

Investigation of Phonon Modes in Silicon Carbide and Polyethylene using Fourier Transform Infrared Spectroscopy

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Abstract

Information from the absorption spectrum of Silicon Carbide (SiC) illustrate its structure like force constant C and velocity of sound v_s for both longitudinal (LA) and transversal (TA) acoustic modes. Due to the high sensitivity and experimental setup, it is expected to not observe exact results because impurities and contamination lead to larger deviations in the end result. The deviations from measured and tabulated values for absorption wavenumbers in CO₂ and H₂O range from approximate 1.4 to 7.8 %, 2.2 to 12.2% in octane, and 0.2 % to 6.5% in polyethylene sample. The measured velocity of sound in Silicon Carbide (SiC) suffered deviations from 66.5 to 85.2%, signifying the importance of experimental setup and using controlled environments.

1. Introduction

Fourier Transform Infrared (FTIR) spectroscopy is a powerful identification tool for both organic and inorganic structures. Infrared radiation (1 μ m to 1mm) is preferred in microscopy since the photon energy (1eV to 1meV) matches best with the energies of phonons. Composite samples produce intricate absorption bands as each constituent and or functional group will contribute with it's characteristic vibration/rotation modes. The detector measures the transmitted radiation and feeds the raw data to an analysing unit that compiles an interferogram in Fourier space [5].

In this study we will use FTIR spectroscopy to determine different properties of materials. We investigate the acoustic and optical phonon modes of Silicon Carbide (SiC) and Polyethylene samples. In addition we run analysis over the main background gases carbon dioxide and water vapour. It is necessary to measure the background absorption spectrum of the air in the detection chamber before proceeding with the experiment. All subsequent measurements will be relative to the background spectrum to exclude irrelevant data, and contrast the peaks corresponding to vibration modes. With background control, one can proceed to measure the absorption of Polyethylene and Silicon Carbide (SiC) and compare the results to tabulated values.

2. Theory

2.1. Blackbody Radiation

A black body is a physical idealized body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence [3]. The radiation that the black body emits in thermal equilibrium is what is known

as black body radiation. Black body radiation is useful in the study of radiation phenomena.

In order to study the peaks of data recorded by the FTIR, it is necessary to use Wien's displacement law. Wien's Law tells us that the frequency of the emission peaks ν_{max} of a black body is proportional to its temperature

$$\nu_{max} = \frac{\alpha k_B T}{h} \approx 5.879 \cdot 10^{10} \text{ Hz K}^{-1} \text{ T} \quad (2.1.1)$$

2.2. Crystals with diatomic basis

Consider elastic vibrations of a crystal with two atoms in the primitive cell. We wish to find the frequency of the wavevector propagating through the material in terms of elastic constants. Assuming that the elastic response of the crystal is a linear function of forces, an approximation is the [111] family of directions in the zinc blende structure [1]. This family of directions is orthogonal to the regularly spaced planes of two distinct atoms in zinc blende, resembling a diatomic chain. Cubic silicon carbide shares the same structure, making it a reasonable approximation. Assume small oscillations about every equilibrium position of the chain of atoms as in figure 1.

We look at the resonance frequency of a diatomic harmonic oscillator

$$\omega = \sqrt{C \frac{(m_1 + m_2)}{m_1 m_2}} \quad (2.2.1)$$

This can be approximated to vibrations with stretching and compression of bonds as in silicon carbide.

For FTIR, we use light dispersion to determine the angular frequencies of the LO and TO modes $\nu = c/\lambda$. Then we use the fact that $\omega = 2\pi\nu = 2\pi c/\lambda = 2\pi c\sigma$, with $\sigma = 1/\lambda$ such that the force constant C of the bond is

$$C = \frac{m_1 m_2}{m_1 + m_2} (2\pi c \sigma)^2 \quad (2.2.2)$$

and we can assume that the force constants can also be used for acoustical modes to find the LA and TA sound velocities

$$v = \sqrt{C/\rho} \quad (2.2.3)$$

where we define the mass density ρ to be

$$\rho = \frac{m_1 + m_2}{d_{hkl}} = \frac{(m_1 + m_2) \sqrt{h^2 + k^2 + l^2}}{a_0} \quad (2.2.4)$$

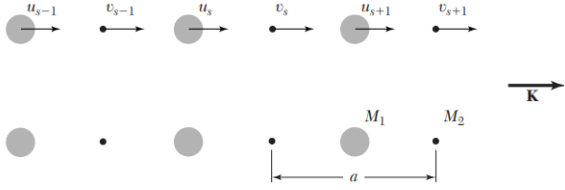


Figure 1: A diatomic crystal structure with masses M_1, M_2 connected by force constant C between adjacent planes. The displacements of atoms M_1 are denoted by u_s, u_{s+1}, \dots , and of atoms M_2 by v_s, v_{s+1}, v_{s+2} . The repeat distance is a in the direction of the wavevector \mathbf{K} . The atoms are shown in their undisplaced positions [2].

2.3. Vibration modes in various materials

For each atom in an molecule, we have $3N$ degrees of freedom, where N is the number of atoms. Since we only account for vibration modes, we have to subtract for uniform translation and rotation, leaving with $(3N - 6)$ degrees of freedom. However, for linear diatomic materials, one of the rotational degrees disappear resulting in $(3N - 5)$ degrees of freedom. In the case for H_2O we have $(3N - 6)$ vibration modes, while for CO_2 we have $(3N - 5)$ vibration modes since it is a linear molecule.

In the case for diatomic chains like silicon carbide SiC and polyethylene, the analysis for vibration modes becomes more complex as we have a long chain of bounded atoms. To approximate this, we can treat as if the carbon atoms are fixed on the chain while the hydrogen or silicon atoms move freely. The vibration modes can then be described as rotations name "wagging", "twisting", and "rocking" in addition to the vibration modes in a free diatomic molecule, for example shown in 2.

3. Method

For our experiment we used the RX1 spectrometer by Perkin Elmer [6]. All the samples used, were pre-made and provided by the laboratory. The background gases we consider in this experiment are vapour and carbon dioxide, because of their large concentration and relatively strong

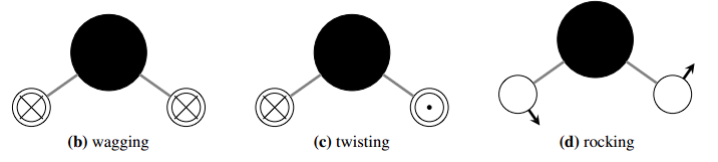


Figure 2: Vibration modes for polyethylene for an individual molecule fragment of the chain. Carbon atoms are drawn in black while hydrogen atoms are drawn in white. [2].

interaction with infrared light. Oscillatory motion of diatomic gasses like oxygen and nitrogen does not contribute to any absorption.

While sampling, the detector might pick up foreign material such as humidity, background gasses and polymeric coating on the lenses. Furthermore, different interferometer models have specific setups and techniques for beam directing. These aspects combine into unique matrix factors and cause measurements to deviate from tabulated values measured in systems with other matrix factors. Comparisons within the subset are not subjected to this problem. Hence, we analyse intensity curves relative to a measured background-noise offset.

3.1. Data Analysis

To simplify the analysis we assume Polyethylene has octane structure ($\text{H}_3\text{C}(\text{CH}_2)_6\text{CH}_3$). Furthermore, we don't consider boundary effects.

We consider a Zinc Blende structure of the Silicon Carbide SiC with a lattice parameter of $a_0 = 4.359\text{\AA}$. To find the sound velocities in SiC we do some further approximations. We use the dispersion relation for the optical phonons to obtain the force constant C for the LO and TO mode. The phonon dispersion of SiC is along the [111] directions, so we can use the formula for interplanar distance. To find the LA and TA sound velocities in the silicon carbide sample, we assume that we can use the same force constant for acoustical modes.

4. Results

Fig. 3 shows the absorption spectrum of the air inside the detection chamber, consisting primarily of CO_2 and H_2O . In fig. 3, the traces of the polymeric coating on the optical lenses are apparent. The gases form two separate clusters in the absorption band with modes of water vapor having higher wave numbers then those of carbon dioxide. The concentration of gases and the polymeric coating translates to increasing depth of the absorption peaks in the interferogram.

This measurement will be an important reference, pinning wave numbers that belong to the background sources. When analysing concrete samples we divide by the background interferogram to display relevant absorption clearly and exclude irrelevant noise. We keep the vertical lines to

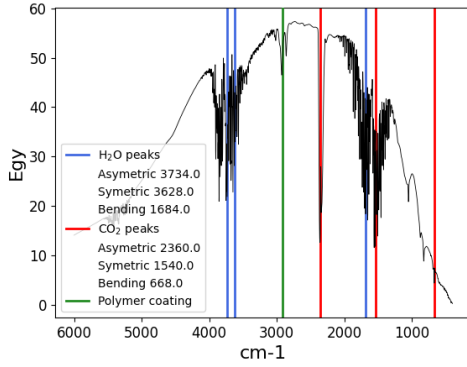


Figure 3: Background FTIR absorption spectrum of the air inside the detector. The absorption peaks of H₂O, CO₂, and polymer coating of the lenses are denoted with vertical lines in different colors.

distinguish vapour and carbon dioxide from intensity peaks of other constituents.

The RX1 spectrometer from Perking Elmer has a Gas Flushing function using Argon and/or Nitrogen to remove some of the background gases inside the cavity. Doing this would further differentiate relevant peaks from the background.

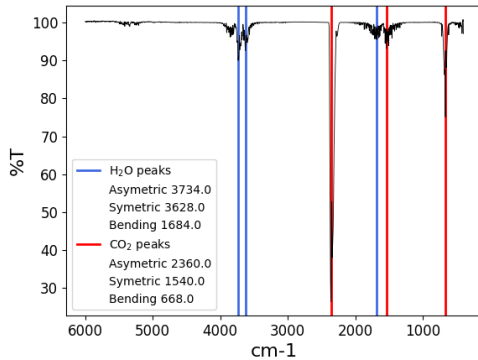


Figure 4: Absorption spectrum of human breath. The spectrum shows transmittance percentage on the vertical axis against wavenumber (in cm⁻¹) on the horizontal axis. The characteristic absorption peaks of water and CO₂ are indicated with vertical lines in different colors.

Table 1: IR absorption wavenumbers [cm⁻¹] for H₂O and CO₂ at room temperature. Different types of vibrational modes asymmetric, symmetric stretch and bending for the chemical compounds. Deviation from [1] is percentwise relative error.

Mode	Tabulated		Measured		Deviation (%)	
	H ₂ O	CO ₂	H ₂ O	CO ₂	H ₂ O	CO ₂
asym.	3945	2463	3734	2360	5.35	4.18
sym.	3811	1428	3628	1540	4.80	7.84
bending	1800	659	1684	668	6.44	1.37

We study CO₂ and H₂O more extensively by breathing directly into the instrument chamber. 4 indicates the wave numbers for symmetric, asymmetric and bending modes of the gas molecules. Carbon dioxide being a linear molecule with double bonds has its vibrational modes at lower wavenumbers compared to those of water vapour. Furthermore Table 1 shows that the symmetric and asymmetric vapour modes are closely grouped $\Delta\lambda \approx 100$ nm.

As mentioned earlier due to difference in matrix factors of the system, one must expect certain deviation between measured and tabulated peak-wave numbers. This will apply for all the subsequent results. In addition, the digital Fourier transform algorithms contribute with a certain numerical error.

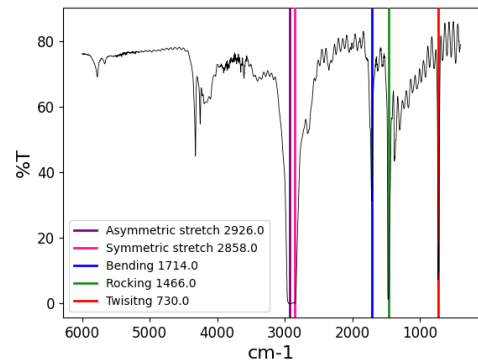


Figure 5: Absorption spectrum of Polyethylene -(C₂H₄)_n-. The transmittance percentage is plotted against the wavenumber (in cm⁻¹). Characteristic absorption peaks of polyethylene are indicated by vertical lines in various colors, each corresponding to a different vibrational mode

Table 2: Calculated IR absorption wavenumbers [cm⁻¹] for octane H₃C(CH₂)₆CH₃ at room temperature. Deviation from tabulated values in [1] is taken to be percentwise relative error.

Vib. mode	Tabulated	Measured	Deviation (%)
asym. stretch	3260	2926	10.25
sym. stretch	3200	2858	10.69
bending	1677	1714	2.21
rocking	1670	1466	12.22
twisting	788	730	7.36

Looking at the tabulated versus measured values for H₂O, CO₂ in table 1 and octane (H₃C(CH₂)₆CH₃) in table 2, it is apparent that octane has much bigger deviations from the tabulated values. The main reason behind the deviation from tabulated values in 2 is because we assume an octane sample to simplify the calculations, but in reality use polyethylene. If actually we had octane, the deviations could be because octane has a much more complicated chemical structure. The purity and exact composition of the octane sample affects the measured values and causes even more deviations from the tabulated values. In larger

molecules like octane, the vibrational modes that are discussed can be coupled, which in return shifts the measured absorption wavenumbers [7]. This causes huge deviations that are outside an acceptable range, which is typically $\pm 5\%$.

Table 3: Calculated IR absorption wavenumbers σ [cm^{-1}] for polyethylene $(\text{CH}_2)_n$. Deviation δ (percentwise relative error) from tabulated values in [8].

Vib. mode	Tabulated	Measured	δ
asym. stretch	2917	2926	0.31%
sym. stretch	2852	2858	0.21%
bending	1377	1466	6.46%
rocking	718	730	1.67%

As we compare the measured values with tabulated polyethylene (CH_2 chain) (c.f table 3), it is apparent that the comparison with octane was the culprit behind the large deviations. The sample we used for the polyethylene may be more uniform and pure than for CO_2 and H_2O . The vibrational modes in polyethylene may be better isolated, which means that there is less coupling between different vibrational modes. This can lead to sharper, more distinct peaks that match closer to theoretical predictions. Other causes could be impurities, calibration and experimental setup.

The spectrum presented in (fig.5) align well with expected IR absorption features for hydrocarbons. The peaks in the spectrum confirm the presence of the various molecular motions consistent with polyethylene’s structure. The slight discrepancies between tabulated and measured wavenumbers in table 3 are possibly attributed to differences in matrix factors but also molecular environment.

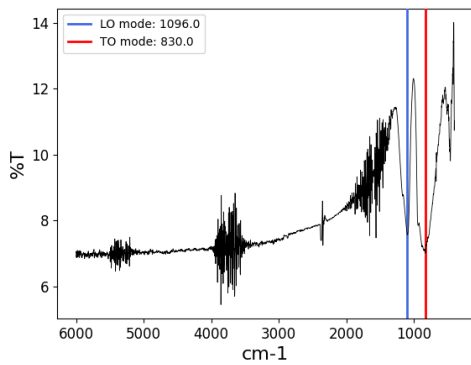


Figure 6: Absorption spectrum of silicon carbide SiC. The transmittance percentage is plotted against the wavenumber (in cm^{-1}). The longitudinal optical and transverse optical modes are denoted by vertical lines in blue and red, respectively.

Absorbing characteristic photons creates a phonon in one of the optical branches. We recognize in the spectral data (fig. 6) the transversal optical mode (TO) as the peak with lower wavenumber, and subsequently lower energy.

The longitudinal optical mode (LO) is the one with slightly higher energy as we expect the material to be stiffer along the axis of the diatomic chain.

Table 4: Wavenumber σ with corresponding calculated angular frequency ω , elastic constant C and sound velocity v_s for the Transverse (TO) and Longitudinal Optical (LO) Phonon Modes along [111] direction family in Silicon Carbide (SiC). Deviation δ (percentwise relative error) from tabulated values in [9].

	TO Mode	LO Mode
σ [cm^{-1}]	830	1096
ω [rad/s]	1.57×10^{14}	2.07×10^{14}
C [N/cm]	3.42	5.96
v_s [cm/s]	1.14×10^5	1.50×10^5
$\delta(v_s)$	66.47%	85.15%

Using Equations (2.2.1), (2.2.2), (2.2.3) and the spectral data from figure 6 we obtain the angular frequency, elastic constant and velocity of sound as presented in table 4. Using $v_s = 3.4 \times 10^5 \text{ cm/s}$ for TO mode and $v_s = 10.1 \times 10^5 \text{ cm/s}$ as tabulated in [9], we observe relative error for TO mode to be 66.47%, and LO mode has relative error of 85.15%. Impurities in the SiC alter the mass density and the stiffness of the material, leading to significantly lower or higher sound velocities. The calculated elastic constant C in table 4, does not take into account combination of elastic moduli.

5. Conclusion

In this experiment, Fourier Transform Infrared (FTIR) Spectroscopy was employed to explore the vibrational modes of Silicon Carbide (SiC) and Polyethylene, along with the main background gases, carbon dioxide and water vapor. The study involved measuring the background absorption spectrum to eliminate irrelevant data, followed by the analysis of SiC and Polyethylene’s absorption, compared against established values. Sensitivities in experimental setup caused significant deviations in most of the measured values. Some simplifications and approximation have also contributed to deviations. This signifies the importance of using cleanrooms in professional settings. We highlighted the structural properties of SiC through its force constant and the velocities of sound for both longitudinal and transversal acoustic modes, underlining the much greater velocity of sound in solids over air.

References

- [1] Breiby, W. D. *Laboratory exercise 2 in TFY4220 Solid State Physics, Lattice Vibrations*, NTNU (2024).
- [2] Kittel, C. *Introduction to Solid State Physics 8th edition*, University of California, Berkeley (2005).
- [3] Gregersen E. "Blackbody" - Britannica <https://www.britannica.com/science/blackbody>
- [4] RTI International. (n.d.). *FTIR Analysis* <https://rtilab.com/techniques/ftir-analysis/>
- [5] LibreTexts. (n.d.). *The Power of the Fourier Transform for Spectroscopists* <https://rtilab.com/techniques/ftir-analysis/>
- [6] Sciencemadness. *PerkinElmer Spectrum RX1 FT-IR Instruction manuals* <http://www.sciencemadness.org/talk/viewthread.php?tid=156910>
- [7] Banwell, C. N., & McCash, E. M. *Fundamentals of Molecular Spectroscopy*, McGraw-Hill (1994).
- [8] Smith, B. C. *The Infrared Spectra of Polymers II: Polyethylene* <https://www.spectroscopyonline.com/view/the-infrared-spectra-of-polymers-ii-polyethylene>
- [9] *Mechanical Properties, Elastic Constants, Lattice Vibrations* <https://www.ioffe.ru/SVA/NSM/Semicond/SiC/mechanic.html>