

Computational Infrared Spectroscopy:
Pentane, Neopentane , Polyethylene and Polyvinylchloride

Eman Mousa Alhajji

North Carolina State University

Department of Materials Science and Engineering

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Qiang Guo

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Abstract

In this experiment, molecular dynamics simulations are used as a tool to calculate IR spectra. The vibrational properties of pentane, neopentane , polyethylene and polyvinylchloride are calculated using Visual Molecular Dynamics (VMD 1.9.2). The frequency for the absorption band of these organic molecules are analyzed and estimated. The different bonds and functional groups of these organic molecules as they give rise to different IR signatures are examined. Pentane and neopentane were found to be isomers, having the molecular formula C_5H_{12} . Polyethylene (C_2H_4) and polyvinyl chloride (C_2H_3Cl) were found to be alkene organic molecules but with different formulas.

Introduction

Computer simulations model phenomena that are too small to be observed directly such as molecules in terms of their structure and the microscopic interactions between them. One of the two main families of simulation technique is molecular dynamics (MD). MD is considered a tool to calculate dynamical properties of the system: transport coefficients, time-dependent responses to perturbations, rheological properties and spectra.¹ The principals of MD simulations rely on calculating the force on each partial, where it is transformed from potential to movement. A single atom is affected by the potential energy functions of every atom in the system: bonded Neighbors and non-bonded Atoms (either other atoms in the same molecule, or atoms from different molecules). There are three types of interaction between bonded atoms: stretching along the bond, bending between bonds and rotating around bonds.² However, the quantum mechanical energy levels observed in Infrared spectroscopy (IR spectroscopy), which is often used to identify structures because functional groups give rise to characteristic bands both in terms of intensity and frequency, are those of molecular vibration.

This vibration is perceived as heat. When a *covalent bond* between two atoms is stated of a certain length, an average, in fact, is cited because the bond behaves as if it were a vibrating spring connecting the two atoms. There are two types of bond vibration: *stretch*, oscillation along the line of the bond, and *bend*, oscillation not along the line of the bond. Vibrational frequency of the chemical bond can be estimated in cm^{-1} using a variation of Hooke's law:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (1)$$

where c is the velocity of light ($3.00 \times 10^{10} \text{cm/sec}$), k is the force constant, related to the strength of the bond (dyne/cm). μ is the reduced mass of the bond, which is given by $\mu = \frac{m_1 m_2}{m_1 + m_2}$ where m_1 and m_2 are the masses of the two atoms (in kilograms per molecule). The vibrational

frequency of a bond in Hooke's law correspond to the frequency of infrared radiation absorbed by that bond. Only vibrations that cause the change in electric dipole moment will be associated with an absorption of infrared radiation. For instance, symmetric mode of vibration has no net change in its dipole moment, while antisymmetric mode has net change in dipole moment. Therefore, the antisymmetric mode would be infrared active and the symmetric mode would not. Absorption regions are classified in a range from 4000 to 0 cm^{-1} based on the type of bonds between the particles in the molecule and their vibration mood. In the region from ≈ 1300 to 400 cm^{-1} , vibrational frequencies are affected by the entire molecule. Absorption in this fingerprint region is characteristic of the molecule as a whole. This region finds widespread use for identification purpose by comparison with library spectra. It is worthwhile to note that the vibrational frequency increases with increasing force constant or increasing bond strength and decreasing atomic mass.²

In this experiment, molecular dynamics simulations are used as a tool to calculate IR spectra. The vibrational properties of pentane, neopentane, polyethylene and polyvinylchloride are calculated using Visual Molecular Dynamics (VMD 1.9.2). The structure of these organic molecules are shown in Figure 1. The frequency for the absorption band of these organic molecules are estimated. The different bonds and functional groups of these organic molecules as they give rise to different IR signatures are examined.

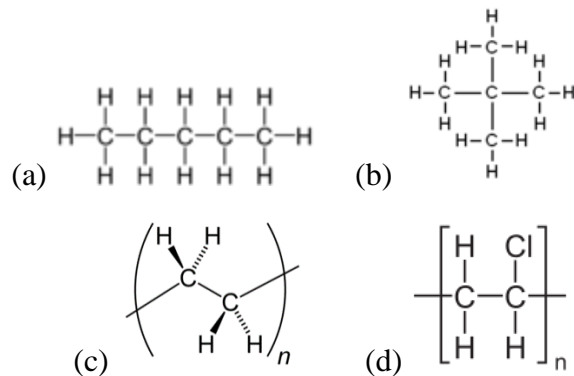


Figure 1: The molecular structures of (a) pentane , (b) neopentane, (c) polyethylene and (d) polyvinylchloride. ²

Experimental Procedure

The IR spectra of pentane, neopentane , polyethylene and polyvinylchloride were visualized and calculated using Visual Molecular Dynamics (VMD 1.9.2) program.

To load each molecule: File - New Molecule-../MDtraj/pentane/pentane.prmtop and Load was pressed; then pentane with file type "AMBER coordinates" was loaded. In order to visualize the interaction of the particles in pentane, Graphics- Representations- "CPK" instead of "Lines" was chosen. The motion was observed by pressing the play bottom. In order to calculate Spectra from 0 to 4000 cm^{-1} : Extensions- Analysis- IR Spectral Density Calculator was pressed. The IR spectrum was generated and then analyzed in excel. These steps were repeated for each of neopentane , polyethylene and Polyvinylchloride.

The frequencies for the absorption band due to the C-C, C-H and C-Cl bonds in in Polyvinylchloride were calculated using Equation 1 and the force constant from the Table 1.

Table 1. Force constants

Bond	$k \cdot 10^5$ (dyn cm^{-1})
C-H	4.24
C-Cl	5.01
C-C	5.8

Results

The IR spectrum calculated for pentane indicated three major peaks, as shown in Figure 2. The first peak with an intensity of 0.147 was at a frequency of 3008 cm^{-1} , representing stretching between C-H bonds. The second one with an intensity of 0.039 was found to be at a frequency of 1367 cm^{-1} , representing stretching between C-C bonds. The third one was at frequency of 1480 cm^{-1} with an intensity of 0.027, representing bending between C-H bonds.

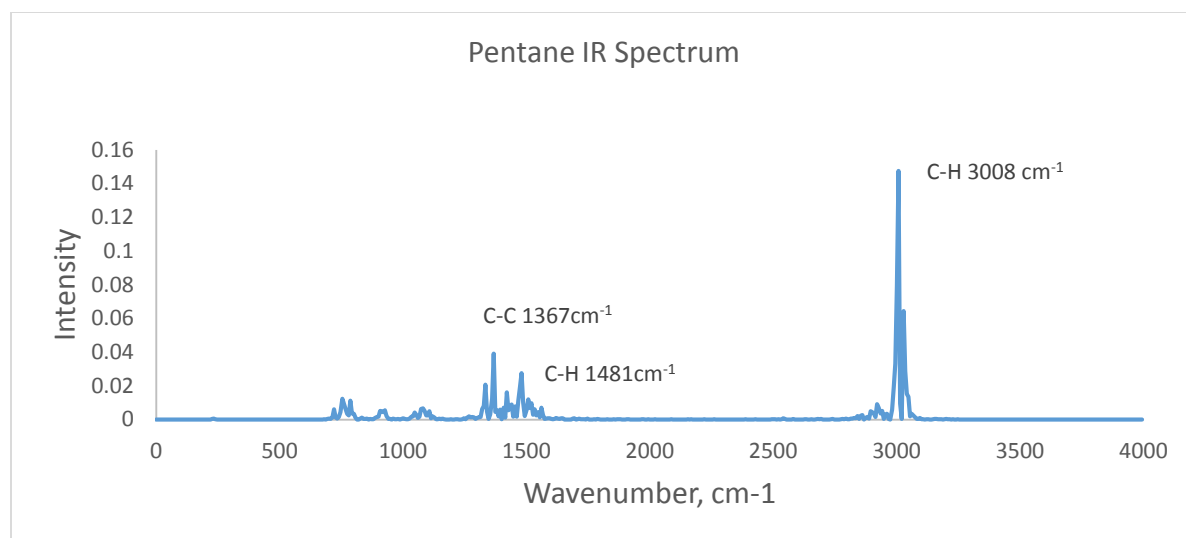


Figure 2: Pentane IR Spectrum

In Figure 3, The IR spectrum calculated for neopentane pointed also to three peaks. The first peak with an intensity of 0.147 was at a frequency of 3015 cm^{-1} , representing stretching between C-H bonds. The second one with an intensity of 0.039 was explored to be at a frequency of 933 cm^{-1} , representing stretching between C-C bonds. The third one was at frequency of 1574 cm^{-1} with an intensity of 0.013, representing bending between C-H bonds.

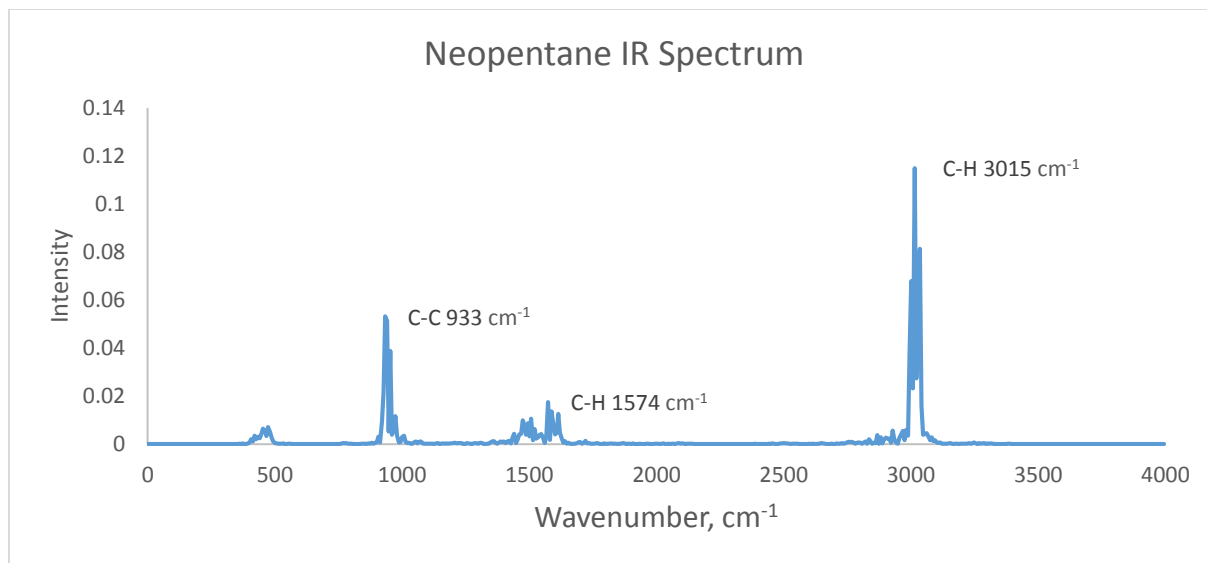


Figure 3: Neopentane IR Spectrum

The IR spectrum, in Figure 4, for polyethylene indicated also three peaks. The first peak with an intensity of 0.168 was detected to be at a frequency of 1347 cm⁻¹, representing stretching between C=C bonds. The second one with an intensity of 0.057 was at a frequency of 3028 cm⁻¹, representing stretching between C-H bonds. The third one was found at frequency of 767 cm⁻¹ with an intensity of 0.039, representing bending between C-H bonds.

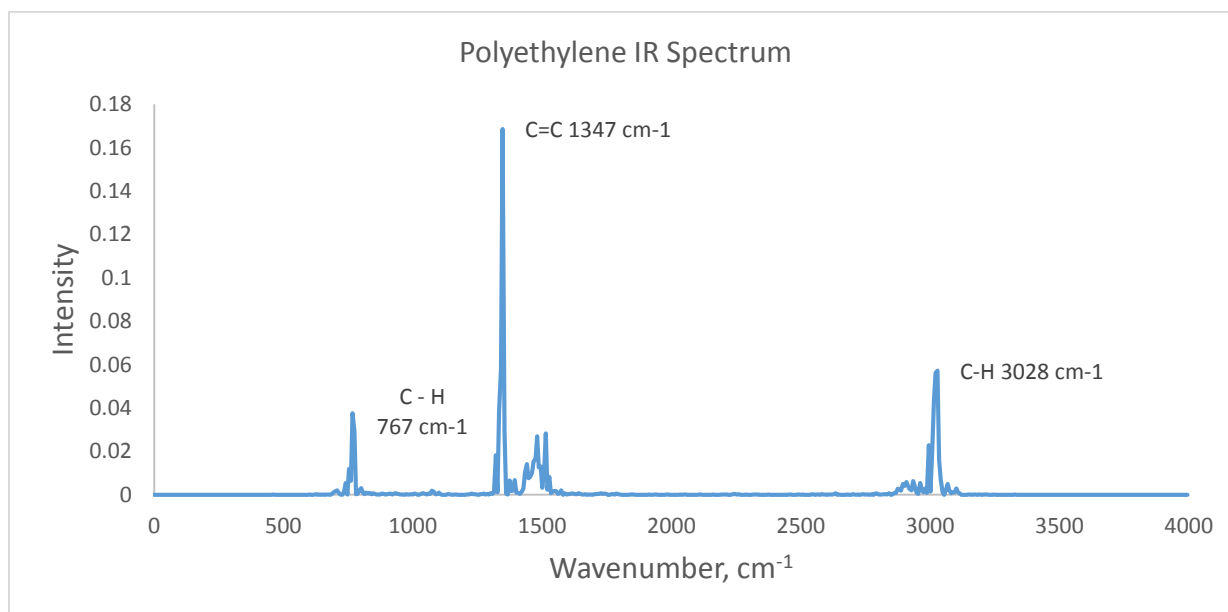


Figure 4: Polyethylene IR Spectrum

The polyvinylchloride IR spectrum calculated showed a great amount of peaks, as seen in Figure 5. The spectrum was found to be more dramatic than the previous ones. The first peak with a high intensity was detected to be at a frequency of 914 cm^{-1} , representing bending between C-H bonds. The second one was with an intensity of 0.02 at a range of frequency from 1394 to 1487 cm^{-1} , representing stretching between C=C bonds. The third one was found at frequency range from 2954 - 3034 cm^{-1} with an intensity of 0.02, representing stretching between C-H bonds. Another peak was found at 1047 cm^{-1} with an intensity of 0.01, representing bending between C-Cl bonds.

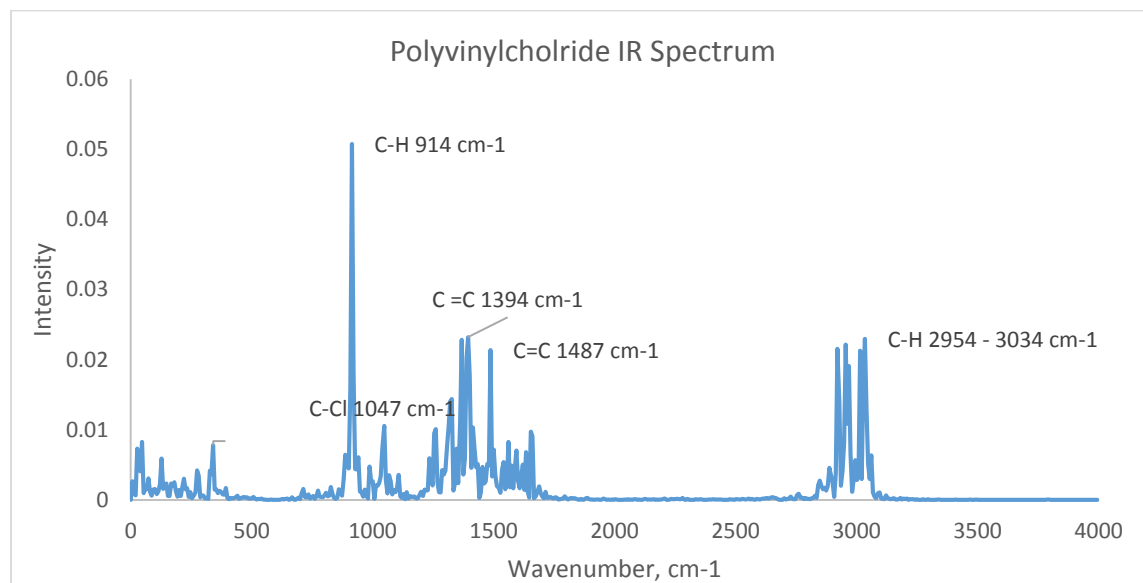


Figure 5: Polyvinylchloride IR Spectrum

The frequencies for the maximum absorption band due to C-C, C-H and C-Cl and C-F were theoretically calculated using Equation 1 and Table 1. First, the masses of C, H, Cl, and Cl were founded to be 1.994×10^{-23} , 1.677×10^{-24} , 5.887×10^{-23} , and 3.155×10^{-23} g/mol, respectively. The reduced mass of the bonds for C-H, C-Cl, C-C, and C-F were 1.547×10^{-29} , 1.484×10^{-23} , 9.970×10^{-24} and 1.222×10^{-29} g/mol, respectively.

²³ g/mol, respectively. The values of frequencies for the maximum absorption band obtained, as shown in Table 2.

Table 2: The frequencies for the maximum absorption band due to C-C, C-H and C-Cl and C-F

Bond	Frequency
C-C	1279.5 cm ⁻¹
C-H	2777.3 cm ⁻¹
C-Cl	973.1 cm ⁻¹
C-F	1021.4 cm ⁻¹

Discussion

Using the Table of Characteristic IR Absorptions in correlation with the IR spectrum of pentane in Figure 2, the cluster of peaks around 3000 cm⁻¹ down to around 2850 cm⁻¹ indicates that there are stretching of sp³-hybridized C-H bonds, which leads to a determination of the functional group of neopentane be alkanes with a chemical formula C₅H₁₂.^{1,3}

The IR spectrum of neopentane shows that a stretching interaction occurs at a frequency range from 3000 to 3100 cm⁻¹ with a strong intensity. The findings agree with the literature; Neopentane is a double-branched-chain alkane with five carbon atoms. Interestingly, similar signatures were observed in pentane and neopentane IR spectra. It can be realized that pentane and neopentane are two compounds with the same molecular formula C₅H₁₂, which then can be classified as isomers.³ Polyethylene is determined to be an alkene because its IR spectrum show both regular alkane peaks from all the sp³ carbons and peaks for the sp² Carbons. It was recognized that one peak was close to 3100 cm⁻¹, which is the peak for sp²-hybridized C-H bonds and a sharp peak was around 1500 cm⁻¹, which represents the C=C double bond.¹ Polyvinyl chloride was determined to be also in alkene. One peak was close to 3000 cm⁻¹ and another sharp one at 914 cm⁻¹, which both are for sp²-hybridized C-H bonds. Another peak corresponding to C-Cl bonds were observed at 1047 cm⁻¹. The last of the most significant one

was at about 1400 cm^{-1} , which represents the C=C double bond and. The data confirms the molecular structures for pentane, neopentane , and polyethylene and polyvinylchloride as shown in Figure 1. ^{2,3}

The theoretical numbers of fundamental vibrations were rarely be observed due to an overtone of the given frequencies and the, or a reduction by the occurrence of a debased band from several absorptions of the same frequency and a lack of change in molecular dipole. Absorption bands for polytetrafluoroethylene are expected to be seen at 1100 cm^{-1} , representing C-F bonds and around 1500 cm^{-1} , representing C=C bonds. ²

Conclusions

IR spectroscopy is a powerful tool for the determination of molecular structure because functional groups give rise to characteristic bands both in terms of intensity and frequency. In this experiment, molecular dynamics simulations were used as a tool to calculate IR spectra. The vibrational properties of pentane, neopentane , polyethylene and polyvinylchloride were calculated using Visual Molecular Dynamics (VMD 1.9.2) and confirmed some of the theoretical number of the frequencies of the absorption bands. The frequency for the absorption band of these organic molecules were analyzed and estimated. The different bonds and functional groups of theses organic molecules as they give rise to different are confirmed and the IR signatures were examined. Overall, the experiment succeeded in showing that that pentane and neopentane are isomers, having the molecular formula C_5H_{12} . It also succeed in proving that polyethylene (C_2H_4) and polyvinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$) are explored to be alkene organic molecules but with different formulas. Further improvements can be done by investigating more in the fingerprint regions, where the frequencies of molecules are more unique.

References

¹M.R. Allen, Introduction to Molecular Dynamics Simulation, Computational Soft Matter: From Synthetic Polymers to Proteins, pp. 1-28, 2004.

²L. Reynolds, Computational Infrared Spectroscopy, MSE 255 experiment description, 2016.

³W.D. Callister Jr., Materials Science and Engineering: An Introduction, Seventh Edition (Wiley, New York, 2007).