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Effect of the intramolecular hydrogen bond on the spectral and optical properties in chitosan oligosaccharide



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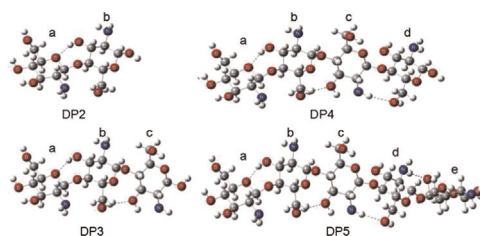
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HIGHLIGHTS

- We establish the chitosan oligosaccharide models DP2–DP5 by density functional theory, the model results are agreed with helical structure which obtained in experiment.
- We have analyzed the statistics of relationship between IR spectra and bond lengths and angles of amino, hydroxyl.
- The nonlinear optical properties of chitosan oligosaccharide display a regular oscillation of occurs with DP increasing, the mean dipole polarizability and the polarizability anisotropy invariant are linear increase.

GRAPHICAL ABSTRACT



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ABSTRACT

The geometric structures, hydrogen bond types, IR spectra and nonlinear optical properties of chitosan oligosaccharide (degree of polymerization 2–5) are studied by density-functional theory (DFT) at B3LYP/6-31+G(d) level. We have analyzed the statistics of relationship between IR spectra and bond lengths, and angles of amino, hydroxyl. The results show that: (1) the active groups C₃-OH, C₆-OH and -NH₂ can form intramolecular hydrogen bond in chitosan oligosaccharide; (2) the IR spectra of three active groups have size effect in growth process, however, its IR intensity increases significantly and IR frequencies are red shifted obviously when the active hydroxyl form hydrogen bonds, because the bond length of active hydroxyl becomes longer; (3) the effect of hydrogen bond on intensity and frequency of the three vibration mode of amino is the main factor and complication. The paper also provides the nonlinear optical properties of chitosan oligosaccharide. The reason why hydrogen bond can make an appreciable difference to IR spectra, and the nonlinear optical properties of chitosan oligosaccharide are discussed. This research has important significance in the characterization of chitosan oligosaccharide, the properties of chitosan material and hydrogen bond by infrared spectroscopy.

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1. Introduction

Chitosan has amino and hydroxyl groups, it is the unique alkaline polysaccharide with positive ions in the nature. So it has a unique functional properties in chemical industry, environmental protection, biomedicine, food etc. [1–4]. Chitosan not only has many biomedical activity and superior function, but also has good water solubility. It has attracted research interest of many researches [5–9]. Many studies on preparing water-soluble chitosan which using degradation procedure have been conducted, yet methods such as acid hydrolysis, oxidation and enzymatic degradation etc. have been developed [1,10,11]. Chitosan oligosaccharide with DP3–DP7 or lower polymerization degree have a unique biomedical activity, for example, they can make the S180 sarcoma cells stop dividing temporarily [12]. Therefore, chitosan is also known as the sixth element for the human body. We have studied on the physical and chemical properties of chitosan oligosaccharide with DP3–DP7, and we have explained why they have unique properties by average binding energy, thermodynamics, density of states and HOMO, LUMO [13]. Nanosystem has its own special properties, such as the size effect and the anisotropy [14–17]. Liang Chen et al. [18–20] studied the IR frequency shift of SiO₂ and MgO inorganic nanotube clusters in the growth process, and they found this kind of nanomaterial exist obvious size effect and nonlinear optical properties. In the previous work, we also research the growth process of oligopeptide chains about the physical and chemical properties, especially the size effect of infrared spectra has been discussed [21–24]. So we have known that there are obvious size effect of IR spectra both in inorganic nanotube clusters and organic oligopeptide chains. The properties of active groups (–OH and –NH₂) on chitosan oligosaccharide we study in this paper show size effect, however, the infrared frequencies are not changed monotonous. Many proton transfer reactions in chemical and biological processes are carried out in the form of hydrogen bonds [25]; protein, fiber, oligopeptides chain and chitosan oligosaccharide largely depend on the geometric configuration which has a lot to do with hydrogen bonds. So we infer that it is the effect of chitosan structure and hydrogen bond that affect the frequency and intensity in IR spectra. The analysis and discussion of IR frequencies and the nonlinear optical properties are given in the paper. The results of our study may be of great importance in studying hydrogen bonding by IR spectroscopy [26], unique activity of chitosan oligosaccharide, chitosan material properties and applications.

We focus our attention on chitosan oligosaccharide DP2–DP7, however, because of the computational resource constraint, this paper only presents the data of DP2–DP5. Even so, it is inferred from physical and chemical properties of DP29DP7 [13] that higher degree of polymerization will not influence the results of qualitative analysis. So we optimize the structure of chitosan oligosaccharide with DP2–DP5 by density-functional theory in this paper. Then we discuss how hydrogen bond influences the geometric structure of chitosan oligosaccharide, the relationship between the IR spectra changes of active groups and hydrogen-bond interaction, and the nonlinear optical properties of chitosan oligosaccharide.

2. Computational methodology

In this work, we optimize the structure of chitosan oligosaccharide, calculate its frequency, study the nonlinear optical properties and covers statistics on the bond lengths and angles of the active hydroxyl and amino by density-functional theory at B3LYP/6-31+G(d) level. The location of the intramolecular hydrogen bond is found out through the typical definition of

hydrogen bond [27]. Besides, we also investigate the connection between chitosan oligosaccharide structure and intensity and frequency of IR spectra, and nonlinear optical properties. Density functional theory using the Thomas–Fermi–Dirac Model [28].

$$E_{TFD}[\rho] = C_k \int \rho(\vec{r})^{5/3} d\vec{r} + \int v_{ext}(\vec{r})\rho(\vec{r}) d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' - \frac{3}{4\pi} (3\pi^2)^{1/3} \int \rho(\vec{r})^{4/3} d\vec{r}$$

Density functional theory is based on Becke's hybrid three-parameter exchange function [29] combined with the LYP correlation functional [30] (B3LYP) method with the 6-31+G(d) basis set. All calculations are performed by using Gaussian 09 software package [31].

3. Results and discussion

3.1. Geometric structure and hydrogen bond

Chitosan oligosaccharide contains many donor and acceptor of hydrogen bond, therefore, helical structure of chitosan is obtained by the degradation in the experiment [32]. The chitosan oligosaccharide models created in this paper tend to form helical structure which exist full of intramolecular hydrogen bond after the optimization [13]. It illustrates that the models we establish accord with the chitosan oligosaccharide obtained in experiment. Frequency calculation shows no imaginary frequency existed, the optimized structures are stable. In order to facilitate the representation of chitosan oligosaccharide intramolecular hydrogen bonding, we are using the letters a–e mark its residues. As shown in Fig.1.

Four intramolecular hydrogen bonds are formed: a-O...H-O-C₃-b, c-C₃-O...H-O-C₆-b, d-C₆-O...H-N-C₂-c, e-C₆-O...H-N-C₂-d. They are all typical strong hydrogen bonds of O-H...O and N-H...O. The intramolecular hydrogen bond lengths and bond angles of chitosan oligosaccharide are counted in our previous work [13]. The range of hydrogen bond length and bond angle of hydrogen bonds are 0.283–0.331 nm and 154.32–169.44 respectively, which are typical strong hydrogen bond. Compared with bond length, bond angle and APT charge of O-H...O and N-H...O, we found that strength of the former is greater than the latter. The existence of hydrogen bond structure also can be verified through the changes of IR strength and frequency.

3.2. Hydrogen bonding and IR spectral characteristics

According to the principle of IR spectral [33], the computation formula of vibration frequency is as follows:

$$\Delta E = hv = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}, \quad \nu = \frac{1}{\lambda} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

In the formula, π and c are constants; ν is the vibration frequency; k is the force constant of chemical bond; μ is a diatomic molecule of reduced mass.

We can know that the peak mobile of one group in an infrared spectroscopy depends largely on its force constant of chemical bond by the above equation, namely the bond length and angle affect IR spectra. It is amino and the hydroxyls on C₃, C₆ that can form intramolecular hydrogen bond in chitosan oligosaccharide. So we count the bond length and bond angle of amino and the hydroxyls on C₃, C₆, as shown in Tables 1-a–1-c.

From Tables 1-a–1-c, we can know that only residue b can form typical hydrogen bond on C₃, bond length of b-C₃-OH is longer than that of a-C₃-OH. Rest –OH groups on residue c, d and e

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