



Conformational change in the C form of palmitic acid investigated by Raman spectroscopy and X-ray diffraction



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ABSTRACT

Fatty acids are substances found in most living beings in nature. Here we report the effect of the low temperature in the vibrational and structural properties of the C form of palmitic acid, a fatty acid with 16 carbon atoms. The Raman spectra were obtained in the temperature interval from 300 to 18 K in the spectral range between 30 and 3100 cm^{-1} . The assignment of the duly observed bands was done based on the density functional theory. On cooling, the main changes observed in the lattice mode region of the Raman spectra were interpreted as a conformational modification undergone by the palmitic acid molecules in the unit cell. The X-ray diffraction measurements were obtained from 290 to 80 K showing a slight modification in the lattice parameters at about 210 K. Differential scanning calorimetry (DSC) measurements were recorded between 150 and 300 K and no enthalpic anomaly in the DSC thermogram was observed. These techniques provided strong evidence of the conformational change in the molecules of palmitic acid at low temperatures.

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1. Introduction

Fatty acids are carboxylic acids with a long chain of carbon atoms and the most common of them have chains with 16 to 22 carbons. They are the second energy source of the animal body and are also part of the chemical composition of several vegetable oils. Among naturally occurring fatty acids, the most commonly found in animal body is the palmitic acid [1], which is also identified in great quantity in vegetable oils, like buriti oil [2], only to cite an example. Palmitic acid (PA) (16:0, hexadecanoic acid), is a long chain saturated fatty acid with 16 carbon atoms [3–10]. In the solid state the molecules are packed as dimers through O–H...O hydrogen bonds. These dimers are ordered in bilayers with terminal methyl groups at both external faces, and these layers are parallel to the crystallographic (100) plane [9,10]. PA is the first fatty acid created in lipogenesis process. It is vital to palmitoylation, a process in which palmitic acid is attached to proteins. Palmitoylation mediates protein–protein interactions and contributes to membrane association. Palmitic acid

has also a wide range of industrial applications, including the use in the production of soaps and cosmetics as well as being utilized as a food additive [2–4].

A comparative study of long chain (C form) fatty acids with an even number of carbon atoms (C_{12} to C_{26}), has been done using infrared and the Raman techniques [5]. These studies were performed varying the temperature from 300 to 90 K; however, they were focused mainly on stearic acid. As far as we know, no meticulous study on palmitic acid under different temperatures has been carried out. Several experimental techniques such as the differential scanning calorimetry (DSC) [6,7], X-ray powder diffraction (XRPD) [8–11], Fourier-transform (FT) Raman spectroscopy [12,13,11,14] or conventional Raman spectroscopy [15,8,5,16] as well as infrared spectroscopy [2,15,6,5,16,14], have been used in the recent years for investigating fatty acids. These studies have the purpose (i) to understand the phase transition [17,18,11] and conformational transformation [17,18,5], (ii) to identify the composition of substances found with fatty acids [2,12,19] and (iii) to search polymorphisms [9], among others [20–22,13]. Raman spectroscopy, in particular, is one of the most powerful available tools, providing information about the molecular structures and giving insights about the symmetry of crystals [23,24,22,11,25,26,5,16,14].

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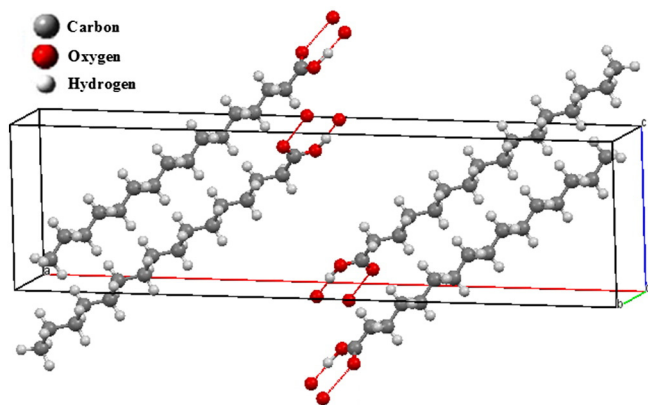


Fig. 1. Representation of the molecules in the crystal structure of palmitic acid at room temperature and ambient pressure.

In the present study, firstly, a discussion about the Raman spectra of the palmitic acid C form in the back scattering geometry recorded at room temperature is given. Secondly, the assignment of the observed Raman bands was done based on the density functional theory. Finally, the Raman active modes and the X-ray powder diffraction (XRPD) measurements as a function of the temperature are used in order to study the stability of the palmitic acid structure. Such a study allows us to understand the occurrence of a conformational phase transformation through the observation of changes both in the Raman modes and in the crystalline lattice parameters.

2. Experimental

2.1. Raman spectroscopy and sample

The palmitic acid, purchased from Aldrich Chemicals, was used as supplied in all the studies described herein. The low temperature Raman studies were performed using a closed helium flux cryostat system (Model DE202S – APD Cryogenics) with a temperature control of ± 0.1 K. The Raman spectra were collected with a triple-grating spectrometer (Jobin Yvon, T64000) in the subtractive mode and the line 514.5 nm of an argon ion laser was used as an excitation source. An Olympus microscope lens with a focal distance of $f = 20.5$ mm and a numeric aperture of $NA = 0.35$ was used to focus the laser beam on the sample surface. The slit was set in order to obtain a resolution of 2 cm^{-1} .

2.2. X-ray diffraction

The *in-situ* XRPD measurements were carried out with a Philips diffractometer (model PW1170), through the Bragg–Brentano geometry with an attached Anton-Par TTK450 temperature chamber, in the temperature range of 290–75 K. A Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) was used with the diffractometer operating at 40 kV/30 mA. The diffraction patterns were obtained in the 2θ angular range of 3° – 45° with a step

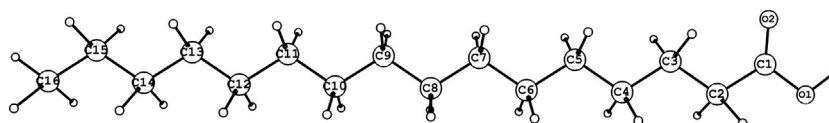


Fig. 2. Molecular structure of palmitic acid with atom numbering.

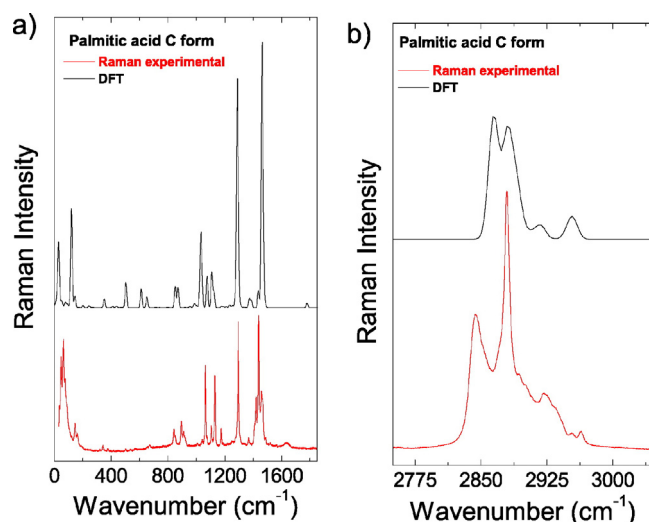


Fig. 3. Experimental and calculated (scaled) Raman scattering spectra of palmitic acid under atmospheric condition in the regions, 40 cm^{-1} to 1850 cm^{-1} and 2750 cm^{-1} to 3050 cm^{-1} .

size of 0.02° and a counting time of 1 s/step. The results were analyzed by the Rietveld refinement using the GSAS program.

2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were recorded using a Netzsch Instrument (DSC 204F1 – Phoenix) equipped with a liquid nitrogen cooling accessory. About 3 mg of sample was monitored between 150 and 300 K, with a 5 K/min heating rate.

3. Computational analysis

The computational methodology can be found with complete detail elsewhere [27]. However, we summarize the most important topics herein. The Density Functional Theory (DFT) [28,29] with B3LYP exchange–correlation functional [30], using the 6-31G(d,p) basis set were carried out using the Gaussian 09 program [31]. Firstly, the geometrical coordinates of the PA molecule, obtained through X-ray diffraction, were optimized. Theoretical Raman Intensities (I^R) were derived from Raman activities obtained with the Gaussian program. The following relationship derived from basic Raman scattering theory was used [32–35]:

$$I^R_i = C (\nu_0 - \nu_i)^4 \cdot \nu_i^{-1} \cdot B_i \cdot S_i,$$

where C is a scaling constant taken as 10^{-13} , ν_0 is the excitation frequency of the argon ion laser, ν_i is the calculated frequency for the i th normal mode and S_i is the corresponding activity. The B_i factor accounts for the contribution of excited vibrational states to the intensities:

$$B_i = (1 - \exp(-h \cdot \nu_i \cdot c / k_B T))$$

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