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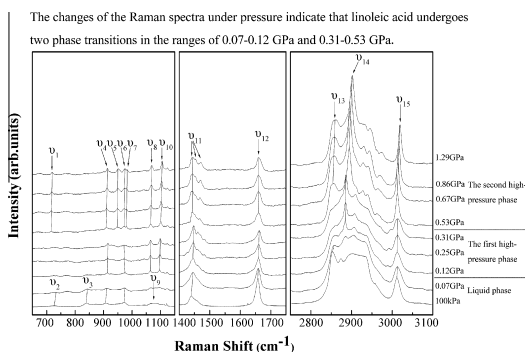
Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saaThe investigation on the pressure-induced phase transition in linoleic acid by in situ Raman spectroscopy [☆]Fan Ya (范雅)^{a,*}, Zhou Jing (周静)^b, Xu Da-Peng (许大鹏)^c^a Department of Physics, Changchun University of Science and Technology, Changchun 130022, China^b National Engineering Research Center for Rare Earth Materials, General Research Institute for Nonferrous Metals, Beijing, China^c College of Physics, Jilin University, Changchun 130012, China

HIGHLIGHTS

- Linoleic acid undergoes two pressure-induced phase transitions below 1.29 GPa.
- The first transition from liquid phase to solid phase takes place in 0.07–0.12 GPa.
- The second phase transition occurs in 0.31–0.53 GPa.
- Some conformational characters of the two high-pressure phases were determined.
- The pressure-induced phase transitions in linoleic acid are reversible.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 November 2013

Received in revised form 11 March 2014

Accepted 11 March 2014

Available online 25 March 2014

Keywords:

Linoleic acid

Pressure-induced phase transition

In situ Raman spectroscopy

ABSTRACT

With diamond anvil cell as a high-pressure apparatus, the in situ Raman spectra of linoleic acid from normal pressure to 1.29 GPa were measured to investigate the effect of pressure on the structural changes. In the pressure ranges of 0.07–0.12 GPa and 0.31–0.53 GPa, the significant changes in Raman spectra show that linoleic acid undergoes two pressure-induced phase transitions. Spectral analysis indicates that the polymethylene chain of linoleic acid molecule transforms from the disordered *gauche* conformation to the ordered *trans* conformation in the range of 0.07–0.12 GPa. And the polymethylene chain of linoleic acid molecule remains the ordered *trans* conformation whereas the conformation of the olefin group significantly changes and the degree of conformational order increases in the range of 0.31–0.53 GPa. The pressure-induced phase transitions in linoleic acid are reversible.

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Introduction

As one well-known essential fatty acid, linoleic acid has many wholesome physiological functions, such as preventing arteriosclerosis, lowering blood fat, decreasing the incidence of coronary heart disease, and so on [1–5]. The application of ultra high pressure

processing technology in food industry has wide perspective of development. As one of the most commonly appearing components of human diets, linoleic acid's phase transition study under pressure is very helpful to improve food preservation technology. On the other hand, the presence of two carbon double bonds in its molecules makes the phase transition very easy to occur during compression [6]. Therefore, the study on the pressure-induced phase transition of linoleic acid has important theoretical values.

So far some physical properties of linoleic acid under pressure have been investigated, such as viscosity, relative permittivity, and so on, which indicated the occurrence of the pressure-induced

[☆] Project supported by the National Natural Science Foundation of China (Grant Nos. 61006065 and 11204020).

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phase transition in linoleic acid [7,8]. However, no high-pressure Raman or any other in situ experimental research on the pressure-induced phase transition in linoleic acid has been reported. Thus, the accurate transition point and structural characterization of the high-pressure phase are still unknown.

Raman spectroscopy, equipped with a diamond anvil cell as a high-pressure apparatus, is a very powerful in situ technology for dynamically investigating the phase transition and conformational change of organic molecules [9–11]. In particular, for CH₂ rich molecules such as linoleic acid, the spectral features in the CH₂ stretching region are highly useful in spectral analysis because they dramatically change with the phase transition. In the present paper, high-pressure in situ Raman spectroscopy was used to investigate the pressure-induced phase transition in linoleic acid.

Experiment

The liquid sample of linoleic acid (C₁₈H₃₂O₂) with a purity above 99% was purchased from SIGMA Co., Ltd. High pressure apparatus used in this experiment is a Mao-Bell diamond anvil cell (DAC) with two diamonds of 500 μm culet size. The liquid sample with a small ruby chip (about 10 μm) was loaded in a hole (its diameter is 200 μm) drilled in a 250 μm thick T301 gasket pre-indented to 90 μm thickness. Then the cell was carefully pressurized in small steps and allowed to stabilize for a few minutes after each pressure change before Raman spectra were taken. The pressure calibration was carried out using the Ruby fluorescence [12]. No pressure-transmitting liquid medium was used in the experiment. We have monitored the separation between the R₁ and R₂ components of the Ruby fluorescence line which was found to remain invariant even at high pressure, indicating a negligible non-hydrostatic component.

Both Raman spectra of linoleic acid and ruby fluorescence measurements were performed with a Raman microscope (Jobin Yvon, HR800) equipped with an Ar⁺ laser (514.5 nm) and a multiple track CCD detector. The laser output power was 20 mW and the integration time was 20 s. Frequency calibration of the Raman spectrum was realized with the characteristic 520 cm⁻¹ line of silicon and the resolution was 1 cm⁻¹. Therefore, the error of pressure calibration was ±0.07 GPa. Experiments were conducted up to 1.29 GPa and were reproduced several times. All measurements were carried out at room temperature. The frequencies of the Raman bands were determined by fitting with Gaussian function.

Results and discussion

The in situ Raman spectra of linoleic acid were recorded at pressures up to 1.29 GPa at room temperature as shown in Figs. 1 and 2 and Table 1 give the frequency–pressure dependency relationships of the main modes and the pressure derivative ($d\omega/dP$) of the Raman modes in different pressure ranges as well as the mode assignments [13–19]. Several unmarked bands have not yet been assigned. In the presence of the predominant first-order diamond peak, we are not able to resolve the peaks around 1300 cm⁻¹ region. And at normal pressure no Raman band was observed in the low wavenumber region of the Raman spectrum of the liquid sample so that we cannot compare it with the corresponding bands at high pressures, thus the spectral region covering the lattice modes was absent from the Raman spectra.

It can be observed that the Raman spectra of linoleic acid totally do not change as the pressure increases to 0.07 GPa. From 0.07 to 0.12 GPa, the significant changes can be observed in the spectra, including the disappearance of two modes (ν_3 , ν_9), appearance of three new modes (ν_8 , ν_{10} , ν_{14}), and sudden changes in the slope of the frequency–pressure curves of some modes, which indicates the occurrence of one phase transition. With the increase in pressure from 0.12 to 0.31 GPa, there is only the linear shift of some Raman modes. But in 0.31–0.53 GPa, we have again found such changes in the spectra as the disappearance of ν_2 and appearance of new modes (ν_1 , ν_5 , ν_7), suggesting the occurrence of the second phase transition. Above 0.53 GPa, some bands linearly shift with the increase in pressure and no other change is observed. The above results indicate that the structural transformations of linoleic acid occur in the ranges of 0.07–0.12 GPa and 0.31–0.53 GPa, respectively.

In linoleic acid molecules, the polymethylene chains are bent at two *cis*-formed C=C bonds and separated into several parts: the big olefin group in centre and the methyl-sided and carboxyl-sided chain in two sides. To analyze the structural transformations, we separate out the modes due to methylene, olefin, carboxylic groups and the modes unassigned.

Methylene chain modes

Below 0.07 GPa, the symmetric CH₂ stretching mode (ν_{13}) remains unchanged. With the increase in pressure from 0.07 to 0.12 GPa, ν_{13} weakens and broadens, so that the accurate peak position cannot be determined. The increase in the half-width of

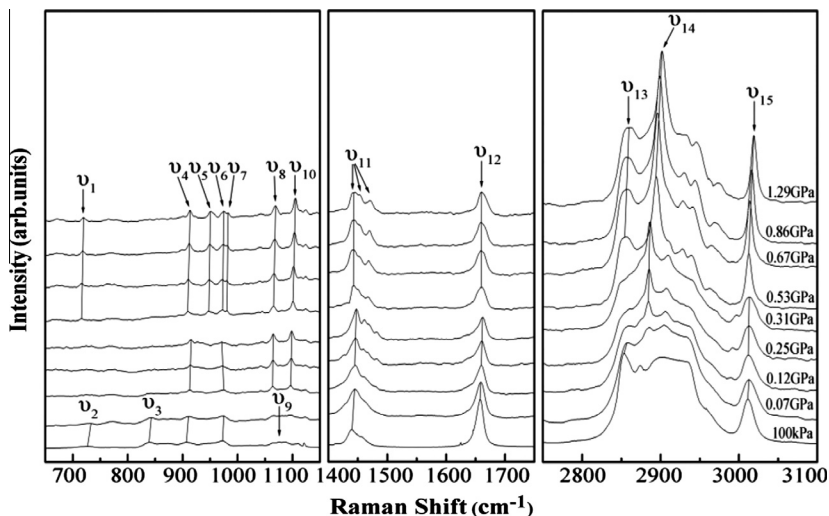


Fig. 1. The Raman spectra of linoleic acid at normal and high pressures.

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