Qualitative differences in the calculated THz absorption spectra of linear and branched polymers as exemplified in amylose and amylopectin

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Abstract. Qualitative absorption spectra of the amylose and the amylopectin molecules were calculated in the THz frequency range within the framework of a simple model of coupled oscillators. The simulations revealed that the absorption of the linear molecule (amylose) was approximately twice as strong as that of the branched molecule (amylopectin) with the same molecular weight. The differences in the fine structure of the obtained spectra were also described. The results can be used to determine the degree of polymer branching using THz spectroscopy.

1. Introduction
Spectroscopy of polymeric molecules in the terahertz (THz) frequency range is a rather young and rapidly developing field of science. Though there still exist some problems with interpretation of the spectroscopy data, THz spectroscopy is a promising method for studying the molecular and supramolecular structure and dynamics, which influence crucially the chemical and physical properties of the substance.

1.1. Importance of the conformational structure and dynamics of polymer molecules
Physical, chemical and biological properties of any substance are determined by interactions between its molecules. Strong intermolecular attraction leads to high melting and boiling points, high viscosity, and slow diffusion and, as a result, to a low response rate in heterogeneous reactions.

The spatial structure and dynamics of molecules influence their interactions. For example, amylose and amylopectin consist of the same monomer, glucose, and have the same functions in the plant cell. Their clathrates with iodine differ in color due to the different structure of the molecules [1]. Structural transitions of amylose molecules are responsible for retrogradation of starch gel [2] and bread staling. Such structural transitions, as DNA looping and RNA hairpins, determine transcription, translation and reparation of DNA in cells [3, 4, 5]. The abnormal structure of PrP protein leads to
neurodegenerative diseases [6]. Thus, investigating the molecular structure and dynamics is an essential task in chemistry, biology, medicine, and food control.

1.2. THz spectra of polymer molecules today

THz spectroscopy of polymeric molecules is developing fast due to its tremendous potential in the investigation of molecular structure, dynamics, and interactions [7 - 12]. THz irradiation is non-ionizing due to the low energy of the THz quantum [7], so the THz field is regarded as non-invasive for molecules including biopolymers and even living organisms, at least if its power is not very high [8,9]. The THz range contains eigenfrequencies of the vibrational modes of polymeric molecules [7-9, 11, 12] and typical frequencies of formation and disruption of hydrogen bonds [10]. Earlier simulations revealed that the eigenfrequencies of regular helix molecules, such as DNA, could depend on the helix pitch distance [11]. THz absorption data contain information about protein flexibility [12] and the hydration shell of solvated molecules [10]. Therefore, THz spectroscopy is becoming a popular method, which can be used for investigation of molecules in various applications in medicine, biology, food control, and polymer science. Nevertheless, there are problems with interpretation of spectral data, since THz spectra are extremely complicated.

2. Purpose of the simulation

Simulations of the THz spectra of some model polymers can make it possible to understand how the molecular structure, dynamics, and interactions affect the spectral features. However, it is impossible to calculate absorption spectra taking into account every electron and every nucleus in such a huge molecule. Thus, essential simplification of the model is necessary.

We aimed to use a simplest model for qualitative understanding of the basic properties of the THz spectra of the model polymeric molecule. Amylose and amylpectin molecules of the same molecular weight were chosen as examples of chemically similar molecules with the same helix pitch but different branching. A comparative study of the simulated absorption spectra revealed the dependence of the THz spectral features of the molecules on the number of branching points in the molecule.

3. Model description

Both amylose and amylpectin molecules consist of glucose residues connected by α-(1,4)-linkages. In a plant cell, both the amylose and amylpectin molecules form semi-crystalline A- and B-structures that consist of double helices [2, 13] with 6 glucose residues per helix lead. The unit cell of the starch crystallite contains 8 water molecules for the A-structure and 36 water molecules for the B-structure [13]. However, amylose molecules are linear while amylpectin molecules have branch points approximately each 17 - 20 glucose residues.

Both the amylose and amylpectin molecules were described as chains of coupled oscillators having the same partial frequency. Each oscillator presents a glucose residue connected to a water molecule by a hydrogen bond. Glucose residues and water molecules were treated as rigid bodies having different masses and opposite charges. Each glucose residue is elastically connected with its neighbors by chemical bonds, and any interactions between water molecules were neglected. It was assumed that the glucose residue and the water molecule of any oscillator could move only along its hydrogen bond. The corresponding equations of motion for each glucose residue and each water molecule out of the branching points are written below:

\[
m_g \ddot{x}_g = -K_H (x_g - x_n) - K_{ch} (2x_g - x_{n-1} - x_{n+1}) - m_g \gamma \dot{x}_g + qE_{x,n} \exp(ik an - i\omega t),
\]

\[
m_w \ddot{x}_w = -K_H (x_w - x_n) - m_w \gamma \dot{x}_n - qE_{x,n} \exp(ik an - i\omega t),
\]

where \(m_g\) and \(m_w\) are the masses of the glucose residue and the water molecule, respectively, \(q\) is the electric charge, \(K_H\) and \(K_{ch}\) are the stiffness of the hydrogen and chemical bonds, respectively, \(x_g\) and \(x_n\) are the displacements of the glucose residue and the water molecule, respectively, and \(E_{x,n}\) is the projection of the THz electrical field onto the hydrogen bond in the \(n\)th pair.
Such a simple model could not be used to predict a precise absorption spectra, but it successfully revealed few qualitative differences between the simulated amylose and amylopectin spectra shown below.

4. Calculation results

The absorption spectra were simulated for three pairs of samples. In each pair, the first sample consisted of amylose molecules and the second, of amylopectin molecules. In the pair of samples, masses of all molecules were identical. The axes of the molecular helixes were parallel, but the molecules were turned around the axes to a random angle from 0 to 2π. All amylopectin molecules in the simulation have branching points after each 17 glucose residues. Molecular masses of the samples were equal to masses of 39, 73, and 143 glucose residues for the first, second, and third pair, respectively.

The calculated spectra consists of two absorption bands, which are called the “main” and “satellite” bands here. The absorption for the main band is approximately 20 times stronger than that for the satellite one. The main band consists of one strong line only, while the satellite band has a fine structure. Both the main and satellite bands are different for the amylose and amylopectin samples.

4.1. The difference in the main bands

![Figure 1](image1.png)

**Figure 1.** Absorption spectra (in arbitrary units) in the range of the main absorption band calculated for all six samples. The numbers in the legend corresponds to the molecular masses of the samples.

The main absorption band calculated for all samples is shown in Fig. 1. Such properties as its central frequency and width are independent of the molecular mass and structure. However, absorption intensity of the unbranched molecules (amylose) is approximately twice as strong as that of the branched ones (amylopectin).

![Figure 2](image2.png)

**Figure 2.** Fine structure of the absorption spectra calculated for the amylose (solid line) and amylopectin (dashed line) samples with length of 73 glucose residues. The absorption coefficients of both samples are expressed in percents of the absorption of the same sample at 1.25 THz.
4.2. The difference in the satellite bands
The fine structure of the satellite band depends on the molecular mass and structure (see Fig. 2).

The absorption between 5.8 and 6.2 THz is stronger for linear molecules, but absorption lines outside this range are stronger for branched molecules. Another difference is that the absorption line at 6.15 is single for the linear molecules and split for the branched molecules.

4.3. Conclusions
The simplified model, used for the simulation, revealed the following spectral features:

- Both amylose and amylopectin absorption spectra consist of two bands, main and satellite ones. The first is approximately 20 times as stronger as the second one.
- The central frequency and width of the main band are the same for all samples. However, the absorption is approximately twice as strong for the linear molecules.
- There is sufficient difference in the fine structure of the satellite band of the linear and branched molecules. First, the central two or three lines from the satellite band are stronger for the linear molecules. Second, the satellite band is wider for the branched molecules. Finally, line splitting appear in the absorption spectra calculated for the branched molecules.

5. Acknowledgements
The presented study was funded by RFBR under research project No. 18-32-00328.

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