barrier is larger for 1-MN

than for 2-MN. In each case, the barrier height is larger for the single-point procedure than for the relaxed procedure, as it must be.

The barriers for methyl groups at the 2 position is relatively the same across MN and DMN for those compounds in which the methyl group is not hindered by an adjacent methyl group, *i.e.* the rotor in 2-MN, both rotors in 2,7-DMN and 2,6-DMN, and the rotors at the 2 position in 1,3-DMN, 1,6-DMN, and 1,7-DMN. Likewise, the barriers for methyl groups at the 1 position is relatively the same across MN and DMN for those compounds in which the methyl group is not hindered by an adjacent methyl group, *i.e.* the rotor in 1-MN, both rotors in 1,4-DMN and 1,5-DMN, and the rotors at the 1 position in 1,3-DMN, 1,6-DMN, and 1,7-DMN.

In compounds where internal rotation is hindered by an adjacent methyl group, the barrier is usually higher than the unhindered rotation, as is the case with both rotors in 2,3-DMN and 1,8-DMN, and the rotor in the 2 position in 1,2-DMN. Surprisingly, we find that the barrier for rotation of the rotor in the 1 position in 1,2-DMN is lower than it is in 1-MN or in isomers of DMN with methyl groups in the 1 position without adjacent rotors. At this time, we attribute this result to the fact that the activation barrier is the difference between the transition state (TS) and the ground state (GS). As one compares, for example, 1,3-DMN with 1,2-DMN, the GS energy of 1,2-DMN is substantially higher. The difference between the TS and the GS is smaller for 1,2-DMN because the GS has distorted the molecule to such a point that rotation of the methyl group is now relatively easier. Certainly, however, the TS energy of 1,2-DMN is much greater than that of 1,3-DMN, relative to the same reference.

The vibrational contributions to entropy are calculated from the normal vibrational frequencies of the equilibrium structures. In Table 1, we report the normal vibrational frequencies for all thirteen compounds, after the scaling factor has been applied.

In Table 2, we provide all of the entropy contributions (translation, rotation, vibration, and internal rotation) for the compounds at 298.15 K. From Figure 4, we see that there are relatively subtle changes in the distribution of contributions to the entropy.

In Table 3, we report the calculated entropies for all thirteen compounds as a function of temperature. The experimental entropy values are available for four compounds: naphthalene [15], 2,7-dimethylnaphthalene [15], 1-methylnaphthalene [16], and 2-methylnaphthelene [16]. In Figures 5-8, we provide plots of the difference between the entropy from theoretical prediction and experiment for the four compounds for which experimental data is available. For all four compounds at all temperatures, the error is always less than 0.4%, which is the same error limit obtained for benzene, toluene and the xylene isomers in I. Moreover, we do not see any systematic discrepancy between the theory and experiment across the four compounds, which provides evidence that whatever sources of error are present, they are not systematic, but rather due to (i) limitations in theory that vary unpredictably from one compound to the next or (ii) statistical noise in the experimental data.

In Figures 9(a) and 9(b), we plot the equilibrium distribution of dimethylnaphthalene compounds in the mixture. In Figure 9(a), the distribution of 2,3-DMN, 1,3-DMN, 1,7-DMN, 2,7-DMN and 2,6-DMN have been shown. The rest of the

DMN compounds that have a relatively small equilibrium distribution have been summed up in Figure 9(b). The distribution among these remaining compounds (1,8-DMN, 1,2-DMN, 1,4-DMN, 1,6-DMN, and 1,5-DMN) is shown in Figure 9(b). The relative abundance of each compound does not strictly follow the trends determined by the relative ground state energies, as shown in Figure 2. For example, 2,7-DMN has the lowest energy, but 2,6-DMN is present in the greatest proportion at all temperatures, because of the fact that 2,7-DMN has a symmetry plane that reduces its entropy by Rln(2). The same can be said for the abundance of 1,5-DMN over 1,4-DMN.

## 4.4 Conclusion

In this work, we have performed a set of quantum mechanical and statistical mechanical calculations to generate the entropy of thirteen aromatic compounds—naphthalene, two methylnaphthalene isomers, and ten dimethylnaphthalene isomers—in the ideal gas state. Using density functional theory (DFT), we have calculated the equilibrium structure and performed a full normal mode analysis. The level of theory used is B3LYP/6-31G(d,p). We have also used DFT to determine relaxed barriers for the internal rotation contribution to the entropy. For four compounds where experimental data is available—naphthalene, 1-MN, 2-MN and 2,7-DMN—we have compared the calculated entropies to the experimental values. The calculated entropies match experiment very well, with the percentage errors close to the experimental uncertainty, less than 0.4%. Finally, we have predicted the equilibrium distribution of DMN isomers

in the mixture, using the calculated entropies and energies from QM and SM calculations in the 300-740 K temperature range.

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## Appendices

A. Tables

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    (b) Calculated equilibrium distribution of 1,8- DMN, 1,2- DMN, 1,4-DMN, and 1,5- DMN in the temperature range of 300-740 K with 20 K increments

Table 1: Calculated frequencies for naphthalene, 1- and 2-dimethylnaphthalene (MN) and ten dimethylnaphthalene (DMN) optimized structures with B3LYP/6-31G(d,p).

| Normal Mode | naphthalene | 1-MN | 2-MN | 2,7-DMN | 2,6-DMN | 2,3-DMN | 1,3-DMN | 1,6-DMN | 1,7-DMN | 1,4-DMN | 1,5-DMN | 1,2-DMN | 1,8-DMN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 171 | 131 | 93 | 85 | 75 | 112 | 92 | 86 | 88 | 120 | 93 | 99 | 44 |
| 2 | 184 | 165 | 121 | 93 | 85 | 116 | 116 | 103 | 101 | 130 | 161 | 121 | 121 |
| 3 | 353 | 182 | 179 | 116 | 94 | 148 | 150 | 144 | 155 | 180 | 179 | 150 | 154 |
| 4 | 385 | 244 | 255 | 129 | 179 | 190 | 173 | 182 | 176 | 184 | 188 | 150 | 232 |
| 5 | 467 | 271 | 276 | 212 | 201 | 256 | 214 | 227 | 212 | 192 | 201 | 220 | 236 |
| 6 | 477 | 408 | 392 | 274 | 215 | 264 | 253 | 240 | 218 | 267 | 252 | 273 | 306 |
| 7 | 502 | 429 | 399 | 277 | 313 | 292 | 277 | 276 | 297 | 296 | 262 | 295 | 314 |
| 8 | 505 | 467 | 440 | 319 | 333 | 298 | 290 | 319 | 336 | 326 | 322 | 339 | 318 |
| 9 | 615 | 469 | 476 | 406 | 394 | 407 | 419 | 413 | 412 | 413 | 452 | 415 | 447 |
| 10 | 616 | 505 | 502 | 413 | 401 | 410 | 426 | 439 | 415 | 443 | 453 | 425 | 460 |
| 11 | 713 | 532 | 512 | 435 | 429 | 437 | 462 | 450 | 462 | 467 | 468 | 455 | 471 |
| 12 | 752 | 560 | 617 | 459 | 480 | 481 | 502 | 480 | 497 | 476 | 478 | 502 | 473 |
| 13 | 761 | 618 | 622 | 477 | 520 | 512 | 517 | 494 | 510 | 496 | 503 | 508 | 508 |
| 14 | 779 | 693 | 691 | 537 | 522 | 527 | 538 | 543 | 531 | 533 | 519 | 530 | 546 |
| 15 | 783 | 727 | 736 | 625 | 572 | 620 | 539 | 567 | 536 | 567 | 565 | 564 | 569 |
| 16 | 828 | 767 | 758 | 630 | 630 | 647 | 623 | 623 | 629 | 620 | 624 | 634 | 610 |
| 17 | 872 | 779 | 761 | 669 | 665 | 648 | 631 | 682 | 691 | 688 | 625 | 672 | 617 |
| 18 | 919 | 788 | 807 | 755 | 744 | 730 | 733 | 707 | 707 | 719 | 728 | 712 | 746 |
| 19 | 923 | 846 | 844 | 756 | 753 | 740 | 742 | 744 | 746 | 751 | 774 | 736 | 762 |
| 20 | 940 | 850 | 870 | 767 | 787 | 755 | 765 | 780 | 770 | 768 | 784 | 765 | 775 |
| 21 | 960 | 886 | 880 | 775 | 808 | 806 | 841 | 809 | 818 | 784 | 796 | 802 | 787 |
| 22 | 967 | 931 | 928 | 829 | 817 | 839 | 854 | 820 | 840 | 817 | 839 | 845 | 802 |
| 23 | 1012 | 949 | 939 | 850 | 870 | 861 | 856 | 865 | 869 | 853 | 865 | 855 | 870 |
| 24 | 1022 | 964 | 943 | 891 | 880 | 885 | 880 | 890 | 886 | 916 | 876 | 858 | 889 |

Table 1, Cont.: Calculated frequencies for naphthalene, 1- and 2-dimethylnaphthalene (MN) and ten dimethylnaphthalene (DMN) optimized structures with B3LYP/6-31G(d,p).

| Normal Mode | naphthalene | 1-MN | 2-MN | 2,7-DMN | 2,6-DMN | 2,3-DMN | 1,3-DMN | 1,6-DMN | 1,7-DMN | 1,4-DMN | 1,5-DMN | 1,2-DMN | 1,8-DMN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 25 | 1120 | 967 | 962 | 928 | 906 | 891 | 930 | 916 | 891 | 931 | 888 | 927 | 934 |
| 26 | 1142 | 1021 | 998 | 935 | 941 | 929 | 947 | 940 | 939 | 931 | 947 | 936 | 943 |
| 27 | 1143 | 1034 | 1018 | 943 | 941 | 960 | 961 | 948 | 949 | 962 | 948 | 962 | 954 |
| 28 | 1153 | 1049 | 1035 | 944 | 952 | 992 | 971 | 968 | 968 | 991 | 976 | 981 | 978 |
| 29 | 1204 | 1073 | 1119 | 985 | 994 | 1006 | 1008 | 999 | 996 | 1024 | 1005 | 1013 | 1022 |
| 30 | 1235 | 1139 | 1145 | 1015 | 1002 | 1018 | 1024 | 1034 | 1033 | 1033 | 1033 | 1021 | 1029 |
| 31 | 1253 | 1155 | 1149 | 1034 | 1034 | 1023 | 1034 | 1035 | 1035 | 1036 | 1034 | 1038 | 1037 |
| 32 | 1366 | 1159 | 1167 | 1035 | 1035 | 1043 | 1036 | 1044 | 1050 | 1047 | 1063 | 1050 | 1037 |
| 33 | 1372 | 1208 | 1207 | 1129 | 1125 | 1081 | 1057 | 1073 | 1073 | 1057 | 1092 | 1067 | 1108 |
| 34 | 1382 | 1231 | 1243 | 1146 | 1144 | 1143 | 1127 | 1154 | 1145 | 1139 | 1129 | 1144 | 1109 |
| 35 | 1456 | 1255 | 1256 | 1168 | 1161 | 1147 | 1154 | 1159 | 1155 | 1151 | 1165 | 1154 | 1154 |
| 36 | 1458 | 1348 | 1353 | 1168 | 1170 | 1178 | 1170 | 1167 | 1185 | 1158 | 1166 | 1172 | 1161 |
| 37 | 1516 | 1367 | 1369 | 1204 | 1214 | 1229 | 1215 | 1214 | 1208 | 1217 | 1211 | 1207 | 1209 |
| 38 | 1579 | 1384 | 1377 | 1246 | 1249 | 1235 | 1232 | 1240 | 1238 | 1240 | 1225 | 1220 | 1226 |
| 39 | 1606 | 1393 | 1385 | 1258 | 1258 | 1260 | 1270 | 1259 | 1257 | 1262 | 1250 | 1253 | 1252 |
| 40 | 1636 | 1433 | 1431 | 1335 | 1338 | 1327 | 1348 | 1348 | 1332 | 1334 | 1340 | 1335 | 1337 |
| 41 | 3077 | 1453 | 1452 | 1376 | 1375 | 1366 | 1366 | 1364 | 1368 | 1364 | 1357 | 1366 | 1340 |
| 42 | 3081 | 1460 | 1465 | 1378 | 1379 | 1377 | 1381 | 1371 | 1380 | 1379 | 1383 | 1379 | 1365 |
| 43 | 3081 | 1471 | 1471 | 1385 | 1385 | 1383 | 1386 | 1384 | 1384 | 1385 | 1384 | 1386 | 1379 |
| 44 | 3084 | 1515 | 1513 | 1386 | 1385 | 1394 | 1397 | 1385 | 1385 | 1388 | 1404 | 1389 | 1394 |
| 45 | 3095 | 1586 | 1577 | 1416 | 1403 | 1437 | 1414 | 1427 | 1436 | 1426 | 1407 | 1424 | 1429 |
| 46 | 3097 | 1606 | 1612 | 1452 | 1452 | 1445 | 1449 | 1452 | 1445 | 1453 | 1452 | 1450 | 1444 |
| 47 | 3108 | 1629 | 1639 | 1452 | 1452 | 1460 | 1452 | 1452 | 1451 | 1453 | 1452 | 1451 | 1449 |
| 48 | 3109 | 2944 | 2945 | 1452 | 1457 | 1461 | 1453 | 1453 | 1452 | 1455 | 1462 | 1470 | 1458 |

Table 1, Cont.: Calculated frequencies for naphthalene, 1- and 2-dimethylnaphthalene (MN) and ten dimethylnaphthalene (DMN) optimized structures with B3LYP/6-31G(d,p).

| Normal Mode | naphthalene | 1-MN | 2-MN | 2,7-DMN | 2,6-DMN | 2,3-DMN | 1,3-DMN | 1,6-DMN | 1,7-DMN | 1,4-DMN | 1,5-DMN | 1,2-DMN | 1,8-DMN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 49 | | 2995 | 2996 | 1469 | 1466 | 1465 | 1466 | 1468 | 1469 | 1467 | 1466 | 1471 | 1473 |
| 50 | | 3033 | 3034 | 1471 | 1485 | 1468 | 1476 | 1477 | 1473 | 1473 | 1475 | 1480 | 1489 |
| 51 | | 3078 | 3074 | 1516 | 1508 | 1504 | 1512 | 1511 | 1511 | 1519 | 1515 | 1514 | 1515 |
| 52 | | 3079 | 3075 | 1574 | 1575 | 1575 | 1582 | 1584 | 1584 | 1594 | 1591 | 1576 | 1589 |
| 53 | | 3086 | 3078 | 1620 | 1619 | 1611 | 1613 | 1610 | 1610 | 1606 | 1606 | 1606 | 1609 |
| 54 | | 3090 | 3082 | 1640 | 1641 | 1641 | 1634 | 1635 | 1634 | 1623 | 1622 | 1627 | 1620 |
| 55 | | 3103 | 3092 | 2945 | 2945 | 2941 | 2944 | 2944 | 2944 | 2943 | 2945 | 2948 | 2961 |
| 56 | | 3104 | 3096 | 2945 | 2945 | 2943 | 2945 | 2945 | 2944 | 2944 | 2945 | 2949 | 2971 |
| 57 | | 3114 | 3108 | 2996 | 2996 | 2990 | 2996 | 2995 | 2995 | 2994 | 2995 | 2994 | 3021 |
| 58 | | | | 2996 | 2996 | 2991 | 2996 | 2996 | 2996 | 2994 | 2996 | 3001 | 3030 |
| 59 | | | | 3032 | 3032 | 3032 | 3032 | 3033 | 3032 | 3032 | 3033 | 3030 | 3036 |
| 60 | | | | 3032 | 3032 | 3033 | 3033 | 3033 | 3033 | 3032 | 3033 | 3064 | 3038 |
| 61 | | | | 3072 | 3071 | 3071 | 3068 | 3074 | 3074 | 3075 | 3078 | 3076 | 3078 |
| 62 | | | | 3073 | 3071 | 3073 | 3075 | 3077 | 3078 | 3085 | 3079 | 3079 | 3079 |
| 63 | | | | 3074 | 3074 | 3078 | 3079 | 3078 | 3085 | 3091 | 3095 | 3089 | 3084 |
| 64 | | | | 3076 | 3075 | 3082 | 3089 | 3086 | 3092 | 3098 | 3095 | 3095 | 3087 |
| 65 | | | | 3091 | 3091 | 3095 | 3103 | 3103 | 3099 | 3113 | 3117 | 3104 | 3105 |
| 66 | | | | 3093 | 3092 | 3108 | 3115 | 3110 | 3104 | 3118 | 3117 | 3118 | 3106 |

Table 2: Entropy contributions for compounds at 298.15 K

| Entropy Contr. | naphthalene | 1-MN | 2-MN | 2,7-DMN | 2,6-DMN | 2,3-DMN | 1,3-DMN | 1,6-DMN | 1,7-DMN | 1,4-DMN | 1,5-DMN | 1,2-DMN | 1,8-DMN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Translational | 20.4 | 20.5 | 20.5 | 20.7 | 20.7 | 20.7 | 20.7 | 20.7 | 20.7 | 20.7 | 20.7 | 20.7 | 20.7 |
| Rotational | 13.2 | 15.0 | 15.0 | 14.7 | 14.6 | 14.6 | 15.4 | 15.3 | 15.3 | 14.6 | 14.6 | 15.3 | 14.6 |
| Vibrational | 6.7 | 8.7 | 8.7 | 10.7 | 10.8 | 10.7 | 10.6 | 10.7 | 10.7 | 10.7 | 10.6 | 10.7 | 11.3 |
| Internal Rotation | 0.0 | 1.4 | 1.8 | 3.5 | 3.5 | 3.0 | 3.1 | 3.1 | 3.1 | 2.7 | 2.7 | 3.4 | 2.2 |
| Total | 40.2 | 45.5 | 45.9 | 49.6 | 49.6 | 48.9 | 49.7 | 49.9 | 49.8 | 48.6 | 48.6 | 50.0 | 48.7 |

Table 3: Calculated entropy for naphthalene, 1- and 2-methylnaphthalene (MN) and ten dimethylnaphthalene (DMN) optimized structures in the temperature range of 300-740 K (plus 298.15 K) with 10 K increments

| Temp.(K) | naphthalene | 1-MN | 2-MN | 2,7-DMN | 2,6-DMN | 2,3-DMN | 1,3-DMN | 1,6-DMN | 1,7-DMN | 1,4-DMN | 1,5-DMN | 1,2-DMN | 1,8-DMN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 298.15 | 40.2 | 45.5 | 45.9 | 49.6 | 49.6 | 48.9 | 49.7 | 49.9 | 49.8 | 48.6 | 48.6 | 50.0 | 48.7 |
| 300 | 40.3 | 45.6 | 46.1 | 49.7 | 49.7 | 49.1 | 49.9 | 50.0 | 50.0 | 48.8 | 48.7 | 50.2 | 48.9 |
| 310 | 40.9 | 46.3 | 46.7 | 50.4 | 50.4 | 49.8 | 50.6 | 50.7 | 50.7 | 49.5 | 49.4 | 50.9 | 49.6 |
| 320 | 41.4 | 46.9 | 47.3 | 51.2 | 51.1 | 50.6 | 51.3 | 51.5 | 51.4 | 50.3 | 50.2 | 51.6 | 50.4 |
| 330 | 41.9 | 47.6 | 48.0 | 51.9 | 51.9 | 51.3 | 52.1 | 52.2 | 52.2 | 51.0 | 50.9 | 52.3 | 51.1 |
| 340 | 42.5 | 48.2 | 48.6 | 52.6 | 52.6 | 52.0 | 52.8 | 52.9 | 52.9 | 51.8 | 51.7 | 53.1 | 51.9 |
| 350 | 43.0 | 48.8 | 49.2 | 53.3 | 53.3 | 52.8 | 53.5 | 53.6 | 53.6 | 52.5 | 52.4 | 53.8 | 52.6 |
| 360 | 43.6 | 49.5 | 49.8 | 54.0 | 54.0 | 53.5 | 54.3 | 54.4 | 54.4 | 53.2 | 53.1 | 54.5 | 53.3 |
| 370 | 44.1 | 50.1 | 50.5 | 54.7 | 54.7 | 54.2 | 55.0 | 55.1 | 55.1 | 54.0 | 53.9 | 55.2 | 54.1 |
| 380 | 44.7 | 50.8 | 51.1 | 55.5 | 55.4 | 55.0 | 55.7 | 55.8 | 55.8 | 54.7 | 54.6 | 55.9 | 54.8 |
| 390 | 45.2 | 51.4 | 51.7 | 56.2 | 56.2 | 55.7 | 56.4 | 56.5 | 56.5 | 55.4 | 55.3 | 56.7 | 55.6 |
| 400 | 45.8 | 52.0 | 52.4 | 56.9 | 56.9 | 56.4 | 57.2 | 57.3 | 57.2 | 56.2 | 56.1 | 57.4 | 56.3 |
| 410 | 46.3 | 52.7 | 53.0 | 57.6 | 57.6 | 57.1 | 57.9 | 58.0 | 58.0 | 56.9 | 56.8 | 58.1 | 57.0 |
| 420 | 46.8 | 53.3 | 53.6 | 58.3 | 58.3 | 57.9 | 58.6 | 58.7 | 58.7 | 57.6 | 57.5 | 58.8 | 57.8 |
| 430 | 47.4 | 53.9 | 54.2 | 59.0 | 59.0 | 58.6 | 59.3 | 59.4 | 59.4 | 58.3 | 58.3 | 59.5 | 58.5 |
| 440 | 47.9 | 54.6 | 54.9 | 59.7 | 59.7 | 59.3 | 60.0 | 60.1 | 60.1 | 59.1 | 59.0 | 60.2 | 59.2 |
| 450 | 48.5 | 55.2 | 55.5 | 60.4 | 60.4 | 60.0 | 60.7 | 60.8 | 60.8 | 59.8 | 59.7 | 60.9 | 60.0 |
| 460 | 49.0 | 55.8 | 56.1 | 61.1 | 61.1 | 60.7 | 61.4 | 61.5 | 61.5 | 60.5 | 60.4 | 61.6 | 60.7 |
| 470 | 49.6 | 56.5 | 56.7 | 61.8 | 61.8 | 61.4 | 62.1 | 62.2 | 62.2 | 61.2 | 61.1 | 62.3 | 61.4 |
| 480 | 50.1 | 57.1 | 57.3 | 62.5 | 62.5 | 62.1 | 62.8 | 62.9 | 62.9 | 61.9 | 61.8 | 63.0 | 62.1 |
| 490 | 50.6 | 57.7 | 58.0 | 63.2 | 63.2 | 62.8 | 63.5 | 63.6 | 63.6 | 62.6 | 62.5 | 63.7 | 62.8 |
| 500 | 51.2 | 58.3 | 58.6 | 63.9 | 63.9 | 63.5 | 64.2 | 64.3 | 64.3 | 63.3 | 63.2 | 64.4 | 63.5 |
| 510 | 51.7 | 58.9 | 59.2 | 64.6 | 64.6 | 64.2 | 64.9 | 65.0 | 65.0 | 64.0 | 63.9 | 65.1 | 64.2 |
| 520 | 52.2 | 59.5 | 59.8 | 65.2 | 65.2 | 64.9 | 65.6 | 65.7 | 65.7 | 64.7 | 64.6 | 65.8 | 64.9 |

Table 3, Cont.: Calculated entropy for naphthalene, 1- and 2-methylnaphthalene (MN) and ten dimethylnaphthalene (DMN) optimized structures in the temperature range of 300-740 K (plus 298.15 K) with 10 K increments

| Temp.(K) | naphthalene | 1-MN | 2-MN | 2,7-DMN | 2,6-DMN | 2,3-DMN | 1,3-DMN | 1,6-DMN | 1,7-DMN | 1,4-DMN | 1,5-DMN | 1,2-DMN | 1,8-DMN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 530 | 52.7 | 60.1 | 60.4 | 65.9 | 65.9 | 65.6 | 66.3 | 66.4 | 66.4 | 65.4 | 65.3 | 66.4 | 65.6 |
| 540 | 53.3 | 60.8 | 61.0 | 66.6 | 66.6 | 66.3 | 67.0 | 67.1 | 67.1 | 66.1 | 66.0 | 67.1 | 66.3 |
| 550 | 53.8 | 61.4 | 61.6 | 67.3 | 67.3 | 66.9 | 67.6 | 67.7 | 67.7 | 66.8 | 66.7 | 67.8 | 67.0 |
| 560 | 54.3 | 62.0 | 62.2 | 67.9 | 67.9 | 67.6 | 68.3 | 68.4 | 68.4 | 67.4 | 67.4 | 68.5 | 67.7 |
| 570 | 54.8 | 62.5 | 62.8 | 68.6 | 68.6 | 68.3 | 69.0 | 69.1 | 69.1 | 68.1 | 68.0 | 69.1 | 68.4 |
| 580 | 55.3 | 63.1 | 63.4 | 69.3 | 69.3 | 69.0 | 69.7 | 69.8 | 69.7 | 68.8 | 68.7 | 69.8 | 69.1 |
| 590 | 55.8 | 63.7 | 63.9 | 69.9 | 69.9 | 69.6 | 70.3 | 70.4 | 70.4 | 69.5 | 69.4 | 70.4 | 69.7 |
| 600 | 56.4 | 64.3 | 64.5 | 70.6 | 70.6 | 70.3 | 71.0 | 71.1 | 71.1 | 70.1 | 70.0 | 71.1 | 70.4 |
| 610 | 56.9 | 64.9 | 65.1 | 71.2 | 71.2 | 70.9 | 71.6 | 71.7 | 71.7 | 70.8 | 70.7 | 71.7 | 71.1 |
| 620 | 57.4 | 65.5 | 65.7 | 71.9 | 71.9 | 71.6 | 72.3 | 72.4 | 72.4 | 71.4 | 71.3 | 72.4 | 71.7 |
| 630 | 57.9 | 66.0 | 66.2 | 72.5 | 72.5 | 72.2 | 72.9 | 73.0 | 73.0 | 72.1 | 72.0 | 73.0 | 72.4 |
| 640 | 58.4 | 66.6 | 66.8 | 73.2 | 73.2 | 72.9 | 73.6 | 73.7 | 73.7 | 72.7 | 72.6 | 73.7 | 73.0 |
| 650 | 58.9 | 67.2 | 67.4 | 73.8 | 73.8 | 73.5 | 74.2 | 74.3 | 74.3 | 73.4 | 73.3 | 74.3 | 73.7 |
| 660 | 59.3 | 67.8 | 67.9 | 74.4 | 74.4 | 74.2 | 74.9 | 74.9 | 74.9 | 74.0 | 73.9 | 75.0 | 74.3 |
| 670 | 59.8 | 68.3 | 68.5 | 75.1 | 75.1 | 74.8 | 75.5 | 75.6 | 75.6 | 74.7 | 74.6 | 75.6 | 75.0 |
| 680 | 60.3 | 68.9 | 69.1 | 75.7 | 75.7 | 75.4 | 76.1 | 76.2 | 76.2 | 75.3 | 75.2 | 76.2 | 75.6 |
| 690 | 60.8 | 69.4 | 69.6 | 76.3 | 76.3 | 76.1 | 76.7 | 76.8 | 76.8 | 75.9 | 75.8 | 76.8 | 76.2 |
| 700 | 61.3 | 70.0 | 70.2 | 76.9 | 76.9 | 76.7 | 77.4 | 77.5 | 77.5 | 76.5 | 76.4 | 77.5 | 76.9 |
| 710 | 61.7 | 70.5 | 70.7 | 77.5 | 77.5 | 77.3 | 78.0 | 78.1 | 78.1 | 77.2 | 77.1 | 78.1 | 77.5 |
| 720 | 62.2 | 71.1 | 71.2 | 78.2 | 78.2 | 77.9 | 78.6 | 78.7 | 78.7 | 77.8 | 77.7 | 78.7 | 78.1 |
| 730 | 62.7 | 71.6 | 71.8 | 78.8 | 78.8 | 78.5 | 79.2 | 79.3 | 79.3 | 78.4 | 78.3 | 79.3 | 78.7 |
| 740 | 63.2 | 72.1 | 72.3 | 79.4 | 79.4 | 79.1 | 79.8 | 79.9 | 79.9 | 79.0 | 78.9 | 79.9 | 79.3 |

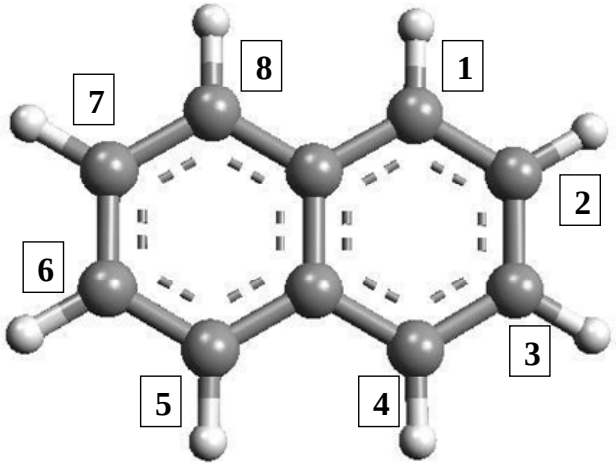


Figure 1: Numbered methyl locations on naphthalene

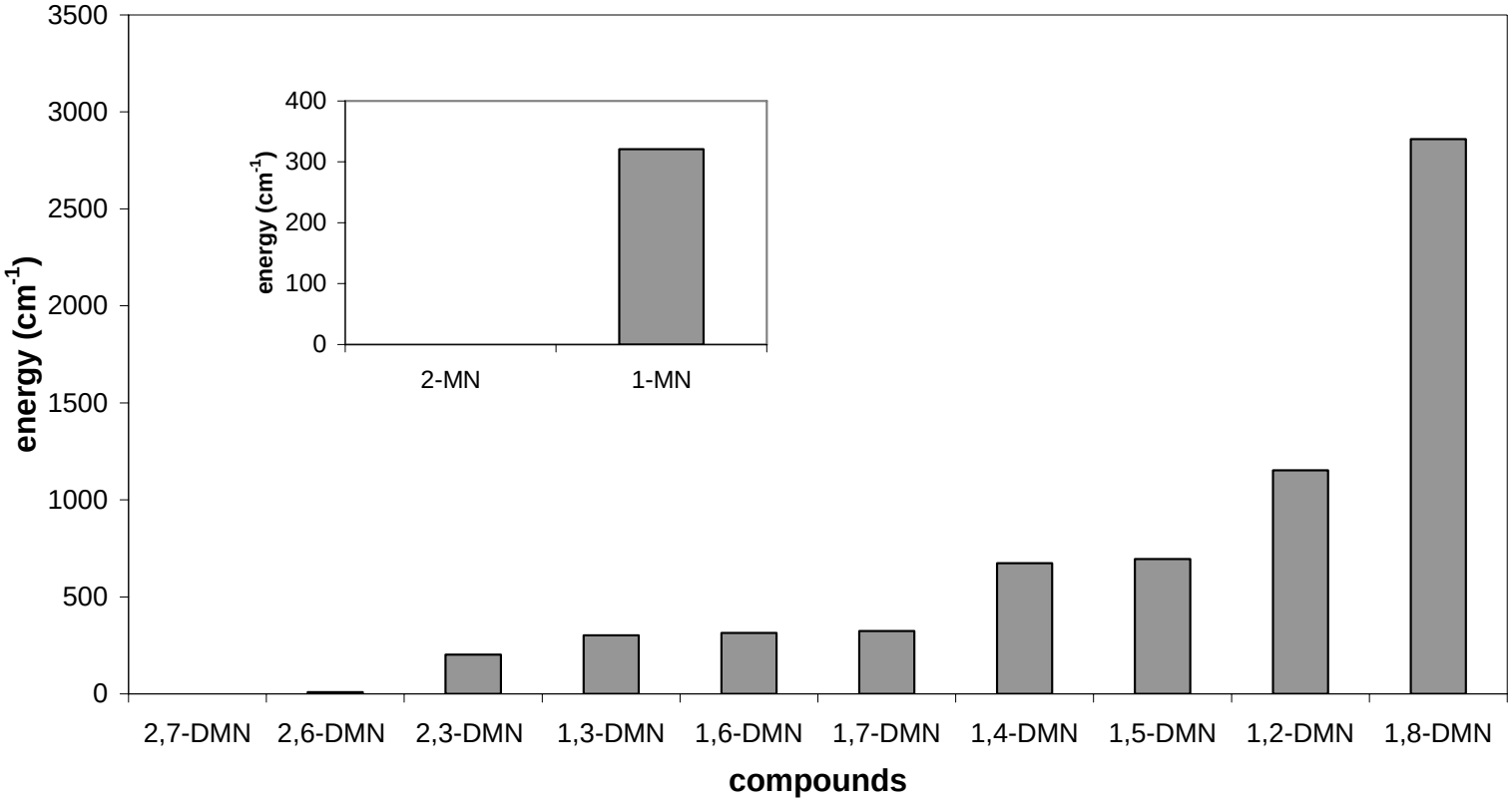


Figure 2: Relative energies for the optimized structures of DMN and MN compounds

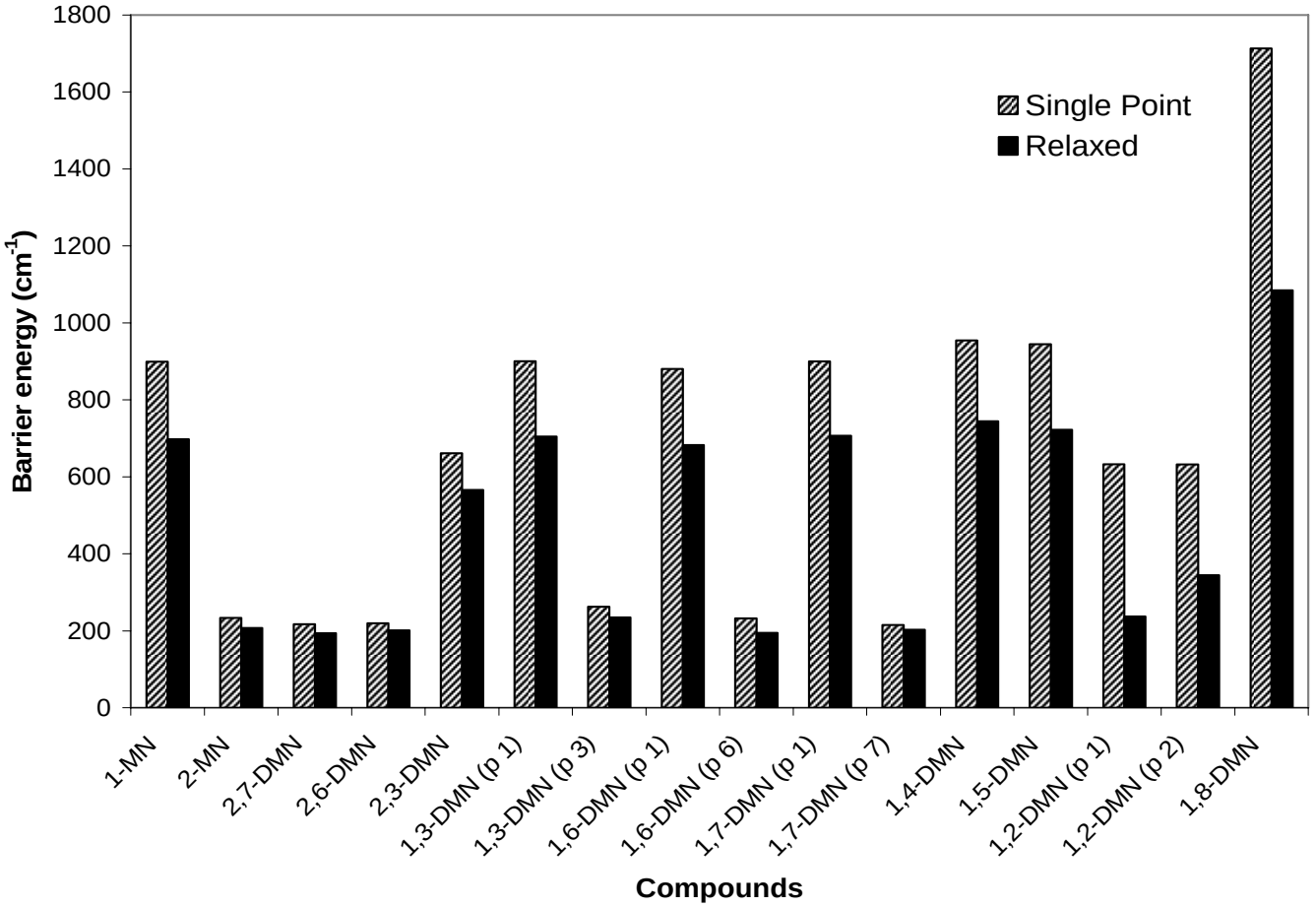


Figure 3: Relaxed vs. single point calculation of energy barriers for dimethylnaphthalene (DMN) and methylnaphthalene (MN) compounds

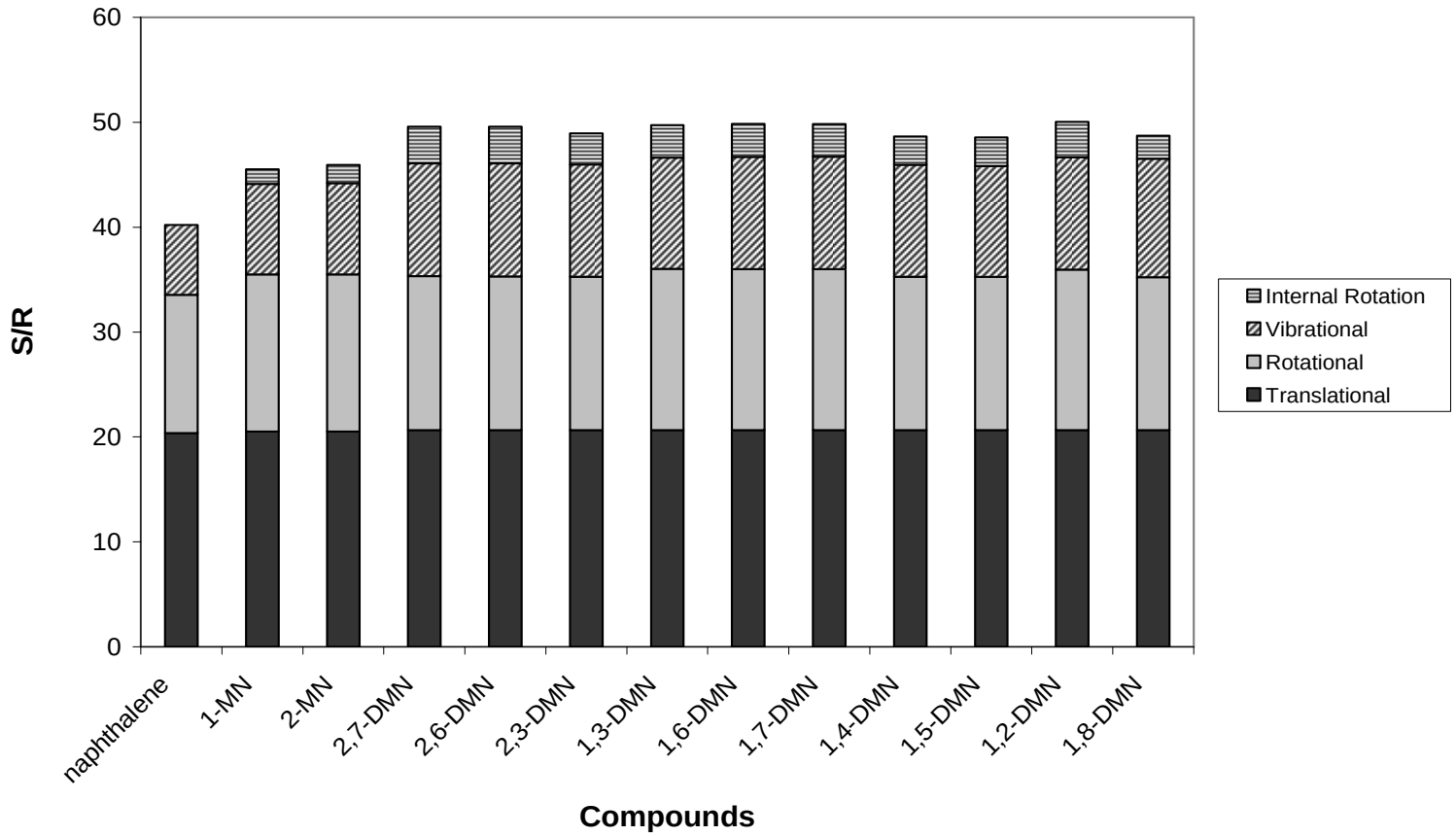


Figure 4: Entropy contributions (translational, rotational, vibrational and internal rotation) of all of the compounds at 298.15 K

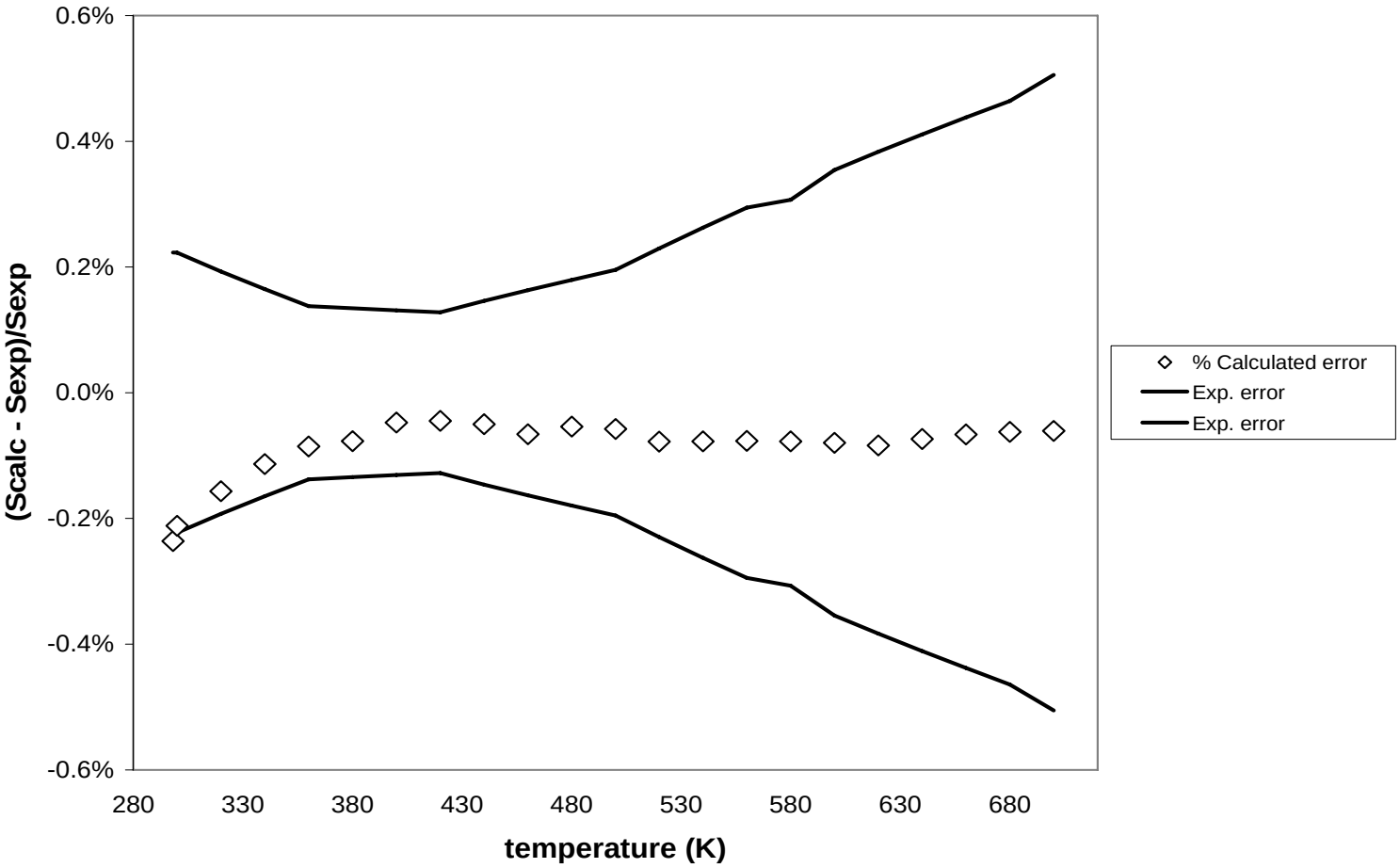


Figure 5: Percentage error of the calculated naphthalene entropy vs. experiment in the temperature range of 300-700 K (plus 298.15 K) with 20 K increments

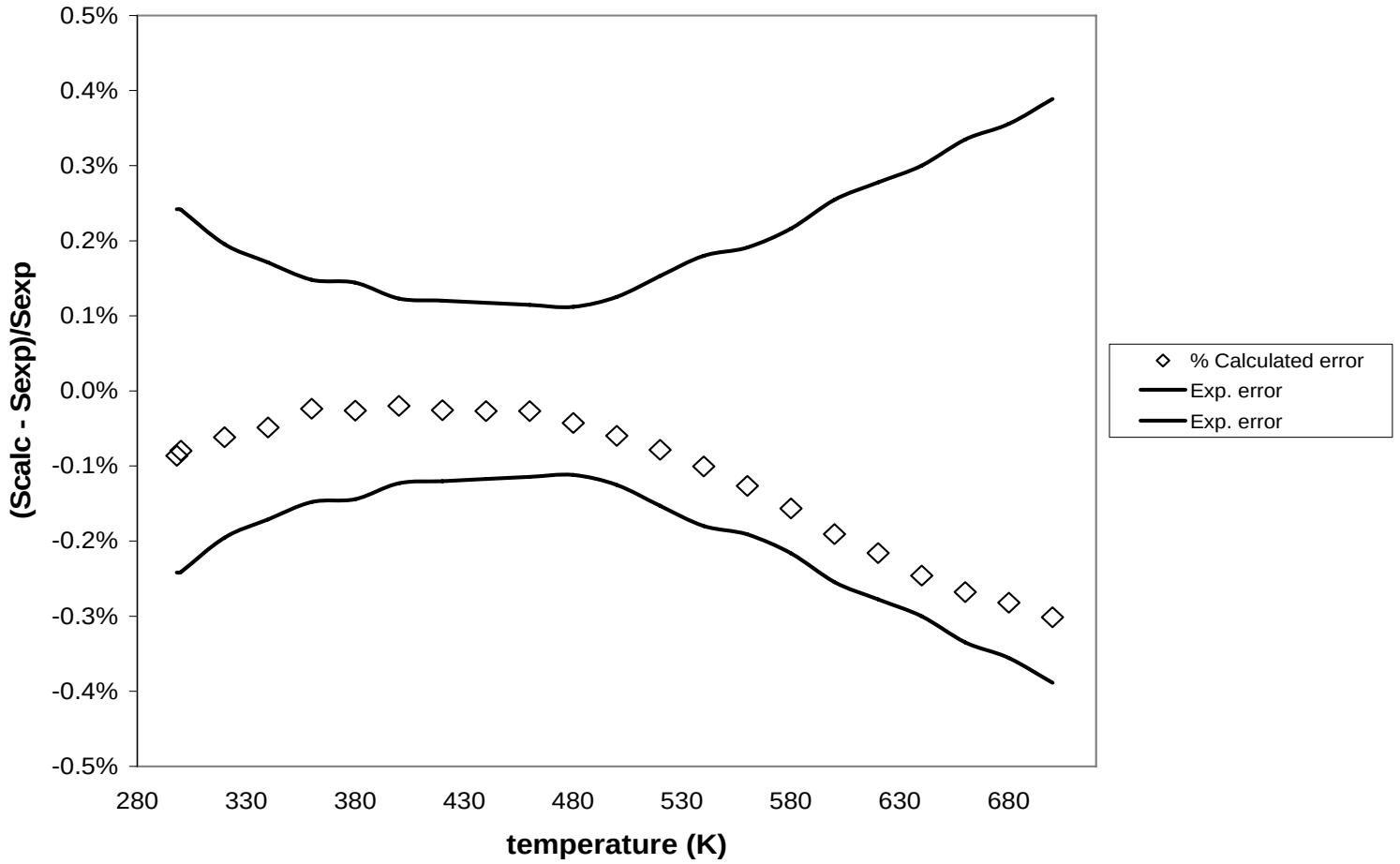


Figure 6: Percentage error of the calculated 2,7-dimethylnaphthalene entropy vs. experiment in the temperature range of 300-700 K (plus 298.15 K) with 20 K increments

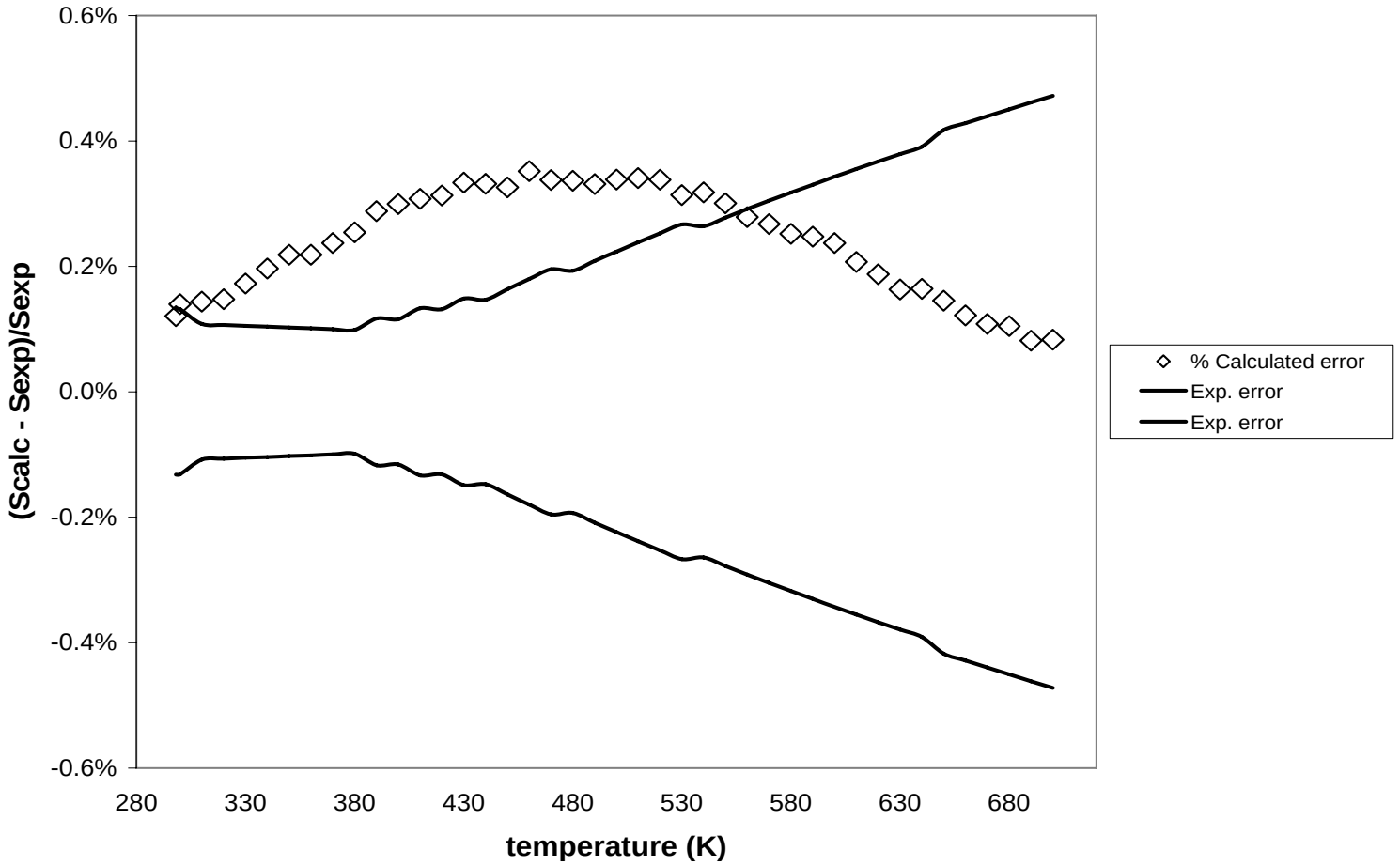


Figure 7: Percentage error of the calculated 1-methylnaphthalene entropy vs. experiment in the temperature range of 300-700 K (plus 298.15 K) with 10 K increments

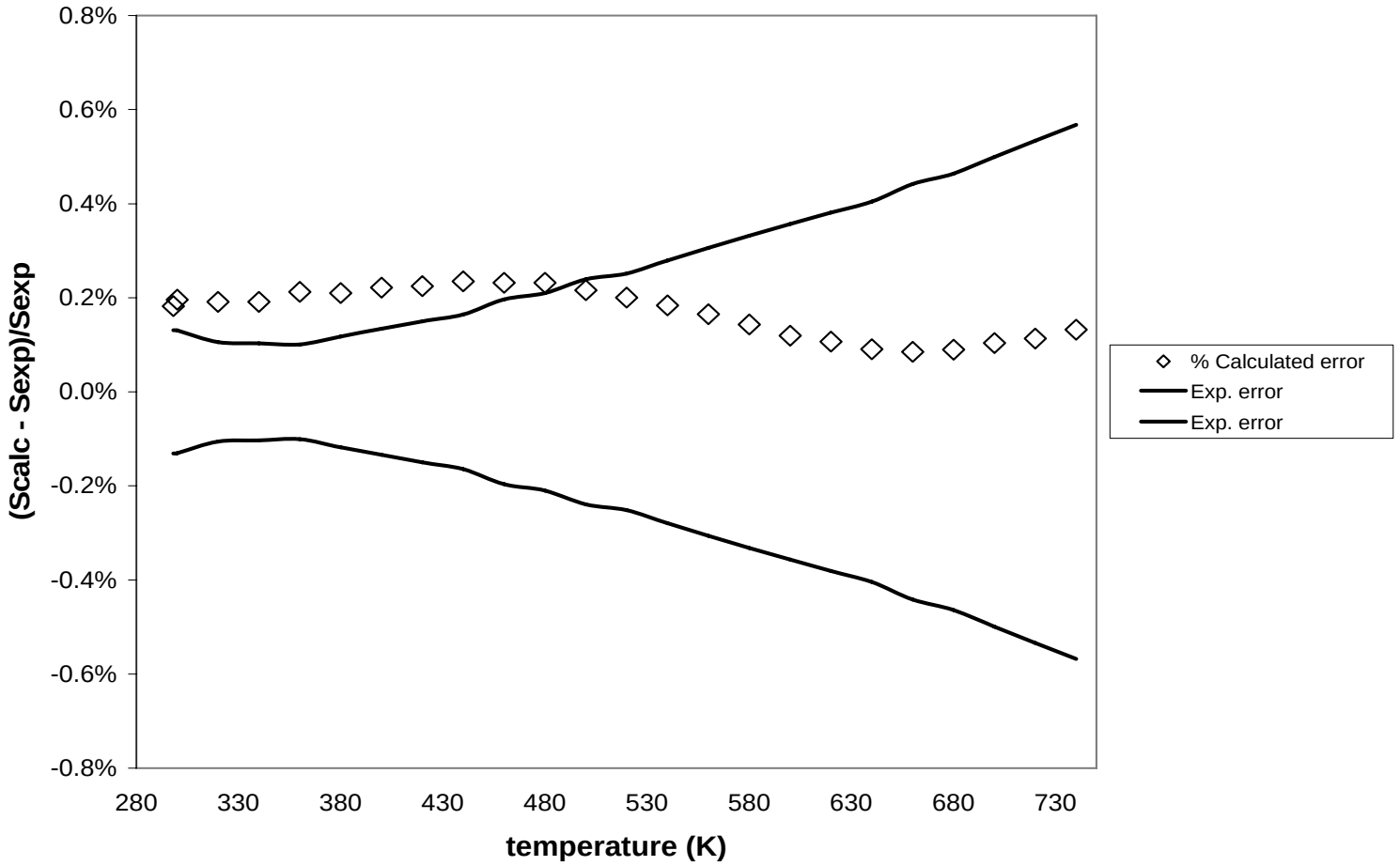


Figure 8: Percentage error of the calculated 2-methylnaphthalene entropy vs. experiment in the temperature range of 300-740 K (plus 298.15 K) with 20 K increments

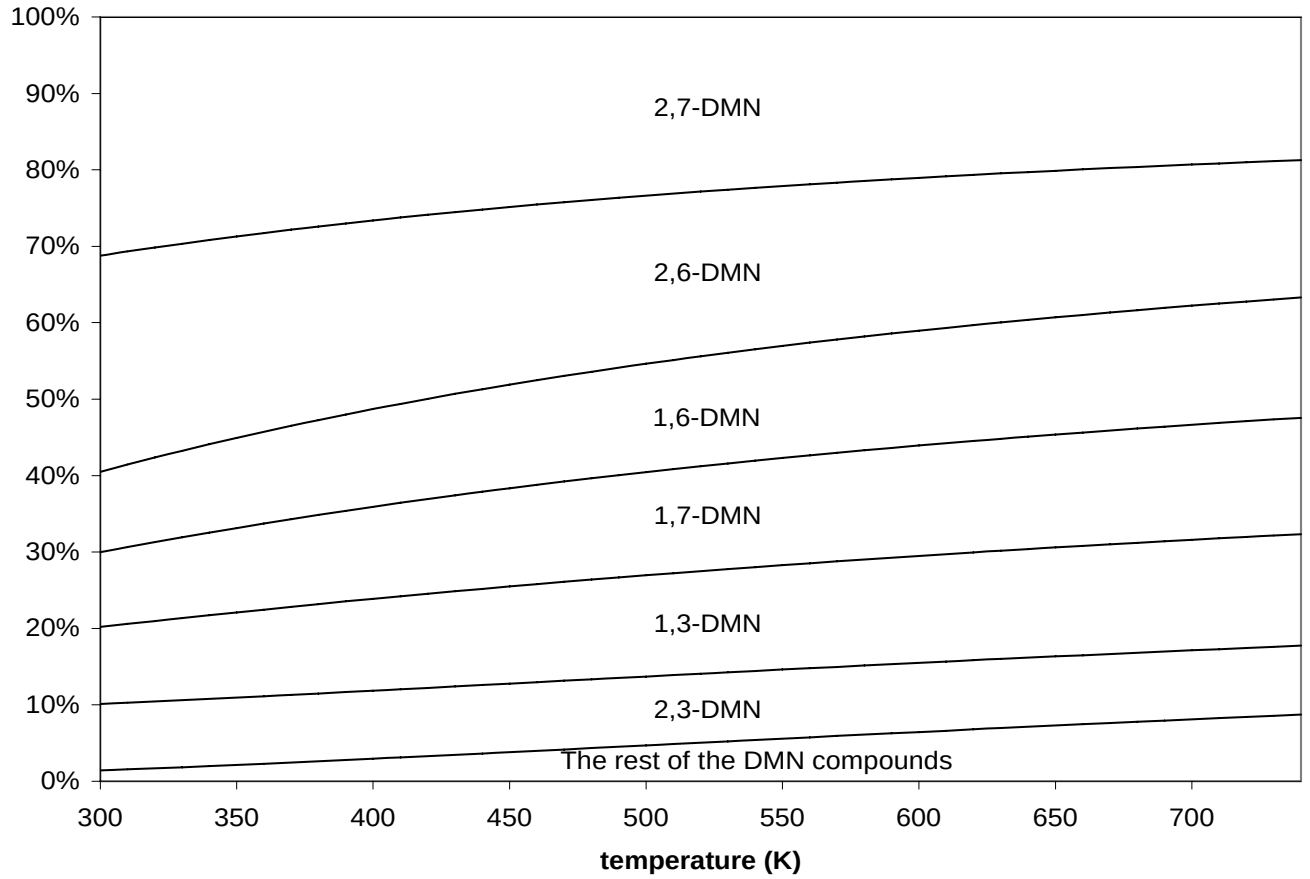


Figure 9 (a): Calculated equilibrium distribution of 2,3-DMN, 1,6-DMN, 1,3-DMN, 1,7-DMN, 2,7-DMN and 2,6-DMN and the sum distribution of the rest of the DMN compounds in the temperature range of 300-740 K with 20 K increments.

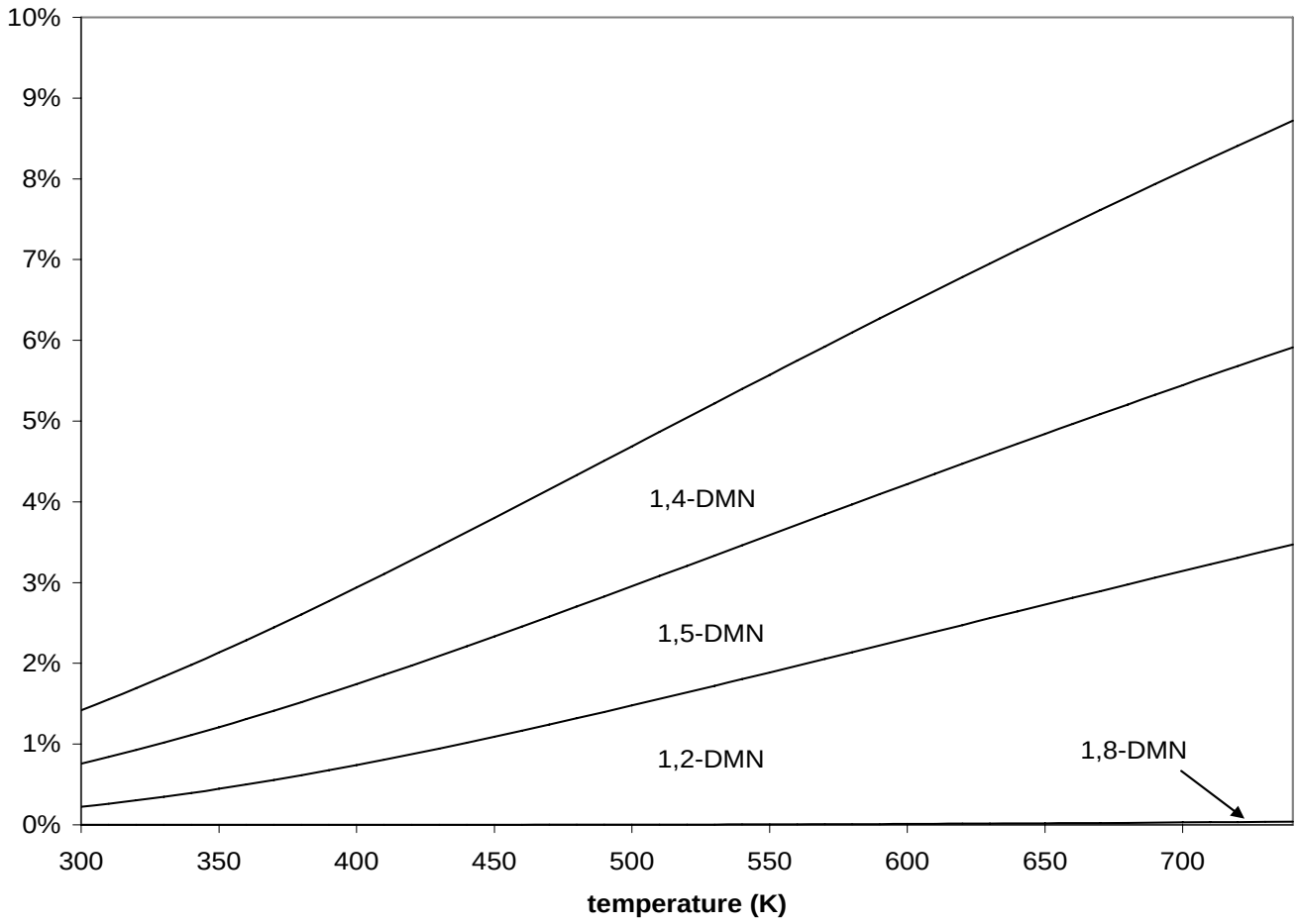


Figure 9(b): Calculated equilibrium distribution of 1,8-DMN, 1,2-DMN, 1,4-DMN, and 1,5-DMN in the temperature range of 300-740 K with 20 K increments.

# PART 4

# Conclusion and Future Work

## 4.1 Summary and Conclusions

In this thesis, a combination of quantum mechanics (QM) and statistical mechanics (SM) is used to generate entropies of aromatic compounds in the ideal gas state. The entropy, along with the energy of the compounds, are necessary for such practical calculations as the determination of the free energy of a reaction involving these compounds and the equilibrium distribution between the isomers.

In Part 2, "A Comparison between Entropies of Aromatic Compounds from Quantum Mechanical Calculations and Experiment," we use QM and SM to generate entropies of simple aromatic compounds—benzene, toluene, *p*-xylene, *m*-xylene and *o*-xylene— in the ideal gas state. Having accurate experimental frequencies and entropies for these compounds from literature, we systematically examine how the choice of quantum mechanical level of theory (method and size of basis set) impacts the agreement between theory and experiment. Six quantum mechanical levels of theory are tested on these five compounds. All of the input for the statistical mechanical evaluation of the entropy, including vibrational frequencies, moments of inertia, and barriers to internal rotation, are generated via quantum mechanical calculations. The vibrational frequencies are scaled based upon comparison with experimentally determined frequencies. We examine the effect of different levels of theory on agreement with experimentally determined entropies.

For all compounds studied in Part 2, we calculate entropies across a temperature range of 250 K to 540 K within 0.5% of experimentally determined values. We also acknowledge that, given the current state of quantum mechanical computations, an

empirical scaling factor for the vibration frequencies is required. This empirical scale factor largely eliminates the advantage in accuracy of increased basis set size. However, the empirical factor does not eliminate the advantage in accuracy of the density functional method (B3LYP) over Hartree-Fock method in QM calculations. Therefore, we recommend that B3LYP with a relatively small basis set is sufficient for accurate entropy calculations, so long as one scales the vibrational frequencies with an appropriate empirical factor. Finally, we find that the variation between scaling factors from one compound to the next is on average 0.3%. This means the reported scaling factors are meaningful up to the third significant digit.

In Part 3, "Theoretical Calculation of Thermodynamic Properties of Naphthalene, Methylnaphthalenes and Dimethylnaphthalenes," we use the same combination of QM and SM to generate the entropy of thirteen aromatic compounds—naphthalene, two methylnaphthalene isomers, and ten dimethylnaphthalene isomers—in the ideal gas state. We compare the calculated entropies to accurate experimental entropies available for four of these compounds: naphthalene, 1-MN, 2-MN, and 2,7-DMN. In QM calculations, we use density functional method (B3LYP/6-31G(d,p)) to calculate the equilibrium structure and also perform a full normal mode analysis. We also determine relaxed barriers for the internal rotation contribution to the entropy in QM calculations. The calculated entropies match the experiment very well, with the percentage errors close to the experimental uncertainty, less than 0.4%. Finally, the equilibrium distribution of DMN isomers in the mixture is predicted using the calculated entropies and energies from QM and SM calculations in the 300-740 K temperature range.

## 4.2 Significance

The work in this thesis demonstrates that given (i) strict adherence to a methodical procedure combining quantum mechanical and statistical mechanical techniques and (ii) a reasonable empirical scaling factor for the vibrational frequencies, one can reliably generate entropies of aromatic compounds in the ideal gas reference state to within 0.5% of precise experimental values. If this level of accuracy is acceptable, then the more expensive experimental techniques for evaluation of entropy can be replaced by this computational technique.

In this thesis, the procedure of combining QM and SM techniques to calculate thermophysical properties such as entropy is clearly described. This procedure is meticulous and describes in detail the generation of each property used in the calculation of the entropy. Some steps of this procedure, such as the determination of energetic barriers in systems with multiple internal rotors, are new. Another step of this procedure that is novel is the use of animated movies of the eigenvectors corresponding to the vibrational modes in order to identify internal rotational modes from vibrational modes. This procedure is used in both Part 2 and Part 3 of the thesis for different compounds.

Given the state of the art of computational quantum mechanics today, all levels of theory require an empirical scaling factor. This empirical scaling factor largely eliminates the advantage in accuracy of more sophisticated levels of theory. This being the case, the approach that we advocate is the use of a mid-range density functional theory, B3LYP, rather than the substantially computationally more expensive higher levels of theory.

In Part 2, the empirical scaling factors for vibrational frequencies are obtained for all five compounds in six QM levels of theory based on comparing with experiment. An average scale factor is determined for each QM level of theory for simple aromatic compounds. These scale factors are better suited for using in more complex aromatics rather using the recommended NIST values. The NIST reports scale factors for select QM levels of theory that are averaged over many different kinds of compounds. In Part 3, we use an averaged scale factor from simple aromatics (xylenes) in QM calculations. Doing so reduces the error significantly compared to using the NIST recommended scale factor.

The normal vibrational frequencies and entropies of five simple aromatic compounds using six QM levels of theory (Part 2) and also frequencies and entropies of thirteen naphthalene derivatives using a QM level of theory (Part 3) are calculated and tabulated. Significantly, the percentage error of calculated entropies compared to experiment is less than 0.5% in Part 2 and less than 0.4% in Part 3.

The equilibrium distribution of the ten dimethyl naphthalene isomers in the temperature range of 300 to 740 K is determined. Part 3 explains the effects of molecular structure on isomers' distribution in nature.

## 4.3 Future Work

The combined QM and SM procedure used in this thesis can be applied to many compounds to get the thermophysical properties. This work is on the aromatic compounds starting with simple one ring compounds in Part 2 and going toward two ring compounds in Part 3. The next step is to investigate the three ring aromatics such as

phenanthrene and its methyl derivatives. Similar to naphthalene derivatives, the experimental entropies are only available for some of the phenanthrene derivatives. Experimental results where available provide a means to approximately predict the error bars for the compounds for which the experimental results are not available.

In this thesis, the thermophysical properties are generated in ideal gas state. As a future work, the effect of solution could be introduced to QM and SM calculations. As a result, the thermophysical properties can also be calculated for compounds in dense phases.

# VITA

Mohamad Hadi Kassaee was born on April 2nd, 1982 in Toledo, OH, USA. In August 2000, he was ranked first at the "the national level," on the chemical engineering entrance exam, among thousands of undergraduate applicants to Azad universities in Iran. In 2003, he got his Associate Degree in Science from the University of Tehran, Iran. In May 2005, Kassaee got the Bachelor of Science degree with highest honors in Chemical Engineering from the University of Tennessee at Knoxville.

In August 2005, he joined the Department of Chemical Engineering at the University of Tennessee as a Master's candidate and also served as a teaching assistant for Chemical Engineering Laboratory and Mass Transfer and Separation Processes courses. He also served as a research assistant in UT Computational Materials Research Group.