BREAKING DOWN THE RAMAN SPECTRA OF POLYETHYLENE WITH QUANTUM MECHANICAL CALCULATIONS

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Polyethylene is presently the highest volume polymer in terms of production, with an extraordinary large amount of applications, ranging from plastic food containers to industrial sheeting. The applications of polyethylene depend largely on the synthesis, which can impact the crystal structure of the final product; more densely packed crystal structures lead to the harder plastic while less densely packed crystal structures lead to more flexible plastic. Understanding the crystallization kinetic pathway that polyethylene takes from the melt stage to the crystal stage could allow for new strategies that improve the processing and properties for this polymer to be developed. This crystallization kinetic pathway has been studied in great detail over the past 30 years, and a three stage model for this kinetic pathway, involving a crystalline stage, a mesomorphic phase, and an amorphous phase, has been proposed. Raman spectroscopy has proven to be a useful tool in examining this kinetic pathway, as peaks that are dependent on the conformation of a sample can be determined. Calculated Raman spectra using quantum mechanical methods has an advantage over experimental methods, in that it can be said with more certainty that peaks at specific frequencies are dependent on specific conformations. This thesis aims to determine peaks in the Raman spectra dependent on specific conformations in an attempt to validate the three phase model for the crystallization kinetic pathway of polyethylene.
The research and writing of this thesis
is dedicated to everyone who helped along the way.

Many thanks,
Maegan Dailey
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1. Introduction

Polyethylene, first accidentally synthesized in 1894 by Hans von Peckmann, has an incredibly wide variety of industrial applications; some of which can be traced back to World War II when it was used as an insulator for underwater cables. Today, polyethylene is the highest volume polymer, with over 90 million metric tons being produced each year.\(^1\) The uses of polyethylene have come a long way since World War II; presently ranging from power emission and electronics to food packaging. By continuing to study polyethylene, efforts can be made to find new and more efficient ways to both modify and control the properties of polyethylene.

Polyethylene is the simplest polymer, as it is repeating methylene (CH\(_2\)) units, illustrated in figure 1.1. Despite the simplicity of its chemical structure, polyethylene can be quite complex in its physical properties, which partly depend on the synthesis. For example, low-density polyethylene (LDPE) is produced by a free radical polymerization of ethylene (scheme 1.1), under high temperatures (160°C to 280°C) and pressures (1.10 kbar to 2.62 kbar).\(^2\)

![Scheme 1.1](image)

The process of free radical polymerization results in a carbon chain containing branching, which is most clearly shown in the final product of scheme 1. Due to the presence of branching, the chains are not able to closely pack in the crystal phase, which leaves voids in the crystal structure and produces a lower density, as well as a low melting point of 100°C. Additionally, this leads to LDPE having a more amorphous crystal structure, where amorphous refers to any deviation from the linear carbon chain that is shown in figure 1.1. Specific applications of LDPE include plastic bags and industrial sheeting.\(^2\) One drawback to the production of LDPE is that it comes with a high
expense; as this production process results in a low yield and requires a sufficiently high amount of energy to compress ethylene at such high temperatures and pressures.

Metal-based catalysts were then introduced to the LDPE polymerization process for a more energy efficient synthesis, which resulted in a process that no longer involved free radical polymerization. This new production process resulted in a white, waxy solid; a substance that at first glance shared no physical properties with LDPE. Further analysis showed that this substance had the same carbon back bone as LDPE, but had less branching, more crystallinity, and a higher melting point.\textsuperscript{2} This substance was then referred to as high-density polyethylene (HDPE), as the lack of branching leads to a more densely packed crystal structure (figure 1.2).\textsuperscript{3}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{image.png}
\caption{The crystal structure of HDPE, as determined by Takahashi; the reference code in the Cambridge Structural Database is QILHU002 and the space group is Pnam.}
\end{figure}

After several generations of trial and error with different organometallic catalysts, the Ziegler Natta catalyst system was determined to be the most successful and is used in the production of HDPE today. Part of the success of the Ziegler Natta catalyst system lies in the fact that polymer size can be controlled through the size of the catalyst and that this reaction occurs at low temperatures and pressures.\textsuperscript{1} Within the general category of HDPE, there exists low molecular weight HDPE, which is the waxy substance first produced as a result of organometallic catalysts, and a higher molecular weight HDPE, which is a tough
plastic. The applications of HDPE are different from those of LDPE due to the difference in physical properties. For example, the uses of the higher molecular weight HDPE include food containers and foam while the uses of the lower molecular weight HDPE include plastic bottles.²

Linear low-density polyethylene (LLDPE) is an additional type of polyethylene that is also produced using organometallic catalysts. While HDPE is produced using the organometallic catalysts and ethylene, LLDPE is produced using ethylene and alkenes, such as 1-butene or 1-octene. (polymer book) Generally, the properties of LLDPE are between those of LDPE and HDPE. LLDPE has the toughness of HDPE, but the flexibility and density are close to that of LDPE. Additionally, by controlling the amount and type of alkene used in the production, the properties of LLDPE can be further tuned.² Adjusting the production process for LLDPE, LDPE, and HDPE allows for additional types of polyethylene to be produced, each with their own unique physical properties. For example, by adjusting the process for HDPE, ultrahigh molecular weight polyethylene can be produced, which has chain lengths of over 100,000 ethylene units. Because the chain lengths are so long, they can tangle, leading to cross-linking and an increase in tensile strength. This cross-linking and increase in tensile strength leads to a material that is incredibly strong; as an example, the applications of ultrahigh molecular weight polyethylene include bullet-proof vests.²

Examining the differences between these various types of polyethylene show that the production process significantly impacts the final product, which in turn determines its applications. One of the most influential properties on the final product is the crystal structure, which is most evident in the differences of applications between HDPE and LDPE. By understanding the crystallization kinetic pathway that polyethylene takes from the melt phase to the crystal phase, new strategies for improving the properties and processing of polyethylene can be developed. With continued improvements, it may even be possible to eventually tailor the properties of polyethylene for specific applications. Additionally, because polyethylene is the chemically the simplest polymer, it can serve as a model for the crystallization kinetic pathway for more complex polymers.
There is a vast amount of literature on attempting to understand the crystallization pathway for polyethylene, some of which dates back to 1949 with Mizushima and Simanouti, who used Raman spectroscopy to study a series of alkanes. The most important observation throughout that study of alkanes was that certain peaks, to be discussed in more detail momentarily, present in the melt stage of the alkane disappeared when the sample was cooled to the crystal stage. Nearly 20 years later, Brown expanded upon this observation. In studying the Raman spectra of deuteriated and non-deuteriated polyethylene solids, Brown observed two shifts: a shift from 1060 cm\(^{-1}\) in the solid state to 1089 cm\(^{-1}\) in the melt state and a shift from 1296 cm\(^{-1}\) in the solid state to 1304 cm\(^{-1}\) in the melt state. The first set of bands refers to C-C stretching modes, while the second set of bands refer to CH\(_2\) twisting modes. The bands at 1060 cm\(^{-1}\) and 1296 cm\(^{-1}\) have been associated with ordered crystal structures that contain straight, linear polyethylene chains. This shift upon heating indicated that the solid phase is predominately linear chains while the melt stage contains chains that are amorphous.

Strobl and Hagedorn expanded on Brown’s analysis by also examining the 1350-1500 cm\(^{-1}\) region of the Raman spectra for a sample of linear polyethylene in the crystal and melt stages. At 1415 cm\(^{-1}\) and 1440 cm\(^{-1}\), there is a doublet of narrow bands which reflect a CH\(_2\) bending mode that is split due to the presence of two structure units in the unit cell. These bands indicate the presence of an orthorhombic crystal structure, where there are straight polyethylene chains arranged in a very linear, ordered fashion. As the polyethylene crystals were melted, the intensity of the 1415 cm\(^{-1}\) band decreased but did not disappear, indicating that there is a stage that precedes the melt stage, where there is no order and the chains are amorphous. Strobl and Hagedorn theorized that this is a rotator phase, where the polyethylene chains are still straight, but no longer possess the order exhibited in the orthorhombic crystal stage. Instead, the polyethylene chains are out of order in a more hexagonal unit cell. Additionally, Strobl and Hagedorn developed a method that used the normalized intensities of the 1060 cm\(^{-1}\), 1129 cm\(^{-1}\), and 1415 cm\(^{-1}\) bands to determine the mass fractions of methylene groups in the crystalline, amorphous, and rotator phases, respectively. Examples of the vibrational modes for the peaks discussed thus far are illustrated in figure 1.3, using both a straight carbon chain and an
amorphous chain for the n=4 alkane. The 1129 cm\(^{-1}\) band was included in this Strobl and Hagedorn method because it represents a C-C symmetric stretching mode associated with straight, linear polyethylene chains.\(^6\)

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**Figure 1.3** Examples of the vibrational modes for a) the 1060 cm\(^{-1}\) asymmetric C-C stretching mode of the linear alkane b) the 1080 cm\(^{-1}\) C-C stretching mode of the disordered alkane c) the 1129 cm\(^{-1}\) C-C symmetric stretching mode of the linear alkane d) the 1296 cm\(^{-1}\) CH\(_2\) twisting mode of the linear alkane e) the 1304 cm\(^{-1}\) CH\(_2\) twisting mode of the disordered alkane f) the 1415 cm\(^{-1}\) bending mode of the linear alkane.

While Strobl and Hagedorn were able to develop a procedure to calculate the mass fraction of methylene groups in the rotator phase, the rotator phase itself was not well characterized. Since the efforts of Strobl and Hagedorn, much work, both experimental and computational, has gone into characterizing this additional mesomorphic phase.\(^7\)\(^{-12}\) By examining both the infrared and Raman spectra of carbon chains ranging in length from 17 to 60 carbons, Kim et al. were able to determine the concentration of amorphous bonds at temperatures above and below the melting point for each alkane.\(^13\) The concentration of amorphous bonds remained low until the transition to the rotator phase occurred, and increased significantly at temperatures past the melting point, indicating that linear chains dominate the crystal stage. Additionally, this indicated that the lack of order associated with the rotator phase occurs because of an increase in longitudinal mobility, which is a consequence of the lateral expansion of the unit cell that occurs during this phase transition.\(^13\)

Tashiro et al. used a combination of time-resolved X-ray diffraction, Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy to analyze both
ordered and amorphous ultra-high molecular weight polyethylene in an effort to experimentally see this mesomorphic hexagonal phase.\textsuperscript{14} The combination of X-ray diffraction and FTIR data showed that this mesomorphic hexagonal phase consisted of an ordered packing of chains that contained both linear and amorphous bonds, the order of which is random. Additionally, analysis of the Raman data showed that chains in the hexagonal phase did not contain more than 5 sequential linear bonds at a time.\textsuperscript{14} Brambilla and Zerbi were able to confirm the findings of Tashiro almost 10 years later by studying alkanes ranging in chain length from 5 to 44 carbons using temperature-dependent Raman spectroscopy.\textsuperscript{15} This analysis included determining the percent concentration of C-C bonds in a linear sequence by using the intensity ratio for peaks at 1295 cm\textsuperscript{-1} and 1129 cm\textsuperscript{-1} over a range of temperatures. In addition to providing conclusions that agreed with the analysis of Tashiro et al., Brambilla and Zerbi also provided a detailed analysis of the Raman spectra for alkanes in both the solid and melt stages; something that proved to be a crucial guideline in this current study on polyethylene.\textsuperscript{15}

Koglin and Meier used quantum mechanical methods to predict the Raman spectra of alkanes containing 8, 12, and 16 carbons; the analysis of which showed an agreement with that performed by Brambilla and Zerbi.\textsuperscript{16} Their analysis also showed that the regions between 0-600 cm\textsuperscript{-1} and 700-1000 cm\textsuperscript{-1} had the most dependence on chain conformation.\textsuperscript{16} In a separate publication, Meier (again by using quantum mechanical methods to predict the Raman spectra) focused on the peaks at 1060 and 1129 cm\textsuperscript{-1}, which are generally associated with the straight chain form of an alkane chain, but not necessarily the crystal state.\textsuperscript{17} Meier began with a straight, linear chain containing 16 carbons, and gradually introduced amorphous bonds into the chain. Based on the intensity measurements of peaks at 1060 and 1129 cm\textsuperscript{-1} for the linear chain and the chains with the amorphous bonds, Meier was able to conclude that 10 consecutive linear bonds in the chain were necessary to produce the sharp peaks consistently observed in the polyethylene spectra.\textsuperscript{17}

Recently, our collaborators at the National Institute of Standards and Technology developed a procedure that improved on the original measurements for the three stages of
polyethylene melting made by Strobl and Hagedorn. Migler et al. analyzed the Raman spectra of a chain containing 21 carbons, combined with turbidity and depolarized transmitted intensity measurements, in terms of the three-state model originally proposed by Strobl and Hagedorn. However, in addition to measuring mass fractions in terms of amorphous and crystalline regions, the measurement of mass fractions was also based on the conformations that are straight but not part of the orthorhombic crystal structure, which are referred to as noncrystalline consecutive trans (NCCT) conformations. These NCCT conformations exist early in the crystallization process at the stage where there are consecutive linear sequences that are not in an orthorhombic structure, but are locally aligned. Additionally, these NCCT conformations may come from the melt stage in a condensed state. Despite the fact that the mass fraction of these NCCT conformers is small (6%), Migler et al. believes that these NCCT conformers are critical to the crystallization kinetic pathway of polyethylene.

Even though there is a significant amount of literature from the past 40 years on the crystallization kinetic pathway for polyethylene, there is still significant debate surrounding the exact physical description of each mesomorphic phase that exists for this crystallization pathway. There are several benefits to using Raman spectroscopy as a tool to investigate this kinetic pathway. Raman spectroscopy does not require the use of thin polymer films as samples, as does infrared spectroscopy. Additionally, the Raman scattering can be used for the determination of orientation distribution functions, which is necessary in the understanding of the mechanical properties of polymers. Additionally, the transmitted light from 180° backscattering can be utilized for additional optical probers, such as small-angle light scattering, as shown by Migler et al. By using the calculated Raman spectra of a wide variety of model systems, peaks that are dependent on amorphous conformations can be identified, ultimately leading to a better understanding of the kinetic pathway that polyethylene takes from the melt stage to the crystal stage. Because the identification of peaks that are dependent on amorphous conformations is an important aspect in understanding the crystallization kinetic pathway, a majority of this thesis will focus on the calculated Raman spectra for chains containing amorphous bonds. However, due to the fact that accurately calculating Raman spectra
involves accurate predictions of the model system energies, a discussion of choosing the appropriate model chemistry will be an important aspect to this thesis.
2. The Model Systems and Their Energetics

2.1 The Determination of Appropriate Model Systems

While polyethylene can have hundreds of repeating CH₂ units, it is not possible to run extensive quantum mechanical calculations on systems this large due to limitations on computational time and resources. However, running extensive quantum mechanical calculations on systems this large is unnecessary, since small chain alkanes can act as low molecular weight polymers and are thus sufficient models for studying polyethylene. For the purposes of this study, it was necessary for the alkanes to be long enough that a variety of defects could be explored, yet small enough that the time necessary for a calculation to finish did not exceed 10 days on 8 processors. Based on this criteria, the alkanes n=4-16, where n is the number of carbon atoms in the alkane, were chosen for this study.

The alkane chains containing amorphous bonds studied in this report are the same as conformational isomers for the alkanes, as each amorphous bond is created by a rotation about a single bond. In many organic chemistry text books, the total number of conformational isomers for an alkane is given by $3^{n-3}$, where n-3 represents the number of torsion angles in the alkane. Recently, Tasi et al. determined that a $5^{n-3}$ rule was more accurate for predicting the number of conformers by taking into consideration three main rotations: a rotation of 180° representing a trans (t) bond, a rotation of ±60° representing a gauche (±g) bond, and a rotation of ±90° representing a perpendicular (±x) bond. These values also describe the “ideal” geometry of any given conformer. Examples of these rotations using a carbon chain of n=4 are shown in figure 2.1.

![Figure 2.1](image)

**Figure 2.1** Examples of torsion angle rotations used to create conformations throughout this thesis, where a) represents the t bond, b) represents the g bond, and c) represents the x bond. All examples above are what is referred to as the "ideal" geometries.
Straight chain alkanes previously mentioned consist of all trans bonds, and any defects are created by combinations of the three angles mentioned above. Tasi et al. also determined “forbidden” sequences of defects. With the $3n^3$ rule, sequences of defects containing g+g-bonds are predicted to occur, however, with the $5n^3$ rule these sequences are actually forbidden due to steric hindrance. Indeed, preliminary calculations performed on conformers containing g+g-bonds revealed an imaginary frequency, indicating that these structures are transition structures and not conformers representing a true minimum on the potential energy surface. Instead, g+x-, x+g-, g-x+, and x-g+ sequences are allowed, as having a 90° angle instead of a 60° angle does not lead to steric hinderance, and in fact are true minima on the potential energy surface. Additionally, x+x-, gx-g, and xgx- are forbidden as well. The conformers created for this study of polyethylene follow the rules established by Tasi et al.\textsuperscript{21,22}

2.2 Choosing an Appropriate Model Chemistry

The density functional theory (DFT) B3LYP with the 6-31G(d,p) basis set was chosen for these initial calculations. The 6-31G(d,p) basis set was chosen because it is a standard basis set large enough to accommodate both the hydrogen and carbon atoms used to create the model systems. The addition of (d,p) adds polarization to the second row elements. This addition of polarization to the 6-31G(d,p) basis set has been shown to improve on both calculated energies and vibrational frequency calculations in comparison to experimental data.\textsuperscript{23} The B3LYP level of theory was initially chosen because it is a robust model suitable for a wide variety of situations, including the calculation of vibrational frequencies.\textsuperscript{24-30} B3LYP is a hybrid DFT that includes a mixture of Hartree-Fock exchange with DFT exchange-correlation, as shown in equation 2.1

$$E_{XC} = E_{XC}^{\text{LSDA}} + a_0 (E_X^{\text{exact}} - E_X^{\text{LSDA}}) + a_X \Delta E_X^{B88} + a_C \Delta E_C^{PW91}$$  \hspace{1cm} (2.1)$$

where LSDA stands for local-spin-density exchange correlation approximation, $E_{XC}$ represents the exchange-correlation approximation, $a_0$, $a_X$ and $a_C$ are semi-empirical coefficients as determined by a fit to experimental data, $E_X^{\text{exact}}$ is the exact exchange energy, $E_X^{B88}$ is the Becke 1988 gradient correction to the LSDA, and $\Delta E_C^{PW91}$ is the 1991 gradient correction for correlation as determined by Perdew and Wang.\textsuperscript{31} The term
at the beginning of the equation represents the LSDA exchange energy. Additional details on the parameters of this theory can be found in reference 31.

In order to determine if this level of theory was suitable for ultimately predicting the Raman spectra, it was necessary to examine the accuracy of both the resulting energies and geometries of geometry optimization calculations performed on straight chain alkanes as well as alkanes containing defects. For the purposes of this report, accuracy refers to results obtained by Gruzman et al., who performed a W1h extrapolation on coupled cluster calculations while studying the alkanes n=4-8 in great detail. Geometry optimization calculations were first performed on various conformers for alkanes n=4-7 using the Gaussian 09 suite. The energy for each conformer was determined by taking the difference between the results of the geometry optimizations for the conformer and the all trans configuration, as the all trans conformer is always the lowest energy conformer. Based on these energies, the order of conformers according to energy can be determined. This is an important and necessary step, as a correct order of conformers based on energy is important in predicting the Raman spectra due to the fact that the energy plays a role in determining what conformers will be accessible at various temperatures. Exactly how the conformer energies relate to the Raman spectra will be discussed in more detail in the Thermodynamics section of this thesis. A similar strategy was used in determining the accuracy of the calculation in terms of geometry. The deviations from these ideal geometries were obtained by subtracting the ideal angles from the angles resulting from the geometry optimization calculations.

For the alkane n=4, only the gauche conformer was examined for the purposes of this thesis, as this was the only conformer examined by Gruzman. The results of the geometry optimization showed that the gauche conformer has an energy of 0.843 kcal/mol; a value that is high when compared to the reference value of 0.598 kcal/mol. Additionally, the resulting angle deviated from the ideal geometry by 5.10°. For n=5, the energies for each of the four lowest energy conformers are shown in figure 2.2 and the deviations from the ideal geometries are shown in figure 2.3. The reference values for the geometries were obtained from calculations performed at the MP2 level of theory. Conformers containing all trans bonds are not shown on the geometry graphs, as the
Figure 2.2 The ordering of n=5 conformers by energy, as determined by geometry optimization calculations performed at the B3LYP/6-31G(d,p) level of theory. The results are compared with reference values obtained by Gruzman, et al.

Figure 2.3 The deviations from the ideal geometries of the four conformers of n=5 upon geometry optimization with the B3LYP/6-31G(d,p) level of theory.
differences upon geometry optimization are zero. As shown in figure 2.2, the energies as predicted by the B3LYP/6-31G(d,p) level of theory are higher than the reference values by an average of 0.473 kcal/mol, consistent with the results for n=4, indicating that this particular model chemistry may not be suitable for these calculations. Figure 2.3 shows that, depending on the conformer, both the B3LYP/6-31G(d,p) level of theory and the reference values have significant deviations from the ideal geometry, despite the fact that the reference values are obtained from calculations performed at a very high level of theory. For alkanes n=6 and n=7, there can be as many as 125 and 625 conformers, respectively, according to the $5^{n-3}$ rule. Many of these conformers are likely to be extremely high in energy and will not be accessible, even at extremely high temperatures. Therefore, for the purposes of this thesis, only the conformers with an energy lower than 7.00 kcal/mol for each alkane will be discussed.

The order of conformers according to energy for n=6 and n=7 are shown in figures 2.4 and 2.5, respectively.

Figure 2.4 The order of the 7 lowest energy n=6 conformers according to energy, as determined at the B3LYP/6-31G(d,p) level of theory.
As with n=4 and n=5, the energies predicted by the B3LYP/6-31G(d,p) level of theory are significantly higher than the reference values by an average value of 0.577 kcal/mol for n=6 and an average value of 0.671 kcal/mol for n=7. Additionally, an interesting note is that for both n=6 and n=7, the order of conformers predicted by B3LYP does not match the order predicted by the reference values. In some instances, this difference in ordering does not have a significant impact on the predicted Raman spectra, as with the ttgt and ttgg conformers for n=7. The B3LYP results predict that the ttgg conformer is lower in energy than the ttgt conformer, while the reference values show the opposite. The reference values also show that these conformers are very close in energy to begin with, and will likely be present in the Raman spectra even at low temperatures. What is also important to consider in differences like this is that while the reference values are obtained at a very high level of theory, they are also subject to error. Therefore, despite the fact that the B3LYP ordering does not match the reference values, no effect on the final Raman spectra will be observed. However, the B3LYP results show that for both

**Figure 2.5** The order of the 10 lowest energy conformers according to energy for n=7, as determined at the B3LYP/6-31G(d,p) level of theory.
n=6 and n=7, the all gauche conformer is higher in energy than the rest of the conformers, suggesting that this conformer would only be present in the predicted Raman spectra at higher temperatures. The reference values suggest that these all gauche conformers are lower in energy, compared to the results produced with the B3LYP/6-31G(d,p) level of theory; so much lower that they are close to conformers that contain gauche bonds separated by trans bonds. These reference values suggest that the all gauche conformer could be present in the predicted Raman spectra at lower temperatures, with a mixture of conformers such as gttg or tggg. This incorrect ordering and energies predicted by the B3LYP method would lead to an incorrectly predicted Raman spectra, further indicating that this method is not suitable for these systems.

This conclusion that B3LYP/6-31G(d,p) is not a suitable method for modeling these systems is further confirmed when examining the geometries for the n=6 and n=7 conformers upon geometry optimization; the geometries for a few select conformers are shown in figure 2.6 while the remaining geometries can be found in the supporting information. Reference values were not available for these alkanes. These results show

![Figure 2.6](image_url)

**Figure 2.6** The deviations from ideal geometries for select conformers for alkanes n=6 and n=7, calculated with the B3LYP/6-31G(d,p) level of theory.
that upon geometry optimization for these select conformers, the deviation from the ideal geometry is on average $4.98^\circ$. These differences are likely due to the lack of parameters for describing intermolecular van der Waals forces in B3LYP, meaning that there are no parameters to stop these angles from moving during geometry optimization. Because of the significant deviations from the ideal geometries and the incorrect ordering of certain conformers according to energy, it was necessary to examine other levels of theory in order to determine a more appropriate model for these systems.

Recent studies have shown that the M06-2x level of theory is very well suited for modeling organic compounds, especially systems containing only carbon and hydrogen. M06-2x is also a hybrid DFT, developed by Truhlar and Zhao as part of the Minnesota functionals. This particular DFT method differs from B3LYP in that the functional is based on meta-GGA approximations and contains parameters for describing intermolecular forces. All calculations performed using the M06-2x level of theory also used the 6-31G(d,p) basis set. Figure 2.7 shows the same conformers from figure 2.6.
upon geometry optimization, where instead calculations were performed using M06-2x. The results for the remaining conformers, as well as the conformers for $n=5$, can be found in the supporting information. With the exception of certain angles for very few conformers, M06-2x out-performs B3LYP in terms of geometry, giving an average value of deviations from the ideal geometries as $4.19^\circ$ for the select conformers in figure 2.7.

However, M06-2x showed a significant problem with the order of conformers according to energy, especially when compared to the B3LYP results and the reference values. An example of these problems can be seen in figure 2.8, which shows the ordering of conformers for alkane $n=5$. Where the predicted energies using B3LYP are higher than the reference values by an average of 0.473 kcal/mol, the predicted energies using M06-2x are lower than the reference values by an average of 0.316 kcal/mol. Additionally M06-2x predicts that the gg conformer for $n=5$ is nearly equal in terms of

![Figure 2.8](image_url)
energy to the tg conformer. This is incorrect, as conformers containing multiple gauche bonds directly next to each other are likely to experience a higher strain than conformers containing a single gauche bond surrounded by trans bonds. This increase in strain would lead to an increase in energy, therefore the gg conformer should not be equal to or lower in energy than the tg conformer.

These problems are not limited to the n=5 alkane, as shown in figures 2.9 and 2.10, which show the ordering of conformers according to energy for n=6 and n=7.

Figure 2.9 The order of conformers for the n=6 alkane according to energy for results obtained using the M062x/6-31G(d,p) level of theory in comparison to results obtained at the B3LYP/6-31G(d,p) level of theory and the reference values.
respectively. Both figures show that the M06-2x functional produces a completely incorrect ordering of conformers when compared to the reference values. Additionally, these figures show that conformers containing multiple gauche bonds are nearly degenerate in energy with conformers containing only one bond. These results indicate that conformers expected to be higher in energy due to the strain of multiple gauche bonds will appear in the predicted Raman spectra even at low temperatures. By predicting that conformers containing multiple gauche bonds are nearly degenerate in energy, M06-2x lacks any kind of additive effect for having multiple gauche bonds in a chain, where B3LYP and the reference values do not. Because the predicted Raman spectra depends on accurate conformer energies, it was determined that the M06-2x/6-31G(d,p) level of theory is not a suitable method for modeling these systems.

After the problems with using the M06-2x/6-31G(d,p) level of theory to model these systems became apparent, it became necessary to find a level of theory that would
prevent the conformers from significantly deviating from the ideal geometry and would also produce energies reasonably close to the reference values. It was then hypothesized that adding dispersion corrections to the B3LYP/6-31G(d,p) level of theory would produce similarly reasonable energy values, yet would improve on the geometries obtained by geometry optimization calculations. Four empirical dispersion corrections were tested for this hypothesis: the Grimme GD2, GD3 and GD3BJ corrections, and the PFD correction. The APFD level of theory was also included in these tests, since the PFD dispersion correction is derived from this level of theory. The 6-31G(d,p) basis set was also used in all calculations involving dispersion corrections. Geometry optimizations were performed on the lower energy conformers for alkanes n=4-7; the energy of each conformer as well as the deviations from the ideal geometries were obtained by taking the appropriate differences, as previously described.

Upon examining the results of these dispersion tests, it was immediately clear that there were problems with the energies predicted by both the GD2 and the GD3BJ dispersion corrections. Figure 2.11 demonstrates these problems using select conformers for the n=6 alkane as an example. The GD2 dispersion correction predicted that the ggg conformer for n=6, where every available torsion angle is a gauche bond, has an energy of 0.1632 kcal/mol; a value that is significantly lower than the reference value of 1.125 kcal/mol. If the reference value is taken as the “absolute” value and the GD2 result is taken as the “experimental” value, these results correspond to a percent error of 85.5%, using the formula shown in equation 2.2.

\[
\text{percent error} = \left| \frac{\text{Reference Value} - \text{DFT Value}}{\text{Reference Value}} \right| \times 100
\]  

(2.2)

Additionally, the GD2 dispersion correction predicts that the ggg conformer is the lowest energy conformer, which is incorrect due to the strain that these gauche bonds put on the structure. Based on these results, it was clear that the GD2 dispersion correction would not lead to any accurate results for the energies of the conformers, and was thus eliminated from consideration as a suitable method. Figure 2.11 also shows that, with the exception of the tgg conformer, the GD3BJ dispersion correction does an excellent job of predicting conformer energies that agree with the reference values. However, the GD3BJ
The result for the tgg conformer produces a percent error of 770.216% when compared to the reference value. This alone is enough to eliminate the GD3BJ dispersion correction from consideration.

The APFD level of theory started out as promising, producing excellent results for the n=4 alkane. This level of theory predicted an energy of 0.602 kcal/mol for the gauche conformer of butane, giving a 0.715% error when compared to the reference value of 0.598 kcal/mol. However, as the size of the alkane increased, there was an increase in the percent errors when results were compared to the reference values. Figure 2.12 shows a comparison between the APFD results and the reference values for the n=5 alkane conformers. While there is good agreement for the tg and gx- conformers, the difference between the APFD result for the gg conformer and the reference value leads to a 19.94%
error. Results for the n=6 alkane conformers (supporting information) also show that the

![Graph](image.png)

Figure 2.12 A comparison of the order of n=5 conformers by energy between results determined at the APFD/6-31G(d,p) level of theory and the reference values.

ggg conformer produces a 20.05% percent error between the APFD result and the reference value. These high percent errors indicate that the APFD level of theory is also insufficient for modeling these systems.

Both the PFD and the GD3 dispersion corrections produced conformer energies close to those of the reference values, as shown in figure 2.13, where the n=6 conformers are used as an example. Both dispersion corrections out-perform the B3LYP functional with no dispersion in terms of energy. Additionally, both dispersion corrections predict conformer energies that are extremely close to the reference values, where the highest percent error, in comparison to the reference values, is 9.15% for the ggg conformer energy predicted by the PFD dispersion. The lowest percent error between the two dispersion corrections is 0.433%, also for the ggg conformer, as predicted by the GD3 dispersion. Figure 2.14 shows a comparison between the PFD and GD3 dispersion
corrections for the geometries of select n=6 conformers (full results in supporting information). There is very little difference between the resulting geometries for the PFD.

**Figure 2.13** The order of select n=6 conformers by energy for results determined by the B3LY/6-31G(d,p) level of theory, results determined by the PFD and GD3 dispersion corrections, in comparison to reference values.
and GD3 dispersion corrections. The GD3 dispersion correction slightly outperforms the PFD dispersion correction; the GD3 correction has an average value of 3.57° for the deviations while the PFD correction has an average value of 3.67°. These averages refer to the conformers shown in figure 2.14. Because the PFD dispersion correction had higher percent errors than the GD3 dispersion correction, a judgement call was made that the B3LYP/6-31G(d,p) level of theory with GD3 dispersion correction is the most sufficient method for modeling these systems because it produces the most reasonably accurate energies. Figure 2.15 shows that this model chemistry produces an accurate ordering of conformers according to energy for the n=7 alkane, despite the fact that the calculated values are slightly lower than the reference values. The order of conformers using this new model chemistry varies slightly from that of the reference values, however this is due to certain conformers being very close in energy. Based on the success in these tests, the B3LYP+GD3/6-31G(d,p) level of theory will be used in further calculations throughout this thesis.
2.3 Model System Energetics

Now that an appropriate model chemistry has been determined, any kind of effective potential that these defects have on the total energy for each conformer can be examined. To do so, the desired defect was introduced into the first torsion angle of alkanes n=6, 7, 9, 12, 16, then moved throughout the chain one torsion angle at a time. A geometry optimization was performed each time the defect was moved, and the total average for every alkane containing the defect was then taken. This average value was taken in order to give an estimate of how much the defect contributes to the overall energy of any given conformer. As will be shown momentarily, not every torsion angle available to the alkane was included in the geometry optimization calculations, as after the center of symmetry the conformers become degenerate in energy. For the purposes of

Figure 2.15 The order of the lowest energy conformers for the n=7 alkane obtained at the B3LYP+GD3/6-31G(d,p) level of theory.
this thesis, only results involving the g, gg, and ggg defects will be discussed here, while the remaining results can be found in the supporting information.

The average values produced as a result of this analysis for the g, gg, and ggg defects are 0.564 kcal/mol, 0.790 kcal/mol, and 1.039 kcal/mol, respectively. What is interesting to note about these results is that there is an increase in the average energy with an increase in the number of gauche bonds, indicating that there is an additive effect. In going from an increase of one gauche bond to two gauche bonds, the energy increases by a factor of 1.40. Additionally, in going from one gauche bond to three gauche bonds, the energy increases by a factor of 2.321. These results are interesting because preliminary calculations performed at the B3LYP/6-31G(d,p) level of theory showed that going from one gauche bond to two gauche bonds would increase the energy by a factor of 2.0. Figures 2.16, 2.17, and 2.18 illustrate the error values for the g, gg, and ggg conformers, respectively. The error value was determined by taking the difference

![Figure 2.16](image-url)  
*Figure 2.16* The error values for a single g defect moving throughout select alkane chains, calculated at the B3LYP+GD3/6-31G(d,p) level of theory.
Figure 2.17 The error values for a gg defect moving throughout select alkane chains, calculated with the B3LYP+GD3/6-31G(d,p) level of theory.

Figure 2.18 The error values for a ggg defect moving throughout select alkanes.
between each individual result and the average value. What these error values are really showing is the deviation from additivity. As shown in the figures, the scale for these error values is quite narrow, indicating an incredibly small deviation from this additivity. These results so far show that there is some kind of effective potential to push the gauche bonds together in a conformer. This idea of the effective potential is also illustrated in figure 2.19, which shows the energy as a function of n=16 conformers, where two gauche bonds are separated by a certain number of trans bonds. What is most interesting to note about this figure is that the conformer where two gauche bonds are directly next to each other and not separated by any trans bonds is the lowest energy conformer, confirming that there is indeed some effective potential that pushes these gauche bonds together. Another interesting result is shown in figure 2.20. This figure shows that there is a linear relationship between energy and the all gauche conformer as chain length increases, which allows for the energy of the all gauche conformer of any given chain length to be predicted.
Figure 2.20 The linear relationship between the energy and carbon chain length of alkane chains of n length, where every torsion angle is in the gauche form; all calculated at the B3LYP+GD3/6-31G(d,p) level of theory.
3. Thermodynamics

3.1 Method

Vibrational frequency calculations cannot only predict the Raman spectra for a particular molecule, but also information that allow thermodynamic quantities to be determined. It is important to note that all results obtained in this section refer to molecules in the gas phase. These thermodynamic quantities include the change in enthalpy (∆H), the change in entropy (∆S), and the Gibb’s free energy (∆G); where the changes in enthalpy and entropy represent changes from the all trans conformer to any other conformer containing a defect. There are three important parameters calculated during the frequency calculations that are used to determine these thermodynamic. The first is the total energy, which is described by the following equation

$$E_{\text{tot}} = E_0 + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}$$  \hspace{1cm} (3.1)

where $E_{\text{vib}}$, $E_{\text{rot}}$, and $E_{\text{trans}}$ represent the vibrational, rotational, and translational contributions to the total energy, respectively. These contributions are calculated from partition functions, which have a dependency on temperature. The temperature is easily controlled through command lines in the files necessary to run the calculations. $E_0$ represents the sum of the electronic energy ($E_{\text{elec}}$) and the zero-point energy. The zero-point energy is a correction that accounts for the effects of molecular vibrations that are present at all temperatures. The $E_{\text{elec}}$ is the result of the geometry optimization calculation, and represents the total energy of the conformer.\textsuperscript{41,42}

The second relevant component is the sum of the electronic and thermal enthalpies, which is determined by adding the $E_{\text{elec}}$ to the thermal correction to enthalpy ($H_{\text{corr}}$). $H_{\text{corr}}$ is determined by the following equation

$$H_{\text{corr}} = E_{\text{tot}} + k_B T$$  \hspace{1cm} (3.2)

where $E_{\text{tot}}$ is the total energy (described in 3.1), $k_B$ is the Boltzmann constant ($3.167 \times 10^{-6}$ Hartree/K) and $T$ is the temperature (K) as input through command lines.\textsuperscript{42} The final relevant component for calculating thermodynamic properties is the total entropy, $S_{\text{tot}}$. The $S_{\text{tot}}$ is calculated very similarly to the way that the $E_{\text{tot}}$ is calculated, as show by the following equation

$$S_{\text{tot}} = S_{\text{elec}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{trans}}$$  \hspace{1cm} (3.3)
where $S_{\text{elec}}$, $S_{\text{rot}}$, $S_{\text{vib}}$, and $S_{\text{trans}}$ represent the electronic, vibrational, rotational, and translational components to the entropy, respectively. These contributions are also calculated from partition functions and also have a temperature dependence.\textsuperscript{42}

When determining the $\Delta S$ and $\Delta H$ of a reaction or the formation of a compound, the difference between the sum of the products and the sum of the reactants are taken. This same line of thought can be applied to determining the $\Delta S$ and $\Delta H$ of any conformer, where the all trans conformer serves as the “reactant” and the conformer serves as the “product”. The all trans conformer is able to serve as the “reactant” because it is the lowest energy conformer for any chain length. Therefore, $\Delta S$ is given by

$$\Delta S = S_{\text{tot(conformer)}} - S_{\text{tot(trans)}}$$

and $\Delta H$ is given by

$$\Delta H = (E_{\text{elec}} + H_{\text{corr}})_{\text{conformer}} - (E_{\text{elec}} + H_{\text{corr}})_{\text{trans}}$$

The determination of $\Delta S$ and $\Delta H$ relies entirely on the components of the calculated thermochemical data as described above. The $\Delta G$ for each conformer can then be determined by

$$\Delta G = \Delta H - T\Delta S$$

The $\Delta G$ can then be used to calculate the Boltzmann factor for each conformer using the following equation

$$N_i = g_i e^{-\frac{\Delta G_i}{k_B T}}$$

where $N_i$ is the Boltzmann factor of any given conformer with respect to the sum of the Boltzmann factors for all conformers, $g_i$ is the degeneracy of the conformer, and $k_B$ is the Boltzmann constant.\textsuperscript{44} Here degeneracy means conformers that produce the same energy upon geometry optimization. For example, the tg conformer of pentane would have a degeneracy of 4, because the following four conformers would all result in the same energy upon geometry optimization: tg\textsuperscript{+}, tg\textsuperscript{-}, g\textsuperscript{+}t, g\textsuperscript{-}t.\textsuperscript{24} At this point, it is also important to note that equations 3.1, 3.2, and 3.5 all have a contribution from the energy determined by geometry optimization calculations. These equations are in turn used to calculate a variety of thermodynamic properties, which are eventually used to determine the Boltzmann factor for each conformer. As will be shown chapter 4, the Boltzmann factors
will have an impact on the Raman spectra, further showing how accurate conformer energies are a necessity for this work.

3.2 Discussion of Select Results

For the alkanes n=4-7, the thermodynamic quantities and Boltzmann factors were calculated for select lowest energy conformers at temperatures ranging from 0°C to 100°C in 10°C increments. Only the results for select conformers of the n=7 alkane will be discussed here; the results for the remaining alkanes n=4-6 and the remaining n=7 conformers can be found in the supporting information. As the all \textit{trans} conformer is the lowest energy conformer for all alkanes, the thermodynamic quantities are all equal to 0.00. The two conformers that will be discussed here are the ttgt and tggt conformers, which have energies of 0.570 and 0.860 kcal/mol, respectively, according to the reference values.\textsuperscript{32} In terms of degeneracy, the ttgt conformer has a degeneracy of 4 while the tggt conformer has a degeneracy of 2.\textsuperscript{32}

These conformers were chosen for this discussion in order to illustrate the first two states that would contribute the most to the Raman spectra at certain temperatures. Figures 3.1 and 3.2 show the ΔG as a function of temperature for the ttgt conformer and

![Figure 3.1](image-url)
tggt conformer, respectively. What is most interesting to note about these is results is that for the ttgt conformer the $\Delta G$ decreases as temperature increases, indicating that the formation of this conformer may be spontaneous at temperatures around 30°C or higher. For the tggt conformer, the $\Delta G$ increases as temperature increases, the opposite trend for the ttgt conformer. These trends are reflected in the Boltzmann factors as a function of temperature; the Boltzmann factors for the ttgt conformer are shown in figure 3.3 and the Boltzmann factors for the tggt conformer are shown in figure 3.4. The Boltzmann factors for the ttgt conformer indicate that even at low temperatures, this conformer has a significant impact on the Raman spectra. The explanation for the decrease in the Boltzmann factors as temperature increases for this conformer is that an increase in temperature increases the number of possible states for the alkane. Increasing the possible number of states for the alkane would increase the number of amorphous conformers that are present at higher temperatures, and the Boltzmann factors for conformers low in energy will decrease relative to the Boltzmann factors for conformers at higher energies.

**Figure 3.2** The $\Delta G$ as a function of temperature for the tggt conformer of the n=7 alkane.
Figure 3.3 The Boltzmann factor as a function of temperature for the ttgt conformer of the \( n=7 \) alkane.

Figure 3.4 The Boltzmann factor as a function of temperature for the tggt conformer of the \( n=7 \) alkane.
Figure 3.4 provides some confirmation of this explanation, because as temperature increases the Boltzmann factor increases as well, even though the change is small. Additionally, the Boltzmann factors for these two conformers differ by a factor of about 15, even though the degeneracy for these two conformers differs by a factor of 2. This indicates that the degeneracy plays some factor in determining the Boltzmann factor, and that the ΔS also plays a significant factor. The ΔS for the ttgt conformer is positive at all temperatures, while the ΔS for the tgtt conformer is negative at all temperatures, due to the fact that the vibrational contribution to the total entropy is less than the vibrational contribution to the total entropy for the all trans conformer. Ultimately, the Boltzmann factors are the most important part of this thermodynamic analysis, as they will be used as weighting factors when examining the predicted Raman spectra.
4. The Raman Spectra

4.1 Peak Identification

As previously mentioned, there are many benefits to using Raman spectroscopy to study the crystallization kinetic pathway of polyethylene. However, one of the possible downsides in experimental Raman spectroscopy is the inability to determine the exact conformations that are present as polyethylene begins to melt. It is in this instance that using computational chemistry to predict the Raman spectra of various alkanes can be extremely beneficial and advantageous. By calculating the Raman spectra of individual conformers and using the Boltzmann factors as weighting factors, individual peaks present in the Raman spectra at any given temperature can be identified as coming from a particular conformer. The use of Boltzmann factors as weighting factors will be discussed momentarily, as the current discussion will focus on identifying peaks in the Raman spectra that are dependent on certain conformations. It should be noted at this point that all spectra were obtained by first applying a Lorentzian broadening to the calculated activities, which takes into account a broadening factor. The equation for the Lorentzian broadening is shown in equation 4.1.\(^\text{44}\)

\[
I_{\nu} = \frac{I_0}{1 + \left(1 - \frac{\nu - \nu_0}{\lambda}\right)^2} \quad (4.1)
\]

In equation 4.1, \(\nu_0\) is the center of the peak, \(I_0\) is the intensity at the center of the peak, \(\nu\) is the half-maximum of the peak, \(I\) is the new intensity of the peak at frequency \(\nu\), and \(\lambda\) is the broadening factor. This broadening factor is determined by the user; for the spectra generated in this thesis the broadening factor has a value of \(\lambda = 3.70 \text{ cm}^{-1}\).

In order to identify peaks that are dependent on conformations, each individual conformation for the \(n=4-7\) alkanes that have been discussed thus far were introduced into the \(n=16\) alkane at the first torsion angle and then moved throughout the chain one torsion angle at a time. After the center of symmetry for the \(n=16\) alkane, these structures become degenerate in energy and are not considered for this analysis. The Raman spectrum was then calculated for each individual structure. For these results, the frequencies of the resulting Raman spectra do not have any scaling factors applied to
them. These $n=16$ chains with the defects were then compared to the all $trans$ chain, which allowed for peaks dependent on having a straight chain alkane and the presence of the defect to be identified. An example of this process is shown in figures 4.1 to 4.3, which aims to identify peaks that are dependent on having a single $gauche$ bond anywhere in an alkane chain. Figure 4.1 shows the full Raman spectra from 0-1600 cm$^{-1}$. The frequencies beyond 1600 cm$^{-1}$ are not included in the following discussions, as it has been shown that this range is related to C-H stretching modes and is not affected by changes in conformation$^{18}$. Figures 4.2 and 4.3 show close ups of the full Raman spectra from 800-1200 cm$^{-1}$ and 1200-1600 cm$^{-1}$, respectively. In these figures, peaks outlined in black boxes represent peaks resulting from the $n=16$ all $trans$ conformer while peaks outlined in pink boxes represent peaks resulting from the $gauche$ defect. The peaks outlined in pink boxes were determined to be unique to the single $gauche$ defect because these peaks appear in all of the calculated spectra shown in these figures that contain a

![Figure 4.1](image-url)
gauche defect yet do not appear in the all trans spectra. Examining the physical vibrational modes, as previously explained in figure 1.3, of these peaks confirm this analysis; thus it is concluded that the gauche defect produces peaks in the Raman spectra at approximately 1136 cm$^{-1}$ and 1429 cm$^{-1}$.

Figure 4.2 The Raman spectra in the range of 800-1200 cm$^{-1}$ for n=16 structures containing a single g defect. For level of theory and legend notation, please see explanation provided in figure 4.1.
This method of analyzing the Raman spectra to identify unique peaks that are dependent on conformation has been performed on several of the unique conformers for $n=4-7$ that have been discussed so far. Additional spectra and results can be found in the supporting information. However, what is interesting to note about these results is that for other conformers containing gauche bonds separated by trans bonds, such as the gtg-conformer, the peak at around 1429 cm$^{-1}$ that is unique to a single gauche bond appear in the spectra for these conformers in addition to the unique peaks created by that conformer. This analysis on the gx-conformer shows that the gauche defect produces the previously mentioned 1429 cm$^{-1}$ peak and that the x-defect produces unique peaks at around 1313 cm$^{-1}$. However, it should be noted here that this peak relating to the x-defect is very low in intensity and will likely not appear in experimental Raman spectra, as conformers containing this defect as generally high in energy and have very low Boltzmann factors despite some conformers having high degeneracies.

Figure 4.3 The Raman spectra in the range of 1200-1600 cm$^{-1}$ for $n=16$ structures containing a single g defect. For level of theory and legend notation, see explanation provided in figure 4.1.
4.2 Scaling Factors

In order to use the calculated Raman spectra to begin examining the crystallization kinetic pathway of polyethylene, the calculated Raman spectra must be comparable to experimental spectra. The results of vibrational frequency calculations generally produce frequencies that are 10-15% higher when compared to the experimental values, which is why it is usually necessary to apply a scaling factor to the resulting frequencies.\(^{45}\) Due to the fact that the scaling factors present in the literature for the B3LYP functional did not provide a scaling factor for calculations obtained with the 6-31G(d,p) basis set, it was necessary to develop a scaling factor. The scaling factors in this section were developed using results obtained at the B3LYP/6-31G(d,p) level of theory, not the B3LYP+GD3/6-31G(d,p) level of theory. As illustrated in figure 4.4, which shows the Raman spectra for the all \textit{trans} conformer of the n=4 alkane, there is an insignificant difference between vibrational frequencies obtained at the B3LYP/6-31G(d,p) level of theory and vibrational frequencies obtained at the B3LYP+GD3/6-31G(d,p) level of theory.
To develop the scaling factor, vibrational frequency calculations for the all trans conformer of alkanes n=4-21 were performed. The results of these calculations included frequencies for both infrared (IR) and Raman spectra. These particular alkanes were chosen because both the symmetry and a description of the vibrational modes for the experimental IR and Raman spectra could be found in the literature. The calculated vibrational frequencies were then matched to the experimental frequencies based on the information provided in the literature. The scaling factor was then determined by equation 4.2,

$$sf = \frac{\sum_{i=1}^{N} (t\nu_i - e\nu_i)}{\sum_{i=1}^{N} (t\nu_i)^2}$$

where $sf$ is the scaling factor, $N$ is the total number of observed frequencies, $t\nu_i$ is the calculated frequency, and $e\nu_i$ is the experimental frequency from the literature. To

Figure 4.4 A comparison of the calculated Raman spectra for the all trans conformer of the n=4 alkane.
determine how well the scaled frequencies matched the experimental frequencies, the root-mean square (RMS) value was calculated, according to equation 4.3:

\[
RMS = \left( \frac{\sum_{i=1}^{N} (sf \times t \nu_i - e \nu_i)^2}{N} \right)^{\frac{1}{2}}
\] (4.3)

This value was calculated for all the alkanes used to determine the scaling factor; the lower the RMS, the better the scaling factor.

The first attempt at determining a scaling factor used 197 total major frequencies for alkanes n=4-21, including both IR and Raman frequencies. This first attempt resulted in a scaling factor of 0.971 with an RMS value of 20.1 cm\(^{-1}\). This large RMS value indicated that some calculated frequencies that were incorrectly matched with the corresponding experimental frequencies. Additionally, calculated frequencies below 500 cm\(^{-1}\) are generally lower than their corresponding experimental frequencies, which also contributed to this high RMS value. The second attempt at determining a scaling factor attempted to resolve these issues by making another attempt at matching calculated frequencies to experimental frequencies and by determining a scaling factor for two separate regions; one region containing frequencies 500 cm\(^{-1}\) and below and another region containing frequencies 500 cm\(^{-1}\) and above.

Determining two scaling factors for two separate regions resulted in a RMS value of 5.43 cm\(^{-1}\) for the region below 500 cm\(^{-1}\) and a value of 20.21 cm\(^{-1}\) for the region above 500 cm\(^{-1}\), indicating either that there were still problems with the assignments or two scaling factors were still not enough to reasonably match the calculated frequencies to the experimental frequencies. Breaking up the spectra into three regions (230-500 cm\(^{-1}\), 700-1099 cm\(^{-1}\), 1100-1600 cm\(^{-1}\)) resulted in RMS values of 5.43 cm\(^{-1}\), 17.90 cm\(^{-1}\), and 20.00 cm\(^{-1}\) for the three regions. The high RMS values for the last two regions are likely due to errors in analyzing the vibrational modes or errors in the experimental data, both of which would result in an incorrect matching between theoretical and experimental frequencies. Despite the fact that these RMS values are still high for all frequencies of alkanes n=4-21, these scaling factors were able to reasonably match calculated frequencies to experimental frequencies, as shown in figure 4.5, which is an experimental
Raman spectra for the all *trans* conformer of the n=21 alkane, collected by our collaborators under ambient lab conditions, compared to the calculated Raman spectra with the applied scaling factors of 1.02, 0.984, and 0.968 for the three regions. There are peaks present at around 1420 cm\(^{-1}\) in the experimental spectra that are not present in the calculated spectra; this is likely due to the experimental spectra having some amorphous bonds and not problems with the frequency calculations.

**4.3 Briefly Examining the Crystallization Kinetic Pathway**

As previously mentioned, there are five main peaks that are used when discussing the crystallization kinetic pathway of polyethylene. To briefly recap, these peaks are 1060 cm\(^{-1}\), 1129 cm\(^{-1}\), 1296 cm\(^{-1}\), 1304 cm\(^{-1}\), and 1415 cm\(^{-1}\), which refer to various stretching, bending, and twisting motions in both the solid stage and the melt stage of all alkanes.\(^{18}\) In order to accurately model the melt stage, it is necessary to consider that all possible conformers are present at this stage and have an impact on the Raman spectra. This was accomplished by weighting the calculated Raman intensity of each conformer with the Boltzmann factor for a given temperature, and then adding the activities for each
conformer to give one final, simulated spectrum at any temperature. The n=5 alkane will be used as an example for this discussion; the remaining alkanes n=4-6 and n=7 can be found in the supporting information. The scaling factors determined in the previous section were applied to all spectra in this section.

Figure 4.6 illustrates the calculated activities of the 1066, 1132, and 1236 cm\(^{-1}\) frequencies, which correspond to the 1060, 1129, and 1296 cm\(^{-1}\) experimental frequencies, respectively. As temperature increases, the calculated activities for all these frequencies decreases. The change in the calculated activities as a function of temperature is very small, however, this can be attributed to the fact that DFT calculations are performed on single molecules in the gas phase. These three frequencies correspond to the all trans conformer of alkanes, and their decrease in activity as temperature increases further validates the experimental observations that as temperature increases the all trans conformer is no longer the dominate conformer. Figure 4.7 shows the calculated activities...
of the 1456 cm\(^{-1}\) frequency, which corresponds to the 1415 cm\(^{-1}\) experimental frequency that comes from having two structural units in the orthorhombic crystal structure, as previously state in the introduction. As illustrated in figure 4.7, the activity of this frequency decreases as temperature increases, indicating that the orthorhombic crystal structure is lost as temperature increases. The decrease in the activity of this frequency also potentially indicates the presence of a rotator phase, which is this additional mesomorphic phase where the hexagonal crystal structure is present before the melt stage. Experimental observations also show that as temperature increases the polyethylene sample becomes dominated by amorphous bonds. Figure 4.8 shows the calculated activities of 1298 cm\(^{-1}\) frequency, which corresponds to the 1304 cm\(^{-1}\) frequency. This particular frequency is included in this analysis because it corresponds to

![Figure 4.7](image-url)
amorphous conformers. Indeed, figure 4.8 shows that as temperature increases, the calculated activity increases, again further validating the experimental observation that as temperature increases the polyethylene sample becomes dominated by amorphous bonds.

The activities of these frequencies were examined in order to attempt to calculate the mass fractions of the amorphous, *trans*, and NCCT conformers at any given temperature using the procedure determined by Migler et al.\textsuperscript{18} However, due to the fact that these calculations are for single molecules in the gas phase and the experimental work performed by Migler et al. involved samples of the n=21 alkane at various stages, such an analysis is not possible at this time. Presently, the discussion of the calculated activities for the five bands has been in terms of how the calculated frequencies correspond to the experimental frequencies, which are determined by examining the Raman spectra of physical polyethylene samples at various temperatures, as discussed in the introduction. As DFT calculations are performed on single molecules in the gas phase, there is no crystal structure to analyze, and there is no way to conclusively state at

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_8}
\caption{The calculated activities of the 1298 cm\textsuperscript{-1} frequency, which is the experimental 1304 cm\textsuperscript{-1} frequency for the n=5 alkane.}
\end{figure}
this time that the decrease in calculated activity for the 1456 cm⁻¹ calculated frequency relates to a loss of an orthorhombic crystal structure. This indicates that the rotator phase and formation of NCCT conformers is due to a type of intermolecular attraction effect; confirming this computationally would require calculations on several molecules.
5. Hairpin Structures

5.1 Definition of a Hairpin Structure and its Energetics

An interesting question that came up throughout this study is if an alkane chain is long enough, will the chain fold in such a way that it will essentially be bent in half at the middle of the chain? These structures, referred to as hairpins structures, were created by introducing a g-ttg+ttg- sequence at the center of symmetry for straight chain alkanes. An example of these defects is shown in figure 5.1 using the n=30 alkane.

![Figure 5.1 An example of a hairpin structure, created by introducing a g-ttg+ttg- sequence at the center of symmetry.](image)

In order to begin exploring the properties of these structures, geometry optimizations were first performed on alkanes n=10 to n=121 using the Forcite Module in Materials Studio 6.0.⁵⁵ These optimizations began with n=10 as this is the smallest alkane for which this hairpin structure can exist. The Forcite Module uses force fields and the principles of classical mechanics to perform calculations. For these initial calculations, the Universal force field was chosen; however, this choice of force field is arbitrary.⁵⁶-⁵⁸ The force fields included in the Forcite Module generally contain parameters that are suitable for modeling a wide range of compounds including anything from organic compounds, to organometallic compounds, and inorganic compounds containing transition metals. With all the calculations involving force fields, the Smart algorithm was used to perform the geometry optimizations with a step size of 0.015 Å. As can be seen in
figure 5.2, which shows the results of these geometry optimizations using three different force fields provided with the Forcite Module, the choice of force field makes very little difference.\textsuperscript{56-58}

The results in figure 5.2 were obtained by taking the difference between the energy of the hairpin structure and the energy of the all \textit{trans} structure. As can be shown in figure 5.2, these hairpin structures are very interesting at first glance. The smaller chains (n=10 to n=31) show that the energy difference between the hairpin structure and the all \textit{trans} structure is positive, meaning that the all \textit{trans} structure is lower in energy and is the preferred conformer; something that was to be expected with these structures. However, upon reaching n=32,33,34, for the Universal, Dreiding, and Compass forcefields respectively, the energy difference between the hairpin structure and the all \textit{trans} structure becomes negative, indicating that the hairpin structure is actually preferred.
past a certain chain length. Additionally, the chain length at which this conversion happens was also unexpected; it was expected that this conversion would happen at chain lengths of at least \( n=100 \) when the alkane chain would be long enough to fold upon itself.

These results obtained with the forcefield optimizations are indeed confirmed by performing geometry optimizations using the B3LYP+GD3/6-31G(d,p) level of theory, as shown in figure 5.3. A possible explanation for this conversion is how the structure changes upon optimization as chain length increases. Before continuing this discussion, briefly refer to figure 5.4 which illustrates a hairpin structure labeled according to terminology that will be used in the remainder of this discussion. Figure 5.5 shows a...
comparison of a hairpin structure before any optimization calculations have been performed, a hairpin structure before the conversion happens, and a hairpin structure after the conversion happens. For structures that contain \( n < 30 \) carbons, the arms of these particular hairpin structures move farther away from each other. This motion corresponds to an average distance of 6.49 Å before optimization and an average distance of 11.74 Å after optimization for optimizations performed at the B3LYP+GD3/6-31G(d,p) level of theory. For hairpin structures containing \( n \geq 30 \) carbons, where \( n=30 \) is the point at which this conversion happens, the arms of the hairpin structure actually begin to cross over each other; the average distance goes from 6.49 Å before optimization to 4.62 Å after optimization at the B3LYP+GD3/6-31G(d,p) level of theory. These differences

**Figure 5.4** An example of a hairpin structure, labeled accordingly to terminology that will be used in the remainder of the hairpin structure discussion.

**Figure 5.5** Examples of hairpin structures where a) is \( n=25 \) before geometry optimization, b) is \( n=25 \) after geometry optimization and c) is \( n=32 \) after geometry optimization.
could be explained by examining the deviations from ideal geometry for these hairpin structures upon optimization, as shown in figure 5.6. This figure shows that before this conversion happens, there is some deviation from the ideal geometry, an average of about 4.0°, at all three gauche angles, yet after this conversion happens this deviation increases to an average 9.89°, 5.39°, and 11.91° for the g1, g2, and g3 angles, respectively. These deviations indicate that in order for this conversion to happen, the angles making up the actual hairpin must break in some way. What is also interesting to note is that after this conversion happens, there is an even/odd effect with both the energetics and the deviations from the ideal geometry.

Figure 5.6 The deviations from the ideal geometries of the three gauche angles that create the hairpin structure upon geometry optimization.
5.2 The Raman Spectra of Hairpin Structures

The Raman spectra of these hairpin structures were also examined to determine if these hairpin structures had any unique spectral features. This analysis is similar to the analysis used for determining unique spectra features from different conformers discussed in section 4.4. For this particular peak determination, the gttg- sequence was used. The results of this analysis are shown in figures 5.7, 5.8, and 5.9, where figure 5.7 is the full Raman spectra and figure 5.8 and 5.9 are close ups in the ranges 800-1200 cm\(^{-1}\) and 1200-1600 cm\(^{-1}\), respectively. In these figures, the peaks outlined in black represent peaks that are common to the \(n=16\) alkane, as these peaks appear in both the all \textit{trans} conformer and the conformers containing the gttg- sequence. The peaks outlined in pink represent the 1429 cm\(^{-1}\) peak that is unique to the single gauche defect. Finally the peaks outlined in purple represent peaks at around 1102 cm\(^{-1}\) and 1364 cm\(^{-1}\) that are potentially

![Figure 5.7](image_url)

**Figure 5.7** The Raman spectra for the \(n=16\) all \textit{trans} conformer as well as conformers containing gttg- sequences. The number next to gttg- in the legend indicates the torsion angle at which the defect is placed.
Figure 5.8 The Raman spectra in the range of 800-1200 cm$^{-1}$ for the n=16 all \textit{trans} conformer as well as conformers containing \textit{gttg}- sequences. See figure 5.7 for legend notation.
Additionally there may be a weak shoulder at 1490 cm$^{-1}$ that may also be unique to the hairpin structures. In order to fully determine if these peaks are in fact unique to the hairpin structures, a comparison was made between the Raman spectra for the n=35 trans conformer and the n=35 hairpin structure. This comparison is shown in figure 5.10, which shows the Raman spectra in the range of 800 cm$^{-1}$ to 1600 cm$^{-1}$. The black boxes in this figure indicate the unique peaks found in the gttg- analysis, as well as the 1429 cm$^{-1}$ peak from the single gauche defect. As illustrated in the figure, the two peaks identified as being unique to the hairpin structure are present in the n=35 hairpin structure and absent in the n=35 trans structure. This comparison also shows several additional peaks present in the n=35 hairpin structure that are absent in the trans structure, however more work would need to be done to determine if these peaks are unique to all hairpin structures or just the n=35 hairpin structure.

Figure 5.9 The Raman spectra in the range of 1200-1600 cm$^{-1}$ for the n=16 all trans conformer and conformers containing gttg- sequences. For legend notation refer to figure 5.7.
Another interesting question that arose when studying these hairpin structures is do these structures pack like regular straight chain alkanes? In examining the crystal structures for straight chain alkanes found in the Cambridge Structural Database, it was found that a majority of the alkanes, with a few exceptions, pack in the trigonal P-1 space group. For comparison purposes, the crystal structure for n=16 alkane was chosen because it not only had the lowest r-factor, but contained all the hydrogens and had no disordered atoms. The hairpin structure for the n=37 alkane was also chosen for comparison purposes, because if the bonds creating the actual hairpin turn are removed, the two remaining arms for the n=37 structure each have 16 carbons.

In order to answer this question, the Polymorph Predictor module in Materials Studio was used. The Polymorph Predictor module allows for the crystal structures of organic and organometallic compounds to be predicted. This module works by going through a set of four processes. The first process is using a Monte-Carlo simulated...
annealing algorithm to search the potential energy surface for possible crystal structures, which has the potential to generate thousands of possible structures. The next process is a clustering step that organizes the predicted structures into groups based on how similar the predicted structures are. The geometries of each structure are then optimized using the chosen force field; a final clustering step then removes duplicates and orders the structures based on lattice energy. If predicting the structure of an already known compound, the success of the generated predictions can be measured by comparing the predicted structures to the known crystal structure, and the powder patterns of the predicted structures to the powder patterns of the known structures.

The first and most important step in generating these crystal structures is determining a suitable method for this process. A suitable method here means choosing an appropriate force field, and deciding whether or not to optimize the structure using classical mechanical or quantum mechanical methods. For these tests, the n=16 alkane was used, since it’s crystal structure is well documented in the Cambridge Structural Database (ref code QQQFBP01). The force fields Dreiding, Universal, and Compass were each tested under the conditions of not optimizing the structure at all before polymorph calculations, optimizing the structure using the Forcite Module, and optimizing the structure using the Dmol3 Module, which uses quantum mechanical methods. For optimizations with the Forcite Module, the Smart algorithm with a displacement of 0.015 Å was used for all calculations involving this module. For all optimizations with Dmol3, the B3LYP level of theory was used with the double numerical polarization plane wave basis set. Additionally, a step size of 0.005 Å was used for the optimizations along with a k-point set of 1x1x1. All Polymorph Prediction calculations used an Ewald summation method for the electrostatics and van der Waals forces.

For all Polymorph Prediction calculations involved in this testing, only the P-1 space group was used, as this is the space group of the n=16 structure in the Cambridge Structural Database. To measure the success of these predictions, crystal similarity measurements were generated for each result. The crystal similarity measurements are based on interatomic distances and acts as a sort of root-mean square value, where the
lower the result, the better the match to the experimental structure. Out of all these predicted structures for the test scenarios mentioned above, calculations performed with the Dreiding force field produced the lowest crystal similarity measurements. The predicted structures that were not optimized before polymorph calculations produced a crystal similarity measurement of 0.137, while the predicted structures optimized with the Forcite and Dmol3 modules produced values of 0.139 and 0.147, respectively. The tests with the Universal and Compass force fields produced values around 1.744 or higher, indicating that the Drieding force field was the best choice for these particular calculations. In order to confirm this choice, the powder patterns of the predicted structures were compared to the power pattern of the experimental structure. Rietveld refinements were performed on the predicted structures in order to generate a comparable powder pattern; these refinements also produced a similarity measurement between the experimental powder pattern and the predicted structure powder pattern. This pattern also acts like a root mean square value, where the lower the value the better the match. The refinement on the non-optimizated structure produced a similarity measurement value of 81%, which is a little high, but still indicated that using the Dreiding force field for Polymorph Prediction calculations without optimizing the structure beforehand would be a suitable method for determining the crystal structure of these hairpins.

The n=37 hairpin structure was first optimized at the B3LYP+GD3/6-31G(d,p) level of theory in order to obtain a hairpin structure where the arms were crossed over each other. The Polymorph Prediction Module was then employed to generate crystal structures, using the Dreiding force field and the same additional parameters used in the testing. As the optimized hairpin structure has C\textsubscript{1} symmetry, the assumption was made that structures predicted in the P-1 space group would be the lowest energy structures and would thus be close to any experimental structure that may exist. This space group was also chosen because the assumption was made that these hairpin structures do in fact pack like alkanes. However, just to confirm that the P-1 space group would in fact produce the lowest energy conformers, calculations were also performed using the P1, P2, P2\textsubscript{1}, and C2 space groups.
The results of these calculations generated a total of 2,285 possible conformers. The results for the five lowest energy conformers are shown in table 5.1. As illustrated in

Table 5.1 The five lowest energy conformers resulting from the Polymorph Prediction on the n=37 hairpin structure.

<table>
<thead>
<tr>
<th>Conformer Number</th>
<th>1</th>
<th>2</th>
<th>1</th>
<th>3</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>P-1</td>
<td>P-1</td>
<td>P1</td>
<td>P-1</td>
<td>P1</td>
</tr>
<tr>
<td>Total Energy (kcal/mol)</td>
<td>4.0130</td>
<td>4.0222</td>
<td>4.0763</td>
<td>4.0764</td>
<td>4.0780</td>
</tr>
<tr>
<td>a (Å)</td>
<td>24.78</td>
<td>29.13</td>
<td>4.48</td>
<td>26.38</td>
<td>10.08</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.88</td>
<td>5.61</td>
<td>22.41</td>
<td>6.58</td>
<td>26.05</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.73</td>
<td>19.07</td>
<td>10.08</td>
<td>11.89</td>
<td>4.48</td>
</tr>
<tr>
<td>α (°)</td>
<td>61.49</td>
<td>81.60</td>
<td>93.31</td>
<td>97.71</td>
<td>56.78</td>
</tr>
<tr>
<td>β (°)</td>
<td>79.96</td>
<td>121.10</td>
<td>106.18</td>
<td>71.95</td>
<td>73.87</td>
</tr>
<tr>
<td>γ (°)</td>
<td>67.15</td>
<td>131.43</td>
<td>76.26</td>
<td>100.43</td>
<td>81.73</td>
</tr>
</tbody>
</table>

the table, three out of the five lowest energy structures pack in the P-1 space group. The table also illustrates that the most likely crystal structure, shown in figure 5.11 for this hairpin is, of the P-1 space group, validating the assumption above. This lowest energy

![Figure 5.11](image-url) The lowest energy predicted structure for the n=37 hairpin structure using the Polymorph Predictor Module in Materials Studio. For unit cell dimensions, refer to table 5.1.
structure was compared to the experimental n=16 alkane using the overlay and crystal similarity features in Materials Studio. The results of these measurements are illustrated in figure 5.12. Because the arms of the n=37 hairpin structure each contain 16 carbons, efforts were made to match the arms of the hairpin structure with the straight chain alkanes in the experimental structure as much as possible. As illustrated in the figure, there is a poor match between the predicted hairpin structure and the experimental n=16 structure. This indicates that despite the fact that the predicted hairpin structure and the experimental structure pack in the same space group, there are several differences between their packings.

Figure 5.12 The results of the overlay between the experimental n=16 crystal structure (black) and the lowest energy predicted structure for the n=37 hairpin. The unit cells dimensions for the n=16 structure are a=4.27 Å, b=4.81 Å, c=22.35 Å, α=84.54°, β=67.43°, and γ=72.99°.

These differences in packing arise from several factors, one of which could be the cell dimensions of the crystal structures. Having to account for the carbons necessary to create the hairpin leads to an increase in cell dimensions when compared to the experimental structure, as illustrated in figure 5.12. The differences in packing can also be related to the fact that the arms of the hairpin structures after this conversion are not straight, as shown in figure 5.13, which compares the hairpin structure to the n=16 alkane with a space filling model. This figure illustrates that there is an obvious curvature in the
hairpin structures, which can affect packing. What is also interesting to note about the energy of this structure is that it a positive value of 4.01 kcal/mol, and the van der Waals energy is lower at -14.88 kcal/mol. This trend is also observed for the predicted structure of the n=16 alkane, which has an energy of -7.47 kcal/mol and a van der Waals energy of -12.73 kcal/mol. These energies for the predicted crystal structure of the hairpin so far indicate that these structures are not likely to be found experimentally. A more intensive, accurate investigate of how these hairpin structures pack will be necessary to determine at what chain length it is possible to crystallize these structures and under what experimental conditions.

Figure 5.13 The space filling models of a) the n=16 experimental structure and b) the lowest energy predicted n=37 hairpin structure.
6. Conclusions and Future Work

The B3LYP+GD3/6-31G(d,p) level of theory has shown to be an appropriate method for modeling these systems, as it was consistently able to predict conformer energies close to those predicted by high level calculations. In the future, when moving on to larger systems that have more torsion angles, it may be worth investigating if there is another model chemistry that still models the conformer energies appropriately, yet would have smaller deviations from the ideal geometry upon optimization.

The quantum mechanical calculations of the Raman spectra involved in this thesis have so far shown that, at least computationally, Raman spectroscopy is in fact a suitable technique for investigating the crystallization kinetic pathway of polyethylene. This is shown through the analysis of the Raman spectra for the individual conformers studied throughout this thesis, as peaks unique to these conformers could be identified in the Raman spectrum. More work will need to be done, such as performing this analysis with additional alkanes, to determine if these peaks are in fact unique to these conformers or if there is some other reason for their appearance in the spectra. Additionally, an important aspect to the future work will involve creating a procedure for computationally determining the mass fractions of the crystalline, amorphous, and NCCT conformers. With the use of Materials Studio, it may be possible to perform calculations on the crystal structures of alkanes that crystallize in an orthorhombic unit cell, which would allow for any intermolecular effects to be observed. These calculations would have to involve accurate geometry optimizations and accurate predictions of the Raman spectra as a function of temperature. The unit cell of the alkane would also have to change as a function of temperature, in order for this rotator phase to be characterized computationally. Determining such a procedure will allow for a greater insight into the crystallization kinetic pathway of polyethylene by showing how important these NCCT conformers are throughout this pathway. Examining the calculated intensities for the 1060 cm\(^{-1}\), 1129 cm\(^{-1}\), 1304 cm\(^{-1}\), and 1415 cm\(^{-1}\) experimental peaks as a function of temperature so far validate some aspects of the proposed three stage model for the crystallization kinetic pathway, though further analysis will be necessary to fully
characterize this model. It may be necessary to examine the intensities as a function of
temperature, or chain length, in any future analysis.

An extensive literature search will also be performed in the future to see if these
hairpin structures exist experimentally. Presently, no crystal structure containing a hairpin
structure has been found in the literature. It is possible that these structures are more
likely to be found in papers that contain surface imaging techniques as part of an analysis
for polyethylene fibers. It may be more likely that these structures are found in fibers that
are so long they tangle compared to trying to crystallize these structures. Performing high
level calculations on a few select hairpin structures, such as structures right before the
conversion, at the conversion, and after the conversion, in order to give a more precise
insight as to why there is a conversion at all. It would be interesting to see if high level
calculations show the same high deviations from ideal geometry upon optimization for
structures after the conversion; this would help to determine if these deviations do in fact
play a roll in the conversion. Additionally, future work for these hairpin structures would
also involve more accurate crystal structure predictions, which would give some insight
as to whether it is actually possible or not to crystallize these structures.
Appendix: Supporting Information

A.1 Supporting Information for Chapter 2. The Model Systems and Their Energetics

All results in this section were obtained using various density functional theories with the 6-31G(d,p) basis set.

Figure A1.1 The deviations from ideal geometry for the remaining conformers of the n=6 alkane. The average deviation from the ideal geometry for all conformers is 3.16°. Geometry optimizations performed with B3LYP.
Figure A1.2 The deviations from the ideal geometry for the remaining $n=7$ conformers. The average deviation for all conformers above is 3.16°. Geometry optimizations performed with B3LYP.
Figure A1.3 The deviations from ideal geometry for the n=5 lowest energy conformers. The average deviation for all conformers is 3.25°. Geometry optimizations calculated with M06-2x.
Figure A1.4 The deviations from ideal geometry for the remaining n=6 conformers. The average deviation for all conformers above is 2.94°. Geometry optimizations performed with M06-2x.
Figure A1.5 Deviations from the ideal geometries for the remaining $n=7$ conformers. The average deviation for all conformers above is 3.86°. Geometry optimizations calculated with M06-2x.
Figure A1.6 The order of the low energy conformers according to energy for the n=6 alkane. Geometry optimizations performed with APFD.
Figure A1.7 The deviations from ideal geometry for the n=5 alkane. The average deviation is 2.17°. Results obtained with B3LYP+PFD.

Figure A1.8 The deviations from the ideal geometry for the remaining n=6 conformers. The average deviation is 3.01°. Geometry optimizations performed with B3LYP+PFD.
Figure A1.9 Deviations from the ideal geometry for the n=5 alkane. The average value for these conformers is 2.13°. Results obtained with B3LYP+GD3.
Figure A1.10 The deviation from ideal geometry for the remaining n=6 conformers. Average deviation: 2.73°. Results obtained with B3LYP+GD3.
Figure A1.11 The deviations from ideal geometry for five $n=7$ conformers. Results obtained with B3LYP+GD3.

Figure A1.12 Deviations from ideal geometry for five $n=7$ conformers. Results obtained with B3LYP+GD3.
Figure A1.13 Deviations from ideal geometries for five \( n=7 \) conformers. Results obtained with B3LYP+GD3.

Figure A1.14 Deviations from the ideal geometry for five \( n=7 \) conformers. Geometry optimizations performed with B3LYP+GD3.
Figure A1.15 The deviations from ideal geometry for five n=7 conformers with results obtained using B3LYP+GD3.

Figure A1.16 Deviations from ideal geometry for three n=7 conformers. The average deviation for all conformers in figures A1.11-A1.16 is 3.25°. Geometry optimizations performed with B3LYP+GD3.
Figure A1.17 The error values for the gx- defect moving throughout select alkanes. Geometry optimizations calculated with B3LYP+GD3. Average value: 2.46 kcal/mol.

Figure A1.18 The error values for the gtg defect for select alkanes. Average value: 1.06 kcal/mol. Geometry optimizations with B3LYP+GD3.
**Figure A1.19** The error values for the gtg- defect moving throughout select alkanes. Average value: 1.22 kcal/mol. Results obtained with B3LYP+GD3.

**Figure A1.20** The error values for the gx-g- defect moving throughout select alkanes. Average value: 3.02 kcal/mol. Calculations with B3LYP+GD3.
Figure A1.21 Error values for the xg-g- defect moving through select alkanes. Average value: 2.43 kcal/mol. Calculations with B3LYP+GD3.

Figure A1.22 The error values for the xg-x defect moving throughout select alkanes. Average value: 3.55 kcal/mol. Results with B3LYP+GD3.
Figure A1.23 The error values for the gttg defect. Average value: 1.06 kcal/mol. Results obtained with B3LYP+GD3.

Figure A1.24 The error values for the gttg- defects. Average value: 1.04 kcal/mol. Results obtained with B3LYP+GD3.
Figure A1.25 Error values for the gtgg defect. Average value: 1.15 kcal/mol. Results obtained with B3LYP+GD3.

Figure A1.26 The error values for the gtg-g defect. Average value: 1.43 kcal/mol. Results obtained with B3LYP+GD3.
Figure A1.27 Error values for the gggg defect. Average value: 1.29 kcal/mol. Results obtained with B3LYP+GD3.

Figure A1.28 Error values for the tggx- defect. Average value: 2.34 kcal/mol. Results obtained with B3LYP+GD3.
Figure A1.29 Error values for the txg-g- defect. Average value: 2.35 kcal/mol. Results with B3LYP+GD3.

Figure A1.30 The error values for the gtxg- defect. Average value: 2.80 kcal/mol. Results obtained with B3LYP+GD3.
Figure A1.31 Error values for the gtgx- defect. Average value: 2.94 kcal/mol. Results with B3LYP+GD3.

Figure A1.32 The error values for the gtx-g defect. Average value: 3.01 kcal/mol. Results obtained with B3LYP+GD3.
Figure A1.33 The error values for the tgxg- defect. Average value: 2.98 kcal/mol. Results obtained with B3LYP+GD3.

Figure A1.34 The error values for the gggx- defects. Average value: 2.87 kcal/mol. Results obtained with B3LYP+GD3.
Figure A1.35 The error values for the ggx-g- defect. Average value: 2.26 kcal/mol. Results obtained with B3LYP+GD3.

Figure A1.36 The error values for the gx-x-g defect. Average value: 4.45 kcal/mol. Results obtained with B3LYP+GD3.
Figure A1.37 The error values for the gxg-x defect. Average value: 4.66 kcal/mol. Results obtained with B3LYP+GD3.

Figure A1.38 The error values for the xg-g-x defect. Average value: 5.13 kcal/mol. Results obtained with B3LYP+GD3.
A2. Supporting Information for Chapter 3. Thermodynamics

All calculations in this section were performed at the B3LYP+GD3/6-31G(d,p) level of theory.

Figure A2.1 The ΔG for the gauche conformer of the n=4 alkane as a function of temperature.
Figure A2.2 The Boltzmann factors for the trans and gauche conformers of the n=4 alkane as a function of temperature.

Figure A2.3 The Boltzmann factors as a function of temperature for the trans conformer of the n=5 alkane. Degeneracy = 1.
Figure A2.4 The $\Delta G$ as a function of temperature for the tg conformer of the n=5 alkane.

Figure A2.5 The Boltzmann factor for the tg conformer of the n=5 alkane as a function of temperature. Degeneracy = 4.
Figure A2.6 The $\Delta G$ as a function of temperature for the gg conformer of the n=5 alkane.

Figure A2.7 The Boltzmann factor as a function of temperature for the gg conformer of the n=5 alkane. Degeneracy = 2.
Figure A2.8 The $\Delta G$ as a function of temperature for the gx- conformer of the n=5 alkane.

Figure A2.9 The Boltzmann factor for the gx- conformer of the n=5 alkane as a function of temperature. Degeneracy = 2.
Figure A2.10 The Boltzmann factors as a function of temperature for the all \textit{trans} conformer of the n=6 alkane. Degeneracy = 1.

Figure A2.11 The $\Delta G$ as a factor as temperature for the ttg conformer of the n=6 alkane.
Figure A2.12 The Boltzmann factors as a function of temperature for the ttg conformer of the n=6 alkane. Degeneracy = 4.

Figure A2.13 The $\Delta G$ for the tgt conformer of the n=6 alkane as a function of temperature.
Figure A2.14 The ∆G for the tgg conformer of the n=6 alkane as a function of temperature.

Figure A2.15 The Boltzmann factors for the tgt (degeneracy = 2) and tgg (degeneracy = 4) for the n=6 alkane as a function of temperature.
Figure A2.16 The $\Delta G$ as a function of temperature for the gtg conformer of the n=6 alkane.

Figure A2.17 The Boltzmann factor as a function of temperature for the gtg conformer of the n=6 alkane, where degeneracy = 2.
Figure A2.18 The ΔG for the gtg- conformation of the n=6 alkane as a function of temperature.

Figure A2.19 The Boltzmann factor as a function of temperature for the gtg-conformer of the n=6 alkane, where degeneracy = 2.
Figure A2.20 The $\Delta G$ as a function of temperature for the all gauche conformer of the \( n=6 \) alkane.

Figure A2.21 The Boltzmann factor as a function of temperature for the all gauche conformer of the \( n=6 \) alkane, where degeneracy = 4.
Figure A2.22 The $\Delta G$ as a function of temperature for the gx-t and tgx- conformers of the n=6 alkane.

Figure A2.23 The Boltzmann factors as a function of temperature for the gx-t and tgx-conformers of the n=6 alkane. The degeneracy for both conformers is 4.
Figure A2.24 The ΔG as a function of temperature for the gx-g- and xg-g-conformers for the n=6 alkane.

Figure A2.25 The Boltzmann factors as a function of temperature for the gx-g- and xg-g-conformers of the n=6 alkane. For both conformers, the degeneracy is equal to 4.
Figure A2.26 The $\Delta G$ as a function of temperature for the $xg$-$x$ conformer of the $n=6$ alkane.

Figure A2.27 The Boltzmann factor as a function of temperature for the $xg$-$x$ conformer of the $n=6$ alkane, for which degeneracy is equal to 4.
Figure A2.28 The Boltzmann factor as a function of temperature for the all *trans* conformer of the n=7 alkane.

Figure A2.29 The ΔG as a function of temperature for the ttgt conformer of the n=7 alkane.
Figure A2.30 The Boltzmann factor as a function of temperature for the ttgt conformer of the n=7 alkane. For this conformer, degeneracy is equal to 4.

Figure A2.31 The $\Delta G$ as a function of temperature for the ttgg conformer of the n=7 alkane.
Figure A2.32 The Boltzmann factor as a function of temperature for the ttgg conformer of the n=7 alkane. For this conformer, degeneracy is equal to 4.

Figure A2.33 The ΔG as a factor of temperature for the tgtg conformer of the n=7 alkane.
Figure A2.34 The Boltzmann factor as a function of temperature for the tgtg conformer of the n=7 alkane. For this conformer, degeneracy is equal to 4.

Figure A2.35 The ΔG as a function of temperature for the gttg conformer of the n=7 alkane.
Figure A2.36 The Boltzmann factor as a function of temperature for the gttg conformer of the $n=7$ alkane. For this conformer, degeneracy is equal to 2.

Figure A2.37 The $\Delta G$ as a function of temperature for the gttg- conformer of the $n=7$ alkane.
Figure A2.38 The Boltzmann factor as a function of temperature for the gttg-conformer of the n=7 alkane. For this conformer, the degeneracy is equal to 2.

Figure A2.39 The $\Delta G$ as a function of temperature for the tgtg- conformer of the n=7 alkane.
Figure A2.40 The Boltzmann factor as a function of temperature for the tgtg-conformer of the n=7 alkane. For this conformer, degeneracy is equal to 4.

Figure A2.41 The $\Delta G$ as a function of temperature for the tggg conformer of the n=7 alkane.
Figure A2.42 The Boltzmann factor as a function of temperature for the tggg conformer of the n=7 alkane. For this conformer, degeneracy is equal to 4.

Figure A2.43 The ∆G as a function of temperature for the gtgg and gtg-g- conformers of the n=7 alkane.
Figure A2.44 The Boltzmann Factor as a function of temperature for the gtgg conformer of the n=7 alkane. For this conformer, degeneracy is equal to 4.

Figure A2.45 The Boltzmann factor as a function of temperature for the gtg-g-conformer of the n=7 alkane. For this conformer, degeneracy is equal to 2.
Figure A2.46 The $\Delta G$ as a function of temperature for the all gauche conformer of the n=7 alkane.

Figure A2.47 The Boltzmann factor as a function of temperature for the all gauche conformer of the n=7 alkane. For this conformer, degeneracy is equal to 4.
Figure A2.48 The $\Delta G$ as a function of temperature for the ttx-g, ttg-x, and tgx-t conformers of the $n=7$ alkane.

Figure A2.49 The Boltzmann factors as a function of temperature for the ttx-g, ttg-x, and tgx-t conformers of the $n=7$ alkane. The degeneracy for all conformers is 4.
Figure A2.50 The $\Delta G$ as a function of temperature for the txg-g- conformer of the n=7 alkane.

Figure A2.51 The Boltzmann factor as a function of temperature for the txg-g- conformer of the n=7 alkane, where degeneracy is equal to 4.
Figure A2.52 The ∆G as a function of temperature for the tggx- and gtx-g conformers of the n=7 alkane.

Figure A2.53 The Boltzmann factors as a function of temperature for the tggx- and gtx-g conformers of the n=7 alkane. For both conformers the degeneracy is 4.
Figure A2.54 The $\Delta G$ as a function of temperature for the gtxg- and gtgx-conformers of the $n=7$ alkane.

Figure A2.55 The Boltzmann factor as a function of temperature for the gtxg- conformer of the $n=7$ alkane. The degeneracy for this conformer is 4.
Figure A2.56 The Boltzmann factor as a function of temperature for the gtgx-conformer of the n=7 alkane. The degeneracy for this conformer is 8.

Figure A2.57 The ΔG as a function of temperature for the tgxg- conformer of the n=7 alkane.
Figure A2.58 The Boltzmann factor as a function of temperature for the tgxg-conformer for which the degeneracy is 8.

Figure A2.59 The ΔG as a function of temperature for the tgx-g-conformer of the n=7 alkane.
Figure A2.60 The Boltzmann factor as a function of temperature for the tgx-g-conformer where the degeneracy is 4.

Figure A2.61 The $\Delta G$ as a function of temperature for the gggx- conformer of the $n=7$ alkane.
Figure A2.62 The Boltzmann factor as a function of temperature for the gggx-conformer, for which the degeneracy is 4.

Figure A2.63 The $\Delta G$ as a function of temperature for the ggx-g- conformer of the n=7 alkane.
Figure A2.64 The Boltzmann factor as a function of temperature for the ggx-g-conformer where the degeneracy is 4.

Figure A2.65 The ΔG as a function of temperature for the txg-x conformer of the n=7 alkane.
Figure A2.66 The Boltzmann factor as a function of temperature for the txg-x conformer, for which the degeneracy is 2.

Figure A2.67 The $\Delta G$ as a function of temperature for the gx-x-g, gxg-x, and xg-g-x conformers of the $n=7$ alkane.
Figure A2.68 The Boltzmann factors as a function of temperature for the gx-x-g, gxg-x, and xg-g-x conformers. The degeneracy for the gx-x-g and gxg-x conformers is 4 and the degeneracy for the xg-g-x conformer is 2.
A3. Supporting Information for Chapter 4. The Raman Spectra

All calculations in this section were performed with the B3LYP/6-31G(d,p) level of theory.

Figure A3.1 The Raman spectra in the range of 0-1600 cm\(^{-1}\) for \(n=16\) structures containing a single \(gx\)- defect. The notation \(gx\)- \(X\) indicates the number of the trans bond at which the defect is placed. No scaling factors have been applied.
Figure A3.2 The Raman spectra in the range of 800-1200 cm$^{-1}$ for n=16 structures containing a gx-defect. Black boxes indicate peaks common to all spectra. For legend notation see figure A3.1.
Figure A3.3 The Raman spectra in the range of 1200 cm\(^{-1}\) to 1600 cm\(^{-1}\) for \(n=16\) structures containing a gx- defect. Black boxes indicate peaks common to all spectra, pink boxes indicate peaks coming from a g defect, and green boxes indicate peaks coming from a x- defect.
Figure A3.4 The Raman spectra in the range of 0-1600 cm\(^{-1}\) for the \(n=16\) structures containing a gtg-defect. No scaling factors have been applied. For legend notation refer to figure A3.1.

Figure A3.5 The Raman spectra in the range of 800-1200 cm\(^{-1}\) for the \(n=16\) structures containing a gtg-defect. No scaling factors have been applied. Black boxes indicate peaks common to all structures. For legend notation refer to figure A3.1.
Figure A3.6 The Raman spectra in the range of 1200-1600 cm$^{-1}$ for the n=16 structures containing a gtg- defect. No scaling factors have been applied. Black boxes indicate peaks common to all structures, pink boxes indicate peaks unique to the g defect, and blue boxes indicate peaks unique to the gtg- defect. For legend notation refer to figure A3.1.
Figure A3.7 The calculated Raman activity as a function of temperature for the 1054.8 cm\(^{-1}\) peak of the n=4 alkane, which corresponds to the 1060 cm\(^{-1}\) experimental frequency. Scaling factors applied.
Figure A3.8 The calculated Raman activity as a function of temperature for the 1139 cm\(^{-1}\) peak of the n=4 alkane, which corresponds to the 1129 cm\(^{-1}\) experimental frequency. Scaling factors applied.

Figure A3.9 The calculated Raman activity as a function of temperature for the 1298.6 cm\(^{-1}\) peak of the n=4 alkane, which corresponds to the 1296 cm\(^{-1}\) experimental frequency. Scaling factors applied.
Figure A3.10 The calculated Raman activity as a function of temperature for the 1286.7 cm$^{-1}$ peak of the n=4 alkane, which corresponds to the 1304 cm$^{-1}$ experimental frequency. Scaling factors applied.

Figure A3.11 The calculated Raman activity as a function of temperature for the 1455.9 cm$^{-1}$ peak of the n=4 alkane, which corresponds to the 1415 cm$^{-1}$ experimental frequency. Scaling factors applied.
Figure A3.12 The calculated Raman activity as a function of temperature for the 1060.7 and 1126.7 cm\(^{-1}\) peaks of the \(n=6\) alkane, which correspond to the 1060 and 1129 cm\(^{-1}\) experimental frequencies, respectively. Scaling factors applied.

Figure A3.13 The calculated Raman activity as a function of temperature for the 1304.8 cm\(^{-1}\) peak of the \(n=6\) alkane, which corresponds to the 1296 cm\(^{-1}\) experimental frequency. Scaling factors applied.
Figure A3.14 The calculated Raman activity as a function of temperature for the 1307.3 cm\(^{-1}\) peak of the n=6 alkane, which corresponds to the 1304 cm\(^{-1}\) experimental frequency. Scaling factors applied.

Figure A3.15 The calculated Raman activity as a function of temperature for the 1458.3 cm\(^{-1}\) peak of the n=6 alkane, which corresponds to the 1415 cm\(^{-1}\) experimental frequency. Scaling factors applied.
Figure A3.16 The calculated Raman activity as a function of temperature for the 1053.4 and 1125.8 cm\(^{-1}\) peaks of the n=7 alkane, which corresponds to the 1060 and 1129 cm\(^{-1}\) experimental frequencies, respectively. Scaling factors applied.

Figure A3.17 The calculated Raman activity as a function of temperature for the 1294.2 cm\(^{-1}\) peak of the n=7 alkane, which corresponds to the 1296 cm\(^{-1}\) experimental frequency. Scaling factors applied.
Figure A3.18 The calculated Raman activity as a function of temperature for the 1302.9 cm$^{-1}$ peak of the $n=7$ alkane, which corresponds to the 1304 cm$^{-1}$ experimental frequency. Scaling factors applied.
Figure A3.19 The calculated Raman activity as a function of temperature for the 1457.8 cm\(^{-1}\) peak of the n=7 alkane, which corresponds to the 1415 cm\(^{-1}\) experimental frequency. Scaling factors applied.
References


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