

VIBRATION STUDY OF THE CHAIN CONFORMATION OF THE n-NONANE WITH ONE GAUCHE CONFORMATION

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Abstract

Ab initio calculations were used to calculate normal mode frequencies and intensities of four stable conformations of n-nonane including all-trans and other three conformations with one gauche. The overall frequency region including IR and Raman spectra was analyzed to get the full spectra information of n-nonane, and to explore the relation between frequency and disorder in the overall frequency region. The bands in the IR spectra and in the Raman spectra were found to be associated with specific conformations, and therefore the character bands of each conformation could be obtained. For the bands with the same vibration modes, the trend with the change of conformation was also discussed which played an important role in the experiments.

Key words: ab initio; vibration spectroscopy; conformation; n-nonane

Introduction

The polymethylene (PM) chain, principal organizing constituent, plays an important role in a variety of synthetic and natural systems. Consequently, the study of conformational properties of chain molecules such as polymethylene had been the focus of considerable attention. Vibration spectroscopy, due to the ability to measure conformation, had been widely used to characterize long chain molecules. A major contribution to the analysis of vibration spectra, in particular the conformational dependence for alkanes and polyethylene, was presented by Snyder and Schachtschneider with the empirically refined force fields.¹⁻³ But such force fields cannot provide detailed insights into the conformation dependence of force constants and spectra. It was therefore very important to have more complete understanding of these properties that could be given by ab initio calculations.⁴⁻⁷ With current ab initio calculations, it had become possible to calculate vibration frequencies and the corresponding intensities when the molecules were not too large. Hence, small alkanes of trans (t) and gauche (g) conformations had been studied widely since their structure

and bonding served as prototypes for carbon-based chemical industry. Ab initio vibration frequencies and optimized geometry researches had been conducted on propane⁸⁻¹³ and n-butane.¹⁴⁻²¹ However, for longer n-alkanes, since their stable conformers provided combinations of t and g rotational states, the disorder in long chain n-alkanes was more complex, so that it was difficult but important to extend these studies. Ab initio methods were also used to calculate pentane and hexane conformations with basis sets of HF/4-21G,^{22,23} HF/4-31G,⁴ and HF/6-31G,^{24,25} which provided spectra studies of four stable conformers of n-pentane and the 10 stable conformers of n-hexane and insights of the influence of conformation on these other molecular properties. In addition, Synder and Kim²⁶ had studied the Raman spectra of liquid n-alkanes C₄-C₉ and presented the overall Raman intensities in the low frequency range as a function of gauche content. Antulio et al.²⁷ calculated the vibration Raman frequencies and intensities of several octane conformations as models for corresponding conformational sequences in polyethylene. E.Koglin et al.²⁸ applied the same method for octane, dodecane and hexadecane conformations. Meanwhile, a wide range of experimental techniques, such as NMR,²⁹⁻³¹ IR,³²⁻³⁴ Raman,³⁵ had been employed to reveal the molecular features of the n-alkyl chains. With the low temperature FTIR spectroscopy, J.P.Gorce and S.J.Spells³⁶ studied long chain n-alkanes. So far, however, the studies mentioned above only gave the amount of conformational disorder at a specific site in the n-alkyl chains. Due to the limitation of experimental conditions, it was very difficult to get the overall frequency information of the conformational order of these systems only by experiments. Hence, ab initio calculations were of importance to solve this problem. At the same time, as a basic unit, by analyzing the results of n-nonane, it could provide some useful information of the conformation for long chain n-alkanes. Therefore n-nonane could be used as a model for long chain n-alkanes, even though there were many more complex conformations. With respect to the current study, the presence of four stable conformations of n-nonane (one of them was all-trans conformation) with one gauche conformation meant that the spectra could be interpreted as resulting from four spectroscopically different species, each having its own set of vibration frequency and intensity parameters. By analyzing the IR and Raman frequencies and their corresponding intensities of each conformation, we could get the detailed spectra information of the specific conformation, and the corresponding correlation between

frequency and vibration mode. Hence, ab initio calculations were useful tools to carry out the vibration study of n-alkanes.

Calculations

Ab initio calculations were performed with the GAUSSIAN 98³⁷ programs. The Hartree-Fock (HF) method and the 6-31G basis set were used to obtain the optimized geometries and frequencies for each molecule in this work. For the n-alkanes, the 6-31G basis set^{24,38} was proved to be the most satisfactory, because it could give more accurate results than other basis sets. The internal and local symmetry coordinates for each molecule followed the definitions of the ttttt conformation of n-nonane (see Figure 1), tttttg, ttttgt, tttgtt conformations were just the same as the above description (see Figure 2, Figure 3, and Figure 4). In general, the HF ab initio calculated frequencies were higher than the corresponding experimental values due to the neglect of contributions from electron correlation. The difference between calculated and experimental frequencies was typically of the order of 10%, which was a well-known deviation of Hartree-Fock calculated vibration frequencies from experimental values. In this work, therefore, the calculated and observed frequencies had not been compared and no scaling of vibration frequencies was applied. But the relation between calculated frequencies and conformations and the change trend of the frequencies were discussed in details.

Results and discussion

It was worthwhile to note that there were three conformations of n-nonane with one gauche bond. And the calculated frequencies of the following molecules were used in the refinement: ttttt, tttttg, ttttgt and tttgtt for n-nonane. In order to minimize the effect of major conformational changes during the minimization process in conformers with a series of consecutive gauche bonds, the corresponding torsion angles were constrained to $\pm 60^\circ$ in n-nonane. For all-trans-nonane, it had C_{2v} symmetry, and for other three conformations of n-nonane, they had lower symmetry, so that the vibrations associated with an assembly of conformational disordered chains were, of course, much more difficult to characterize. But they all had 81 fundamental frequencies including

vibration modes with IR and Raman active, those only with IR active or only with Raman active.

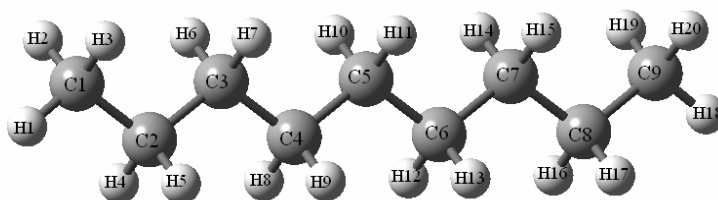


Figure 1. Internal coordinates of ttttt conformation of n-nonane.

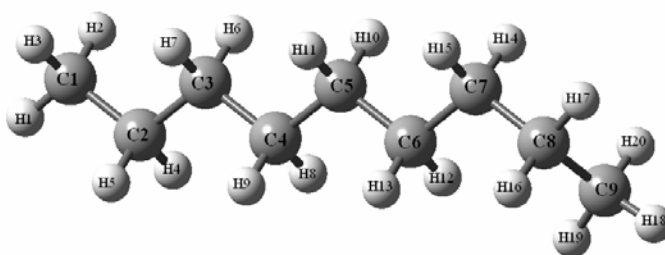


Figure 2. Internal coordinates of ttttg conformation of n-nonane.

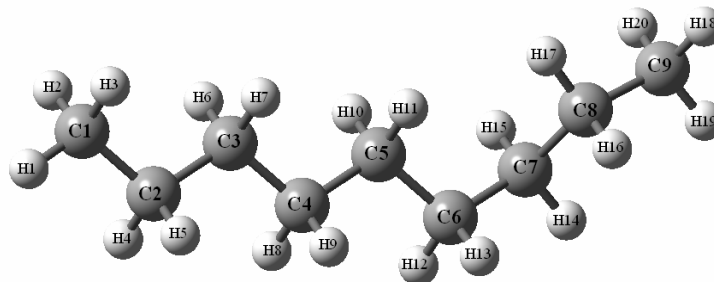


Figure 3. Internal coordinates of tttgt conformation of n-nonane.

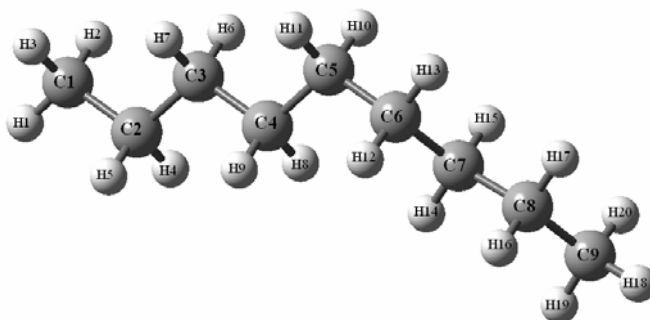


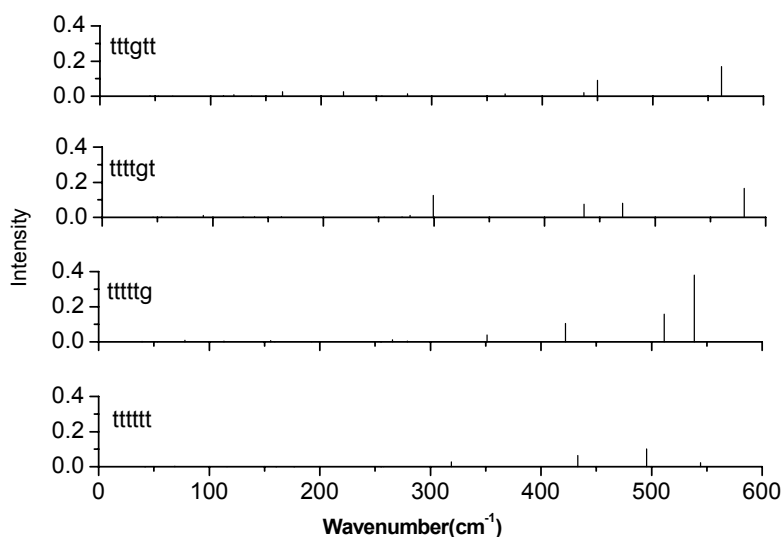
Figure 4. Internal coordinates of ttgtt conformation of n-nonane.

The low frequency region ($0-600\text{cm}^{-1}$) of the IR and Raman spectra was useful for analyzing polymethylene chain conformation. There remained some problems, however,

concerning the interpretation of the spectra obtained by experiments. So the present analysis of the calculated spectra of n-nonane was aimed at improving band assignments and exploring the relation between frequencies and conformations in this frequency region. With the changes of the conformation, the vibration modes would become more complex. In order to characterize the vibrations of an assembly of disordered chains in details, the coordinates are defined as follows: s is stretching; ss is symmetric stretching; as is antisymmetric stretching; b is bending; sb is symmetric bending; ab is antisymmetric bending; r is rocking; w is wagging; tw is twisting; t is torsion. The calculated IR spectrum was shown in Figure 5 and the assignments of main bands were listed in Table 1. For all-trans conformation there were two bands with appreciable intensity, one was at 433.3 cm^{-1} , another was at 495.6 cm^{-1} , in the calculated IR spectrum of n-nonane. Hence, they could be considered as the character bands of all-trans conformation in this region. And the tttgtt conformation also had two main features: 450.0 cm^{-1} , and 562.1 cm^{-1} , whereas for ttttg and tttgt conformation there were three and four bands with appreciable intensity respectively. It was obvious that the intensity of ttttg conformation was higher than other three conformations, and the band with the highest intensity was at 538.6 cm^{-1} . Especially interesting was that the vibration modes mentioned above all belonged to CCC bending mode, but the difference was that the vibration occurred at different site, thus according to this, we could think those vibrations which mainly occurred at specific site (including gauche segment) as the character bands of n-nonane with one gauche conformation. Therefore, for ttttg conformation, the character band was at 538.6 cm^{-1} ; for tttgt conformation, the character bands were at 299.4 cm^{-1} and 580.6 cm^{-1} ; for tttgtt conformation, the character band was at 562.1 cm^{-1} . As far as the effect of changes in conformation was concerned, the change trend of the same vibration modes was only discussed. But in this region, due to the increase of the chain length, the coupling of vibration modes became more complex, so that it was very hard to find the same vibration mode. In order to describe in-phase and out-of-phase of the vibration mode in details, the definition was as follows: the vibration mode in the same parentheses meant in-phase, e.g., the vibration mode of $b(C_{1,2,3},C_{2,3,4})$ stood for CCC bending in-phase; the vibration mode in the different parentheses meant out-of-phase, e.g., the vibration mode of $b(C_{1,2,3})b(C_{2,3,4})$ stood for CCC bending out-of-phase.

Table 1.

conformation	Calculated frequency (cm ⁻¹)	Description
ttttt	433.3	b(C _{1,2,3} ,C _{2,3,4}),b(C _{6,7,8} ,C _{7,8,9})
	495.6	b(C _{2,3,4} ,C _{3,4,5}),b(C _{5,6,7} ,C _{6,7,8})
ttttg	422.2	t(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),b(C _{1,2,3} ,C _{7,8,9})
		b(C _{2,3,4} ,C _{3,4,5} ,C _{4,5,6} ,C _{6,7,8})
	511.5	B(C _{1,2,3} ,C _{2,3,4}),b(C _{4,5,6} ,C _{5,6,7})
	538.6	t(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),b(C _{1,2,3} ,C _{5,6,7} ,C _{6,7,8})
	b(C _{2,3,4} ,C _{3,4,5} ,C _{4,5,6} ,C _{7,8,9})	
tttgt	299.4	b(C _{2,3,4} ,C _{7,8,9}),b(C _{6,7,8})
	435.8	b(C _{2,3,4} ,C _{3,4,5}),b(C _{5,6,7} ,C _{6,7,8} ,C _{7,8,9})
	470.7	b(C _{1,2,3} ,C _{5,6,7}),b(C _{3,4,5} ,C _{6,7,8})
	580.6	b(C _{1,2,3} ,C _{2,3,4} ,C _{6,7,8} ,C _{7,8,9}),b(C _{4,5,6} ,C _{5,6,7})
tttgt	450.0	b(C _{1,2,3} ,C _{2,3,4} ,C _{3,4,5}),b(C _{4,5,6} ,C _{5,6,7} ,C _{6,7,8} ,C _{7,8,9})
	562.1	b(C _{1,2,3} ,C _{2,3,4} ,C _{5,6,7} ,C _{6,7,8}),b(C _{3,4,5} ,C _{4,5,6})

Figure 5. Calculated IR spectrum of n-nonane in the region of 0-600 cm⁻¹.

The calculated Raman spectrum in the region of 0-600 cm⁻¹ was shown in Figure 6 and the description of main bands was listed in Table 2. Compared with the calculated IR spectra, it was obvious that there were great difference between all-trans conformation and other three conformations. For ttttt conformation there was only a single band, at 257.6 cm⁻¹, with the highest intensity in this region in the calculated Raman spectrum of n-nonane, hence it could be considered as the characteristic band. Whereas with the site of gauche bond changed from ttttg to tttgtt conformation, the number of the bands with higher intensities became increases. For ttttg and tttgt conformation there were two main bands with appreciable intensity, and for tttgtt

conformation there were five bands with higher intensity. But all vibration modes had something in common, viz., the mode of vibration was only CCC bending. In the same way, the characteristic bands of conformations with one gauche bond could be obtained by the method mentioned above, thus in the Raman spectra of this region, for ttttg conformation whose characteristic band was at 279.2 cm^{-1} ; and for tttgt conformation, the characteristic bands were at 278.4 cm^{-1} and 435.8 cm^{-1} ; there were also two characteristic bands for tttgtt conformation, 278.3 cm^{-1} and 562.1 cm^{-1} . As far as the effect of changes in conformation was concerned, the change trend of the same vibration modes was only discussed. For the vibration mode of $b(C_{1,2,3}, C_{2,3,4}, C_{3,4,5}, C_{4,5,6}, C_{5,6,7}, C_{6,7,8}, C_{7,8,9})$ (stood for CCC bending in-phase),

Table 2. Calculated Raman frequency and description.

conformation	Calculated frequency (cm^{-1})	Description
ttttt	257.6	$b(C_{1,2,3}, C_{2,3,4}, C_{3,4,5}, C_{4,5,6}, C_{5,6,7}, C_{6,7,8}, C_{7,8,9})$
ttttg	265.7	$b(C_{2,3,4}, C_{5,6,7})$
	279.2	$b(C_{1,2,3}, C_{2,3,4}, C_{3,4,5}, C_{4,5,6}, C_{5,6,7}, C_{6,7,8}, C_{7,8,9})$
tttgt	278.4	$b(C_{1,2,3}, C_{7,8,9}), b(C_{4,5,6})$
	435.8	$b(C_{2,3,4}, C_{3,4,5}), b(C_{5,6,7}, C_{6,7,8}, C_{7,8,9})$
tttgtt	278.3	$b(C_{1,2,3}, C_{2,3,4}), b(C_{4,5,6}, C_{5,6,7})$
	366.4	$b(C_{1,2,3}, C_{4,5,6}), b(C_{2,3,4}, C_{3,4,5})$
	437.6	$b(C_{1,2,3}, C_{2,3,4}, C_{7,8,9}), b(C_{5,6,7})$
	450.0	$b(C_{1,2,3}, C_{2,3,4}, C_{3,4,5}), b(C_{5,6,7}, C_{6,7,8}, C_{7,8,9})$
	562.1	$b(C_{1,2,3}, C_{2,3,4}, C_{5,6,7}, C_{6,7,8}), b(C_{3,4,5}, C_{4,5,6})$

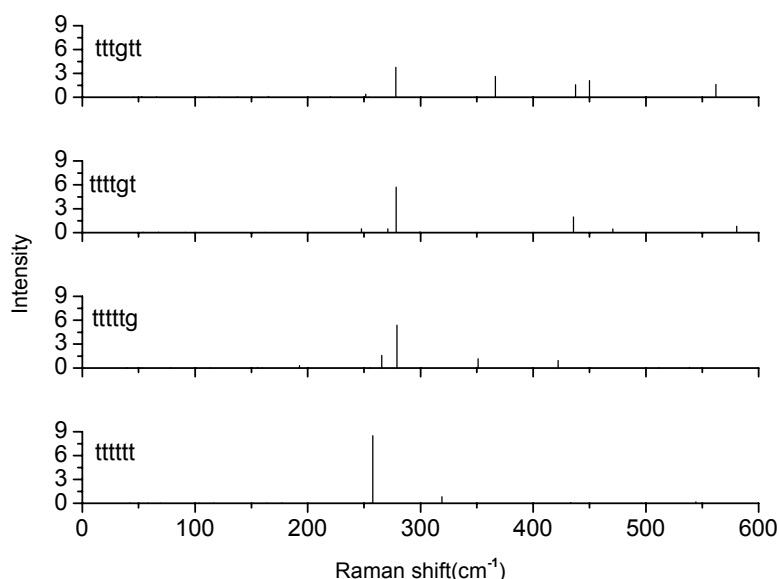


Figure 6. Calculated Raman spectra of n-nonane in the region of $0\text{--}600\text{ cm}^{-1}$.

while the intensity decreased with the change of conformation from tttttt to ttttgg, the frequency increased from 257.6 cm^{-1} to 279.2 cm^{-1} . For ttttgt and ttttgg conformation, the vibration mode mentioned above could not be found due to the coupling of the vibration modes, although they all had a band with higher intensity at about 278 cm^{-1} . At the same time, because it was very hard for other vibration modes to find the same kind, they were not discussed in this region.

According to the intermolecular interactions, many vibrations could have coupling in some degree. Thus the bands in the region of $700\text{--}1300\text{ cm}^{-1}$ were becoming more and more complex, especially for the conformations with low symmetry. Hence the approximate nature of the vibration modes was only described. The calculated IR spectrum was shown in Figure 7 and the assignments of main bands were listed in Table 3. From our results, two main kinds of band could be found, one was CH rocking mode (including methyl and methylene), the other was CC stretching mode. In general, both of them existed together. One of the most intriguing phenomena in the spectra was that there were some vibration modes with nearly the same frequency at around 800 cm^{-1} and 1220 cm^{-1} respectively. For those four conformations, the vibration mode of $r(\text{C}_1\text{H}_{1,2,3}, \text{C}_9\text{H}_{18,19,20})s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4})s(\text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$ appeared at 1220.2 cm^{-1} , 1221.2 cm^{-1} , 1218.72 cm^{-1} , and 1216.1 cm^{-1} from tttttt to ttttgg conformation respectively, which could testify that the change of conformation could hardly affect the frequency of this kind of vibration, in contrast to the intensity of each conformation, affected by conformation greatly, decreased from tttttt conformation to ttttgg conformation. But it was very strange that the vibration mode of $r(\text{C}_2\text{H}_{4,5}, \text{C}_3\text{H}_{6,7}, \text{C}_4\text{H}_{8,9}, \text{C}_5\text{H}_{10,11}, \text{C}_6\text{H}_{12,13}, \text{C}_7\text{H}_{14,15}, \text{C}_8\text{H}_{16,17})$ only lay in the tttttt conformation (798.7 cm^{-1}) and ttttgg conformation (799.2 cm^{-1}), and the corresponding intensity varied a little with the change of conformation. For other two conformations, although the corresponding frequency appeared at about 800 cm^{-1} , the vibration modes were different, the mode of $r(\text{C}_2\text{H}_{4,5}, \text{C}_4\text{H}_{8,9}, \text{C}_6\text{H}_{12,13})$, $r(\text{C}_3\text{H}_{6,7}, \text{C}_5\text{H}_{10,11})$ belonged to ttttgt conformation, and the mode of $r(\text{C}_2\text{H}_{4,5}, \text{C}_4\text{H}_{8,9}, \text{C}_7\text{H}_{14,15})$, $r(\text{C}_3\text{H}_{6,7}, \text{C}_5\text{H}_{10,11}, \text{C}_6\text{H}_{12,13}, \text{C}_8\text{H}_{16,17})$ belonged to ttttgg conformation. This might be caused by the effect of intermolecular interactions with the change of conformation. At the same time, it was becoming more difficult to find the characteristic band in this region, thus some bands which either had higher intensity or appeared at some special sites were only considered as the characteristic band of each conformation. In view of this, the feature characteristics of tttttt conformation were at 798.7 cm^{-1} and 1220.2 cm^{-1} ;

for tttttg conformation, the band at 862.7 cm^{-1} , although its intensity was relatively low, might be considered as the characteristic band because the vibration mainly took place in the gauche component. In the same way, for ttttgt and tttgtt conformations, its corresponding characteristic bands were at 824.4 cm^{-1} , 1184.4 cm^{-1} respectively.

Table 3. Calculated IR frequency and description.

conformation	Calculated frequency (cm^{-1})	Description
ttttt	798.7	$r(\text{C}_2\text{H}_{4,5}, \text{C}_3\text{H}_{6,7}, \text{C}_4\text{H}_{8,9}, \text{C}_5\text{H}_{10,11}, \text{C}_6\text{H}_{12,13}, \text{C}_7\text{H}_{14,15}, \text{C}_8\text{H}_{16,17})$
	978.4	$r(\text{C}_1\text{H}_{1,2,3}), r(\text{C}_9\text{H}_{18,19,20}), s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4}), s(\text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$
	1220.2	$r(\text{C}_1\text{H}_{1,2,3}, \text{C}_9\text{H}_{18,19,20}), s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4}), s(\text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$
tttttg	799.2	$r(\text{C}_2\text{H}_{4,5}, \text{C}_3\text{H}_{6,7}, \text{C}_4\text{H}_{8,9}, \text{C}_5\text{H}_{10,11}, \text{C}_6\text{H}_{12,13}, \text{C}_7\text{H}_{14,15}, \text{C}_8\text{H}_{16,17})$
	836.8	$r(\text{C}_2\text{H}_{4,5}, \text{C}_5\text{H}_{10,11}), r(\text{C}_4\text{H}_{8,9}, \text{C}_7\text{H}_{14,15}, \text{C}_8\text{H}_{16,17})$
	862.7	$r(\text{C}_2\text{H}_{4,5}, \text{C}_6\text{H}_{12,13}, \text{C}_8\text{H}_{16,17}), r(\text{C}_4\text{H}_{8,9})$
	1221.2	$r(\text{C}_1\text{H}_{1,2,3}, \text{C}_9\text{H}_{18,19,20}), s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4}), s(\text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$
tttgt	798.4	$r(\text{C}_2\text{H}_{4,5}, \text{C}_4\text{H}_{8,9}, \text{C}_6\text{H}_{12,13}), r(\text{C}_3\text{H}_{6,7}, \text{C}_5\text{H}_{10,11})$
	824.4	$r(\text{C}_2\text{H}_{4,5}, \text{C}_5\text{H}_{10,11}, \text{C}_7\text{H}_{14,15}, \text{C}_8\text{H}_{16,17}), r(\text{C}_3\text{H}_{6,7}, \text{C}_4\text{H}_{8,9}, \text{C}_6\text{H}_{12,13})$
	1095.0	$s(\text{C}_{1,2}, \text{C}_{5,6}, \text{C}_{8,9}), s(\text{C}_{2,3}, \text{C}_{3,4}, \text{C}_{4,5}, \text{C}_{6,7}, \text{C}_{7,8})$
	1218.7	$r(\text{C}_1\text{H}_{1,2,3}, \text{C}_9\text{H}_{18,19,20}), s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4}), s(\text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$
	1266.0	$\text{C}_1\text{H}_{1,2,3}, \text{C}_9\text{H}_{18,19,20}), s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4}, \text{C}_{4,5}, \text{C}_{5,6}, \text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$
tttgtt	798.4	$r(\text{C}_2\text{H}_{4,5}, \text{C}_4\text{H}_{8,9}, \text{C}_7\text{H}_{14,15}), r(\text{C}_3\text{H}_{6,7}, \text{C}_5\text{H}_{10,11}, \text{C}_6\text{H}_{12,13}, \text{C}_8\text{H}_{16,17})$
	807.3	$r(\text{C}_2\text{H}_{4,5}, \text{C}_4\text{H}_{8,9}, \text{C}_6\text{H}_{12,13}, \text{C}_8\text{H}_{16,17}), r(\text{C}_3\text{H}_{6,7}, \text{C}_7\text{H}_{14,15})$
	981.8	$r(\text{C}_9\text{H}_{18,19,20}), s(\text{C}_{6,7}, \text{C}_{8,9})$
	1184.4	$\text{tw}(\text{C}_2\text{H}_{4,5}, \text{C}_4\text{H}_{8,9}, \text{C}_6\text{H}_{12,13}, \text{C}_8\text{H}_{16,17}), \text{tw}(\text{C}_3\text{H}_{6,7}, \text{C}_5\text{H}_{10,11}, \text{C}_7\text{H}_{14,15})$
	1216.1	$r(\text{C}_1\text{H}_{1,2,3}, \text{C}_9\text{H}_{18,19,20}), s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4}), s(\text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$
	1266.5	$\text{C}_1\text{H}_{1,2,3}, \text{C}_9\text{H}_{18,19,20}), s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4}, \text{C}_{4,5}, \text{C}_{5,6}, \text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$

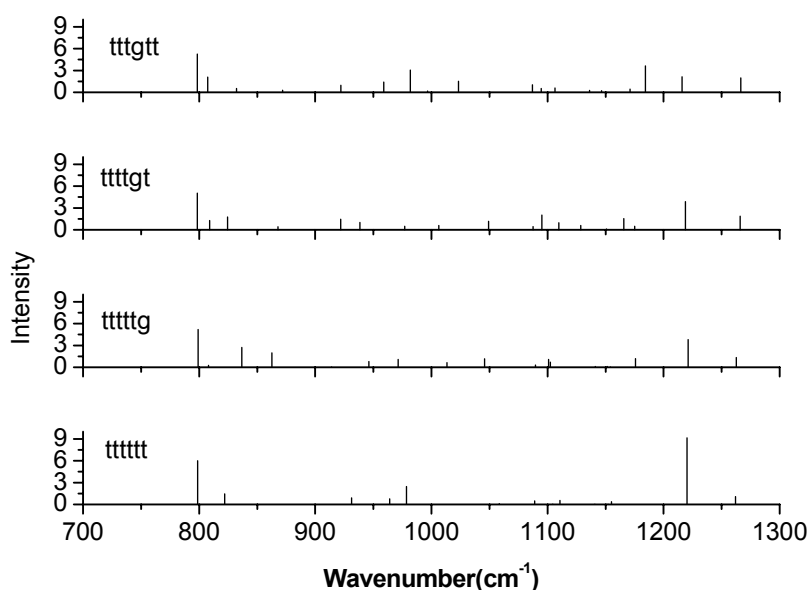


Figure 7. Calculated IR spectra of n-nonane in the region of $700\text{--}1300\text{ cm}^{-1}$.

Table 4. Calculated Raman frequency and description.

conformation	Calculated frequency (cm ⁻¹)	Description
ttttt	964.1	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),s(C _{1,2} ,C _{2,3} ,C _{7,8} ,C _{8,9}),s(C _{5,6} ,C _{6,7})
	1110.6	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),s(C _{1,2} ,C _{4,5} ,C _{5,6} ,C _{8,9}), s(C _{2,3} ,C _{3,4} ,C _{6,7} ,C _{7,8})
	1140.2	s(C _{1,2} ,C _{3,4} ,C _{4,5} ,C _{7,8}),s(C _{2,3} ,C _{5,6} ,C _{6,7} ,C _{8,9}), w(C ₂ H _{4,5} ,C ₅ H _{10,11} ,C ₈ H _{16,17}),w(C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₆ H _{12,13} ,C ₇ H _{14,15})
	1151.8	s(C _{1,2} ,C _{3,4} ,C _{5,6} ,C _{7,8}),s(C _{2,3} ,C _{4,5} ,C _{6,7} ,C _{8,9})
	1262.0	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}), s(C _{1,2} ,C _{2,3} ,C _{3,4} ,C _{4,5} ,C _{5,6} ,C _{6,7} ,C _{7,8} ,C _{8,9})
tttttg	914.0	s(C _{6,7}),s(C _{7,8} ,C _{8,9})
	946.2	s(C _{6,7} ,C _{7,8} ,C _{8,9})
	971.5	r(C ₁ H _{1,2,3}),s(C _{1,2} ,C _{2,3})
	1101.0	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),s(C _{1,2} ,C _{7,8}), s(C _{2,3} ,C _{3,4} ,C _{4,5} ,C _{5,6} ,C _{6,7})
	1102.4	r(C ₁ H _{1,2,3}),s(C _{3,4} ,C _{6,7} ,C _{7,8}),s(C _{4,5} ,C _{5,6} ,C _{8,9})
	1151.5	s(C _{1,2} ,C _{3,4} ,C _{5,6} ,C _{7,8}),s(C _{2,3} ,C _{4,5} ,C _{6,7} ,C _{8,9})
	1154.1	s(C _{1,2} ,C _{3,4} ,C _{5,6} ,C _{7,8}),s(C _{2,3} ,C _{4,5} ,C _{6,7} ,C _{8,9}), tw(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15})
	1175.951	s(C _{5,6} ,C _{7,8}),s(C _{6,7} ,C _{8,9})
1262.6	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}), s(C _{1,2} ,C _{2,3} ,C _{3,4} ,C _{4,5} ,C _{5,6} ,C _{6,7} ,C _{7,8} ,C _{8,9})	
ttttgt	921.9	r(C ₉ H _{18,19,20}),r(C ₁ H _{1,2,3}), s(C _{1,2} ,C _{2,3} ,C _{3,4}),s(C _{5,6} ,C _{6,7} ,C _{7,8} ,C _{8,9})
	977.2	r(C ₁ H _{1,2,3}),r(C ₉ H _{18,19,20}),s(C _{1,2} ,C _{2,3})
	1087.6	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),s(C _{1,2} ,C _{3,4} ,C _{4,5} ,C _{5,6} ,C _{6,7})
	1109.7	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),tw(C ₂ H _{4,5} ,C ₄ H _{8,9}),tw(C ₃ H _{6,7}), s(C _{4,5} ,C _{5,6} ,C _{8,9}),s(C _{6,7} ,C _{7,8})
	1150.8	s(C _{1,2} ,C _{3,4} ,C _{5,6} ,C _{7,8}),s(C _{2,3} ,C _{4,5} ,C _{6,7} ,C _{8,9})
	1175.1	s(C _{4,5} ,C _{6,7} ,C _{8,9}),s(C _{5,6} ,C _{7,8}), w(C ₄ H _{8,9} ,C ₆ H _{12,13} ,C ₈ H _{16,17}),w(C ₅ H _{10,11} ,C ₇ H _{14,15})
	1266.0	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}), s(C _{1,2} ,C _{2,3} ,C _{3,4} ,C _{4,5} ,C _{5,6} ,C _{6,7} ,C _{7,8} ,C _{8,9})
tttgtt	981.8	r(C ₉ H _{18,19,20}),s(C _{6,7} ,C _{8,9})
	996.7	r(C ₁ H _{1,2,3}),s(C _{1,2} ,C _{2,3} ,C _{3,4} ,C _{4,5} ,C _{5,6} ,C _{6,7})
	1136.3	s(C _{4,5} ,C _{7,8}),s(C _{5,6} ,C _{6,7} ,C _{8,9}),w(C ₇ H _{14,15} ,C ₈ H _{16,17}), tw(C ₃ H _{6,7} ,C ₅ H _{10,11}),tw(C ₂ H _{4,5} ,C ₄ H _{8,9})
	1146.6	s(C _{1,2} ,C _{3,4} ,C _{5,6} ,C _{7,8}),s(C _{2,3} ,C _{4,5} ,C _{6,7} ,C _{8,9})
	1171.1	s(C _{3,4} ,C _{5,6}),s(C _{4,5} ,C _{6,7}), w(C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₇ H _{14,15}),w(C ₄ H _{8,9} ,C ₆ H _{12,13})
	1216.1	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),s(C _{1,2} ,C _{2,3} ,C _{3,4} ,C _{6,7} ,C _{7,8} ,C _{8,9}), w(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11}),w(C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	1266.5	r(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}), s(C _{1,2} ,C _{2,3} ,C _{3,4} ,C _{4,5} ,C _{5,6} ,C _{6,7} ,C _{7,8} ,C _{8,9})

The calculated Raman spectrum in the region of 700-1300cm⁻¹ was shown in Figure 8 and the assignments of main bands were listed in Table 4. Compared with the calculated IR spectra, the number of bands with appreciable intensity increased. And therefore it was hard to analyze the Raman spectra in this region. From Figure 8, we could find that the intensity of ttttg conformation was lower than that of other three conformations, whereas the ttttt conformation had the highest intensity. Relatively, the

characteristic bands of tttttt conformation were easy to be made certain, thus the bands at 964.1 cm^{-1} , 1151.8 cm^{-1} , and 1262.0 cm^{-1} could be considered as its characteristic bands. According to the rule mentioned above, we suggested that tttttg conformation should have two characteristic bands, 946.2 cm^{-1} and 1176.0 cm^{-1} ; tttgtt conformation also had two featured bands, 1087.6 cm^{-1} and 1175.1 cm^{-1} ; for tttgtt conformation, there were two characteristic bands at 1136.3 cm^{-1} and 1171.1 cm^{-1} . With respect to the change trend of the same vibration modes, the apparent character was at near 1260 cm^{-1} , the $r(\text{C}_1\text{H}_{1,2,3}, \text{C}_9\text{H}_{18,19,20})s(\text{C}_{1,2}, \text{C}_{2,3}, \text{C}_{3,4}, \text{C}_{4,5}, \text{C}_{5,6}, \text{C}_{6,7}, \text{C}_{7,8}, \text{C}_{8,9})$ vibration mode varied regularly with the conformation changing from tttttt to tttgtt conformation, the calculated frequency would shift about 5 cm^{-1} at most, 1262.0 cm^{-1} for tttttt conformation, 1262.6 cm^{-1} for tttttg conformation, 1265.9904 cm^{-1} for tttgtt conformation, 1266.5 cm^{-1} for tttgtt conformation. Similar with this mode, the calculated frequency of vibration mode of $s(\text{C}_{1,2}, \text{C}_{3,4}, \text{C}_{5,6}, \text{C}_{7,8})s(\text{C}_{2,3}, \text{C}_{4,5}, \text{C}_{6,7}, \text{C}_{8,9})$ shifted to the low frequency region with the change of conformation, tttttt at 1151.8 cm^{-1} , tttttg at 1151.5 cm^{-1} , and tttgtt at 1150.8 cm^{-1} , tttgtt at 1146.6 cm^{-1} .

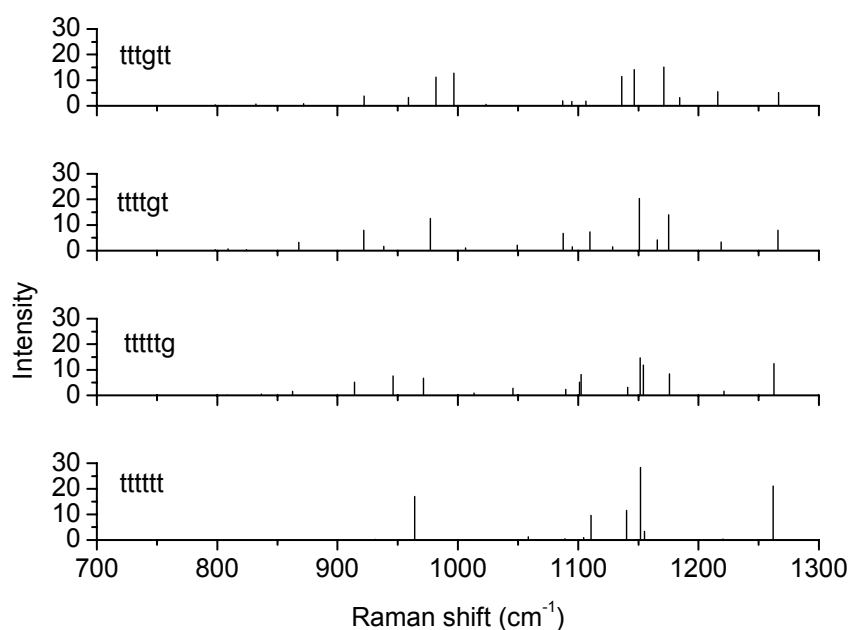


Figure 8. Calculated Raman spectra of n-nonane in the region of $700\text{-}1300\text{ cm}^{-1}$.

The calculated IR spectrum in the range $1300\text{-}1700\text{ cm}^{-1}$ was shown in Figure 9 and the description of main bands was listed in Table 5. In general, the bands in this region of the spectrum of n-nonane were much better defined than those in the region of

700-1300 cm^{-1} . The vibration modes mainly included the methylene wagging and bending, the methyl symmetric and antisymmetric bending. From Figure 8, we could see that the intensities of the bands in the lower-frequency were distinctly weaker than those of in the higher-frequency. Hence emphasis was put on the higher-frequency. One of the most intriguing phenomena was that the band at about 1578 cm^{-1} , whose vibration mode was methyl symmetric bending, and the band at around 1657 cm^{-1} , which belonged to methyl antisymmetric bending in-phase and out-of-phase, was strong and clearly discernable shoulder. According to the calculated values, the frequency and the intensity of both modes were independent of conformation. In the higher-frequency region, the vibration mode was the coupling of methyl bending and methylene bending. The effect of conformation was great with the decrease of symmetry and the coupling would become more serious, which would lead to the split of the bands. Among of them, the ttttg conformation was affected greatly. And therefore it was very difficult to find the same vibration modes, so it was not discussed in this paper. As to the characteristic bands, by analyzing the site that the vibrations took place and the relative intensity in details, we could conclude that 1657.3 and 1673.8 cm^{-1} belonged to ttttt conformation; 1524.3, 1548.3 and 1660.8 cm^{-1} to ttttg conformation; 1668.5 cm^{-1} to tttgt conformation; 1549.7 cm^{-1} to tttgtt conformation.

From the calculated Raman spectrum in the region of 1300-1700 cm^{-1} (shown in Figure 10) and the assignments of main bands (listed in Table 6), we could find that the bands with higher intensity were mostly located at two sites: one at near 1450 cm^{-1} , the other at near 1660 cm^{-1} . For the former, one methylene twisting mode played an important role. However, it comprised three kinds of vibration modes for the latter, viz. methyl symmetric bending, methyl antisymmetric bending and methylene bending. Similar with the IR spectra in this region, for methyl antisymmetric bending, the effect of change of conformation was very little, ttttt at 1657.3 cm^{-1} , ttttg at 1657.2 cm^{-1} , tttgt at 1657.2 and 1657.3 cm^{-1} , tttgtt at 1657.2 cm^{-1} , but each intensity had some little difference. One of the most interesting was that the band of this kind of mode for tttgt conformation was split into two components, and both methyl vibrations did not affect each other. There was no good reason to confirm; we could only suggest that this might be correlated with the conformation. On the contrary, for the vibration mode of methylene twisting mode in-phase, the calculated Raman frequency was affected by the

conformation, the value of tttgtt conformation was larger than those of other conformations by 10 cm^{-1} , the minimum value 1450.8 cm^{-1} appeared in the ttttgt conformation, and the intensity of each conformation decreased from tttttt to ttttgt conformation. As far as the characteristic bands were concerned, among four conformations, each conformation had its own bands, so that they could be considered

Table 5. Calculated IR frequency and description.

conformation	Calculated frequency (cm^{-1})	Description
tttttt	1578.6	sb(C ₁ H _{1,2,3}),sb(C ₉ H _{18,19,20})
	1578.9	sb(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20})
	1657.3	ab(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20})
	1673.8	sb(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}) b(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
tttttg	1524.3	w(C ₂ H _{4,5} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17}),w(C ₄ H _{8,9})
	1548.3	w(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₇ H _{14,15} ,C ₈ H _{16,17}),w(C ₃ H _{6,7} ,C ₆ H _{12,13})
	1578.6	sb(C ₁ H _{1,2,3})
	1578.9	sb(C ₉ H _{18,19,20})
	1657.2	ab(C ₁ H _{1,2,3})
	1660.8	sb(C ₁ H _{1,2,3}),ab(C ₉ H _{18,19,20}),b(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₅ H _{10,11}) b(C ₄ H _{8,9} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	1665.3	sb(C ₁ H _{1,2,3}),ab(C ₉ H _{18,19,20}) b(C ₂ H _{4,5} ,C ₃ H _{10,11} ,C ₇ H _{14,15} ,C ₈ H _{16,17}),b(C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₆ H _{12,13})
	1667.7	sb(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),b(C ₂ H _{4,5} ,C ₃ H _{10,11} ,C ₇ H _{14,15}) b(C ₃ H _{6,7} ,C ₆ H _{12,13} ,C ₈ H _{16,17})
1673.1	sb(C ₁ H _{1,2,3}),b(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₆ H _{12,13}),b(C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₇ H _{14,15})	
ttttgt	1578.5	sb(C ₁ H _{1,2,3})
	1578.7	sb(C ₉ H _{18,19,20})
	1657.2	ab(C ₁ H _{1,2,3})
	1657.3	ab(C ₉ H _{18,19,20})
	1668.5	sb(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),b(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₇ H _{14,15}) b(C ₃ H _{6,7} ,C ₆ H _{12,13} ,C ₈ H _{16,17})
	1672.7	sb(C ₁ H _{1,2,3}),b(C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₇ H _{14,15}) b(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₆ H _{12,13} ,C ₈ H _{16,17})
tttgtt	1549.7	w(C ₄ H _{8,9} ,C ₇ H _{14,15}),w(C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₈ H _{16,17})
	1578.5	sb(C ₁ H _{1,2,3}),sb(C ₉ H _{18,19,20})
	1578.5	sb(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20})
	1657.2	ab(C ₁ H _{1,2,3})
	1657.2	ab(C ₉ H _{18,19,20})
	1670.1	sb(C ₉ H _{18,19,20}),sb(C ₁ H _{1,2,3}),b(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₇ H _{14,15}) b(C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₈ H _{16,17})
	1672.1	sb(C ₁ H _{1,2,3}),b(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₆ H _{12,13} ,C ₈ H _{16,17}) b(C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₇ H _{14,15})

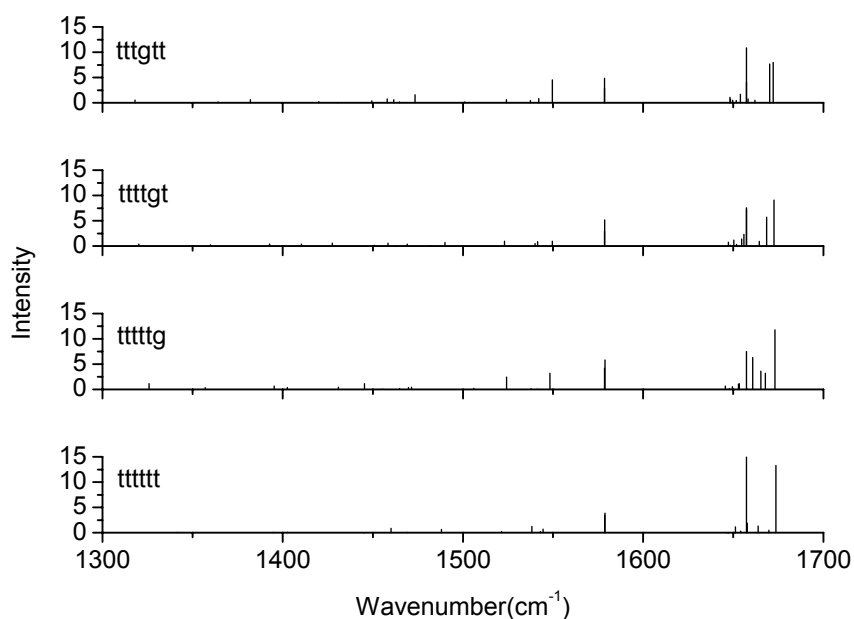


Figure 9. Calculated IR spectra of n-nonane in the region of 1300-1700 cm^{-1} .

as the characteristic bands. Hence, 1454.0 and 1654.0 cm^{-1} belonged to tttttt conformation; 1653.3 cm^{-1} belonged to tttttg conformation; 1458.5, 1650.3, and 1654.7 cm^{-1} to ttttgt; 1648.4, 1658.2 cm^{-1} to tttggt conformation. Of course, these results would be approved by the experiments in the further work.

The calculated IR spectrum in the region of 3150-3270 cm^{-1} was shown in Figure 11 and the assignments of main bands were listed in Table 7. In this region, there were mainly two kinds of vibration modes, including CH symmetric stretching and antisymmetric stretching. Snyder³ thought that the frequencies and intensities for CH stretching tended to remain independent of chain length. However what we were interested in was the trend of the frequencies and the intensities with the change of conformation. In general, it was obvious that the bands of symmetric stretching lay in the lower-frequency region, on the contrary, the bands of antisymmetric stretching lay in the higher-frequency region. Similar to other frequency regions, the number of bands with higher intensity of tttttt conformation was much less than that of other conformations. But the intensities in this region were much stronger than those of other regions. And the number of antisymmetric stretching was more than that of symmetric stretching. From our calculated results, we can find that in the region of symmetric stretching, methylene symmetric stretching was an important vibration mode, but the

vibration mode of methylene symmetric stretching in-phase only existed in the ttttt conformation which had C_{2V} symmetry. Hence the band at 3175.4 cm^{-1} could be considered as its characteristic band. In the higher-frequency region, the methyl antisymmetric stretching and methylene antisymmetric stretching were the significant vibration modes. For the mode of CH antisymmetric stretching in-phase, its frequency had a big shift, tttttt at 3249.9 cm^{-1} , tttttg at 3231.5 cm^{-1} , ttttgt at 3231.2 cm^{-1} , but tttgtt had not the same vibration mode, so the band at 3249.9 cm^{-1} was considered as a

Table 6. Calculated Raman frequency and description.

conformatio n	Calculated frequency (cm^{-1})	Description
ttttt	1438.5	tw($C_2H_{4,5}$, $C_5H_{10,11}$, $C_8H_{16,17}$)
	1454.0	tw($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_7H_{14,15}$, $C_8H_{16,17}$)
	1650.7	b($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_7H_{14,15}$, $C_8H_{16,17}$)
	1654.0	sb($C_1H_{1,2,3}$, $C_9H_{18,19,20}$), b($C_3H_{6,7}$, $C_7H_{14,15}$)
	1657.3	b($C_2H_{4,5}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_8H_{16,17}$) ab($C_1H_{1,2,3}$), ab($C_9H_{18,19,20}$)
ttttg	1455.3	tw($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_7H_{14,15}$, $C_8H_{16,17}$)
	1649.5	b($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_6H_{12,13}$, $C_7H_{14,15}$)
	1652.9	sb($C_1H_{1,2,3}$), b($C_7H_{14,15}$)
	1653.3	sb($C_9H_{18,19,20}$), b($C_8H_{16,17}$), b($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_7H_{14,15}$)
	1657.2	ab($C_1H_{1,2,3}$)
1658.0	sb($C_1H_{1,2,3}$), ab($C_9H_{18,19,20}$), b($C_3H_{6,7}$, $C_6H_{12,13}$), b($C_4H_{8,9}$, $C_7H_{14,15}$)	
tttgt	1450.8	tw($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_7H_{14,15}$, $C_8H_{16,17}$)
	1458.5	tw($C_7H_{14,15}$, $C_8H_{16,17}$), w($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$), w($C_5H_{10,11}$, $C_6H_{12,13}$)
	1462.5	tw($C_3H_{6,7}$, $C_4H_{8,9}$), tw($C_7H_{14,15}$, $C_8H_{16,17}$)
	1650.3	b($C_7H_{14,15}$, $C_8H_{16,17}$)
	1651.8	sb($C_1H_{1,2,3}$)
	1654.7	ab($C_9H_{18,19,20}$), b($C_8H_{16,17}$), b($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_7H_{14,15}$)
	1657.2	ab($C_1H_{1,2,3}$)
	1657.3	ab($C_9H_{18,19,20}$)
tttgtt	1461.6	tw($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$), tw($C_6H_{12,13}$, $C_7H_{14,15}$, $C_8H_{16,17}$)
	1464.8	tw($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_7H_{14,15}$, $C_8H_{16,17}$)
	1648.4	b($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$, $C_6H_{12,13}$, $C_7H_{14,15}$), b($C_5H_{10,11}$)
	1649.7	b($C_2H_{4,5}$, $C_3H_{6,7}$, $C_4H_{8,9}$), b($C_5H_{10,11}$, $C_6H_{12,13}$, $C_7H_{14,15}$)
	1651.6	sb($C_9H_{18,19,20}$), b($C_7H_{14,15}$), b($C_3H_{6,7}$, $C_4H_{8,9}$, $C_5H_{10,11}$, $C_6H_{12,13}$, $C_8H_{16,17}$)
	1653.9	sb($C_1H_{1,2,3}$), b($C_2H_{4,5}$, $C_5H_{10,11}$)
	1657.2	ab($C_9H_{18,19,20}$), ab($C_1H_{1,2,3}$)
	1658.2	sb($C_9H_{18,19,20}$), b($C_6H_{12,13}$), b($C_7H_{14,15}$, $C_8H_{16,17}$)

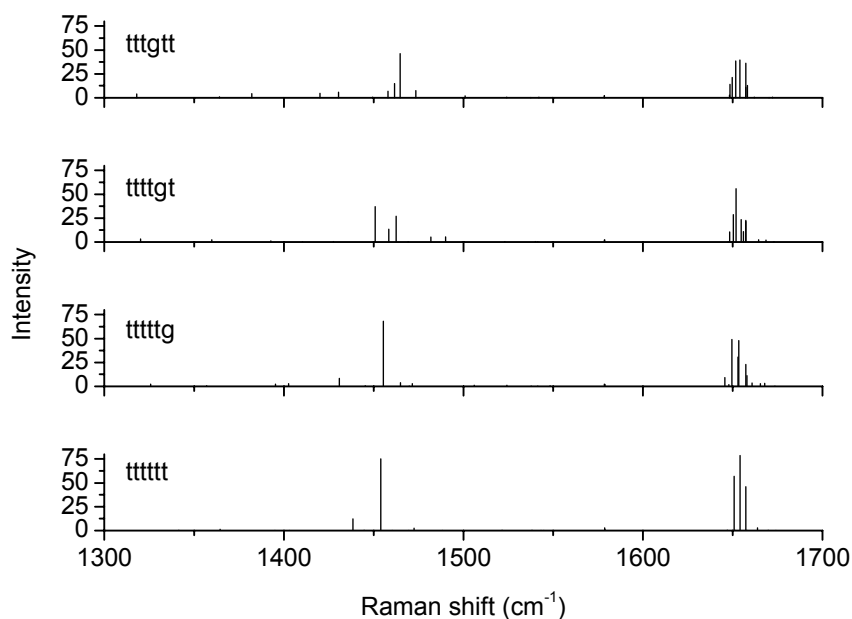


Figure 10. Calculated Raman spectra of n-nonane in the region of 1300-1700 cm^{-1} .

characteristic band of tttttt conformation, another featured band was at 3228.8 cm^{-1} . And the characteristic bands of other three conformations were as follows: 3261.4 cm^{-1} belonged to tttttg, 3220.1 cm^{-1} to ttttgt, and 3225.0 cm^{-1} to tttggt conformation. In addition, one of the most intriguing bands was near 3220 cm^{-1} , it formed the division between symmetric stretching and antisymmetric stretching (dashed in Figure 11).

The calculated Raman spectrum in the region of $3150\text{-}3270 \text{ cm}^{-1}$ was shown in Figure 12 and the assignments of main bands were listed in Table 8. Different from the calculated IR spectrum, the bands with higher intensity lay in the lower-frequency region, but because of the coupling of vibration mode, it was very difficult to find the same mode. Although some bands with the approximate frequency, their vibration modes were different. On the other hand, the division between symmetric stretching and antisymmetric stretching shifted to near 3182 cm^{-1} (dashed in Figure 12), but there appeared an exception at about 3177 cm^{-1} , viz. the frequency of antisymmetric stretching was smaller than that of symmetric stretching. In the higher-frequency region, the bands were converged at about 3250 cm^{-1} , while in the lower-frequency region, the bands scattered relatively, hence the number of symmetric stretching seemed to be more than that of antisymmetric stretching. The vibration at about 3250 cm^{-1} was the methyl antisymmetric stretching mode, although the detailed vibrations varied with the change

of conformations, its values and change trend were the same with that in IR spectra. With respect to the characteristic bands, in the spectrum of tttttt conformation, the characteristic bands were at 3177.1 and 3181.1 cm^{-1} with the higher intensities. For tttttg conformation, the characteristic bands were at 3170.8, 3192.0 and 3204.9 cm^{-1} . The band at 3192.0 cm^{-1} belonged to the character of ttttgt, the bands at 3165.0 and 3190.9 cm^{-1} belonged to the feature of ttttgt conformation.

Table 7. Calculated IR frequency and description.

conformation	Calculated frequency(cm^{-1})	Description
tttttt	3175.4	ss(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	3180.7	ss(C ₁ H _{1,2,3} ,C ₂ H _{4,5}),ss(C ₉ H _{18,19,20} ,C ₈ H _{16,17})
	3228.8	as(C ₁ H _{2,3} ,C ₉ H _{19,20})
	3249.9	as(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	3250.0	as(C ₁ H _{1,2,3}),as(C ₉ H _{18,19,20})
	3250.1	as(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20})
tttttg	3174.5	ss(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₆ H _{12,13}),ss(C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₇ H _{14,15})
	3231.5	as(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	3247.7	as(C ₉ H _{18,19,20})
	3250.0	as(C ₁ H _{2,3} ,C ₂ H _{4,5} ,C ₃ H _{6,7})
	3250.4	as(C ₁ H _{1,2,3})
	3261.4	as(C ₉ H _{18,19,20})
ttttgt	3174.1	ss(C ₁ H _{1,2,3} ,C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₇ H _{14,15} ,C ₉ H _{18,19,20})
	3174.5	ss(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₆ H _{12,13} ,C ₈ H _{16,17})
	3220.1	ss(C ₁ H _{1,2,3} ,C ₃ H _{6,7} ,C ₈ H _{16,17}),ss(C ₂ H _{4,5} ,C ₇ H _{14,15} ,C ₉ H _{18,19,20})
	3231.2	as(C ₉ H _{19,20}),as(C ₇ H _{14,15} ,C ₈ H _{16,17})
	3250.1	as(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	3250.5	as(C ₁ H _{2,3} ,C ₂ H _{4,5} ,C ₃ H _{6,7})
tttgtt	3252.2	as(C ₁ H _{1,2,3})
	3173.1	as(C ₉ H _{18,19,20}),as(C ₆ H _{12,13} ,C ₈ H _{16,17}),ss(C ₇ H _{14,15})
	3173.7	ss(C ₁ H _{1,2,3}),ss(C ₂ H _{4,5} ,C ₄ H _{8,9}),ss(C ₃ H _{6,7} ,C ₅ H _{10,11})
	3181.0	ss(C ₁ H _{1,2,3}),ss(C ₈ H _{16,17} ,C ₉ H _{18,19,20})
	3225.0	as(C ₉ H _{19,20}),as(C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	3229.4	as(C ₁ H _{2,3}),as(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11})
	3250.2	as(C ₁ H _{1,2,3}),as(C ₉ H _{18,19,20}),as(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9})
	3250.4	as(C ₉ H _{18,19,20}),as(C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
3250.7	as(C ₁ H _{1,2,3}),as(C ₉ H _{18,19,20})	

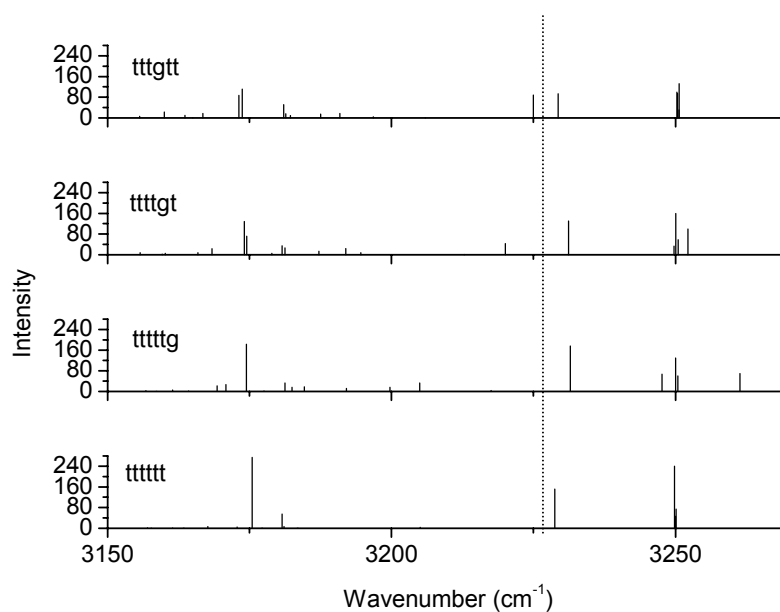


Figure 11. Calculated IR spectra of n-nonane in the region of 3150-3270 cm^{-1} .

Conclusions

In the present work, we investigated the overall IR and Raman spectra of n-nonane by ab initio calculations. The Hartree-Fock (HF) method and the 6-31G basis set provided the good description of normal mode frequencies and intensities of three stable conformations of n-nonane. By analyzing the IR and Raman spectra respectively, and dividing the frequency region into four parts: 0-600 cm^{-1} , 700-1300 cm^{-1} , 1300-1700 cm^{-1} and 3150-3270 cm^{-1} , each region was discussed in details, and the characteristic bands with corresponding vibration modes were reassigned. For different conformations, there were different characteristic bands, and some of these bands could not be obtained by experiments, especially for some broad bands. But this question could be resolved in the present work, so that it was possible to find the overall spectra information including IR and Raman of each conformation. The bands in the IR spectra were found to be associated with specific conformations: 433.3, 495.6, 798.7, 1220.2, 1657.3, 1673.8, 3175.4, and 3249.9 cm^{-1} for tttttt conformation; 538.6, 862.7, 1524.3, 1548.3, 1660.8, and 3261.4 cm^{-1} for tttttg conformation; 299.4, 580.6, 824.4, 1668.4, 3220.1 cm^{-1} for ttttgt conformation; 562.1, 1184.4, 1549.7, 3225.0 cm^{-1} for tttggt conformation. In the Raman spectra, the bands were as follows: 257.6, 964.1, 1151.8, 1262.0, 1454.0, 1654.0,

Table 8. Calculated Raman frequency and description.

conformation	Calculated frequency (cm ⁻¹)	Description
ttttt	3163.3	ss(C ₂ H _{4,5} ,C ₈ H _{16,17})
	3167.7	ss(C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15})
	3177.1	ss(C ₁ H _{1,2,3} ,C ₄ H _{8,9} ,C ₆ H _{12,13} ,C ₉ H _{18,19,20})
	3181.1	ss(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	3183.4	as(C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₇ H _{14,15}),as(C ₄ H _{8,9} ,C ₆ H _{12,13})
	3205.0	ss(C ₁ H _{1,2,3} ,C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17} ,C ₉ H _{18,19,20})
	3250.0	as(C ₂ H _{4,5} ,C ₅ H _{10,11} ,C ₈ H _{16,17}),as(C ₃ H _{6,7} ,C ₇ H _{14,15})
	3250.1	as(C ₁ H _{1,2,3}),as(C ₉ H _{18,19,20})
ttttg	3164.3	ss(C ₁ H _{1,2,3} ,C ₈ H _{16,17}),ss(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₆ H _{12,13})
	3170.8	ss(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),ss(C ₂ H _{4,5} ,C ₅ H _{10,11} ,C ₈ H _{16,17})
	3177.6	as(C ₂ H _{4,5} ,C ₄ H _{8,9}),as(C ₃ H _{6,7} ,C ₅ H _{10,11})
	3181.2	ss(C ₁ H _{1,2,3} ,C ₂ H _{4,5} ,C ₃ H _{6,7})
	3182.5	ss(C ₉ H _{18,19,20}),as(C ₂ H _{4,5} ,C ₅ H _{10,11} ,C ₇ H _{14,15}), as(C ₃ H _{6,7} ,C ₆ H _{12,13})
	3184.7	ss(C ₉ H _{18,19,20}),as(C ₂ H _{4,5} ,C ₅ H _{10,11}),as(C ₃ H _{6,7} ,C ₄ H _{8,9})
	3192.0	ss(C ₈ H _{16,17} ,C ₉ H _{18,19,20}),as(C ₆ H _{12,13} ,C ₇ H _{14,15})
	3204.9	as(C ₈ H _{16,17})
	3247.7	as(C ₉ H _{18,19,20})
	3250.4	as(C ₁ H _{1,2,3})
tttgt	3165.9	ss(C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15})
	3178.9	as(C ₂ H _{4,5} ,C ₄ H _{8,9}),as(C ₃ H _{6,7})
	3180.8	ss(C ₉ H _{18,19,20})
	3181.3	ss(C ₁ H _{1,2,3})
	3192.0	as(C ₆ H _{12,13} ,C ₈ H _{16,17}),as(C ₇ H _{14,15})
	3249.7	as(C ₈ H _{16,17} ,C ₉ H _{19,20})
	3250.5	as(C ₁ H _{1,2,3})
tttgtt	3165.0	ss(C ₂ H _{4,5}),ss(C ₄ H _{8,9} ,C ₆ H _{12,13} ,C ₇ H _{14,15} ,C ₈ H _{16,17})
	3166.8	ss(C ₁ H _{1,2,3}),ss(C ₄ H _{8,9})
	3173.1	ss(C ₂ H _{4,5} ,C ₃ H _{6,7} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₇ H _{14,15})
	3181.4	ss(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20}),ss(C ₆ H _{12,13} ,C ₈ H _{16,17}),ss(C ₇ H _{14,15})
	3182.2	ss(C ₁ H _{1,2,3}),ss(C ₉ H _{18,19,20})
	3187.6	as(C ₂ H _{4,5} ,C ₄ H _{8,9} ,C ₇ H _{14,15}),as(C ₃ H _{6,7} ,C ₆ H _{12,13} ,C ₈ H _{16,17})
	3190.9	as(C ₂ H _{4,5} ,C ₅ H _{10,11} ,C ₆ H _{12,13} ,C ₈ H _{16,17})
	3250.6	as(C ₃ H _{6,7} ,C ₄ H _{8,9} ,C ₇ H _{14,15})
	3250.7	as(C ₄ H _{8,9} ,C ₆ H _{12,13}),as(C ₅ H _{10,11} ,C ₇ H _{14,15})
	as(C ₁ H _{1,2,3}),as(C ₉ H _{18,19,20})	
	as(C ₁ H _{1,2,3} ,C ₉ H _{18,19,20})	

3177.1, and 3181.1 cm^{-1} for tttttt conformation; 279.2, 946.2, 1176.0, 1653.3, 3170.8, 3192.0, 3204.9 cm^{-1} for ttttgg conformation; 278.4, 435.8, 1087.6, 1175.1, 1458.5, 1650.3192, 1654.7, 3192.0 cm^{-1} for ttttgt conformation; 278.3, 562.1, 1136.3, 1171.1, 1648.4, 1658.2, 3165.0, 3190.9 cm^{-1} for tttggt conformation. Likewise, the trend of frequency change with the same vibration mode was also discussed. According to the trend, we could predict the change of conformation for experiments. At the same time, we also wanted to demonstrate the applicability and usefulness of ab initio calculated spectra for elucidating the spectra of long chain n-alkanes and their conformations in the future work. In short, the results could be directly compared to experimental data, and therefore provided a future rationalization of the experimentally observed features. And the early interpretations presented could now be confirmed by the feasibility of ab initio calculations which could provide frequencies and intensities.

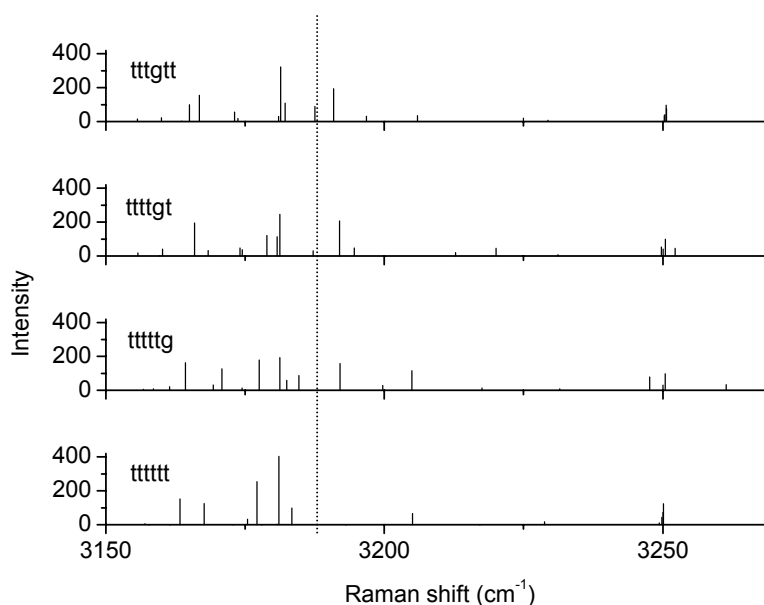


Figure 12. Calculated Raman spectra of n-nonane in the region of 3150-3270 cm^{-1} .

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Povzetek

Za izračun frekvenc in intenzitet normalnih nihanj štirih stabilnih konformacij *n*-nonana, ki so vključevale all-trans in še tri druge konformacije z eno gauche, smo uporabili ab initio nivo teorije. Raziskali smo vse območje IR in ramanskih frekvenc *n*-nonana z namenom ugotoviti povezavo med frekvencami in neredom v celotnem frekvenčnem področju. Ugotovili smo, da so pasovi infrardečih in ramanskih spektrov povezani s specifičnimi konformacijami, zato se da določiti karakteristične pasove posameznih konformacij. Analizirali smo tudi spreminjanje frekvenc pasov posameznih načinov nihanja s spreminjanjem konformacije, kar igra pomembno vlogo pri eksperimentih.