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Phase transformation in the C form of myristic-acid crystals and DFT calculations☆

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ABSTRACT

In this study, the vibrational frequencies of myristic acid (CH_3—$(CH_2)_{12}$—COOH) were obtained using density functional theory calculations, and the results were compared with experimental Raman and infrared data. Additionally, Raman spectra of crystalline myristic acid were recorded in the 300–20 K range. Raman spectroscopy gives important insights into the effect of low temperatures on its monoclinic phase. X-ray diffraction was performed from 298 to 133 K to provide additional information about the cryogenic behavior of the crystals. These undergo a phase transformation, which was confirmed by differential scanning calorimetry through an enthalpy anomaly observed at low temperatures. Raman spectra and X-ray diffraction refinement of the cell parameters in combination with differential scanning calorimetry at low temperatures revealed slight modifications, confirming a conformational change in the myristic acid molecules involving rearrangement of dimers within the unit cell.

1. Introduction

Fatty acids have important properties that can be utilized in various areas of science and technology, in food, pharmaceuticals, cosmetics, medicine, and catalysis [1–4]. They are also fundamental to human nutrition and the functional activity of biological membranes, being present in phospholipids in the glycerol skeleton [5–7]. In addition, free fatty acids constitute the extracellular matrix of the outer layer of human skin, preventing the unregulated water loss from the body through the skin and playing a crucial role in the human physiology [8,9]. Myristic acid (14:0, tetradecanoic acid, MA) is a saturated fatty acid with the molecular structure CH_3—$(CH_2)_{12}$—COOH. Like other fatty acids, MA is abundant in nature as a constituent of several vegetables; for example, it presents 75% trimyristin of the total amount of triglycerides in palm kernel oil, coconut oil and butterfat [10]. It is a minor component in animal fats, e.g., it comprises 8%–14% of bovine milk and 8.6% of breast milk [11]. Regarding human epidemiological studies, MA is strongly associated with average serum cholesterol concentrations [12]. It is also correlated with higher cholesterol levels and is believed to be much more cholesterolemic than palmitic acid.

MA was applied as a complexing agent to produce a low-cost route to synthesizing nanorods of CdE (E = Se, Te) [13]. Additionally, a recent study reported the reduction of silver myristate (AgMy) under mild thermal reaction conditions in a polar solvent [14]. It was also used in a nanocomposite synthesis involving a eutectic mixture of capric, myristic, and palmitic acids with expanded graphite as supporting material, for potential use as a solution for energy storage systems [15]. Another interesting application of MA involves fatty acid-albumin interactions, where human serum albumin is co-crystallized with long-chain fatty acids, including MA [16–18].

Studies of selected fatty acids at extreme temperatures and pressures were recently reported. For instance, the vibrational properties of stearic acid (C form) and palmitic acid (C form) were investigated at different pressures and temperatures [19–22]. Additionally, computational calculations based on density functional theory (DFT) were performed to confirm the mode assignments of both crystals, increasing understanding of their vibrational properties [23].

While several literature reports discuss the properties of MA, there are no detailed studies on the stability of MA crystals at low temperatures that incorporate theoretical calculations using DFT to assign their vibrational modes. Our work attempts to close this gap by furnishing a

☆ This paper is dedicated to the memory of Prof. Dr. Josué Mendes Filho.

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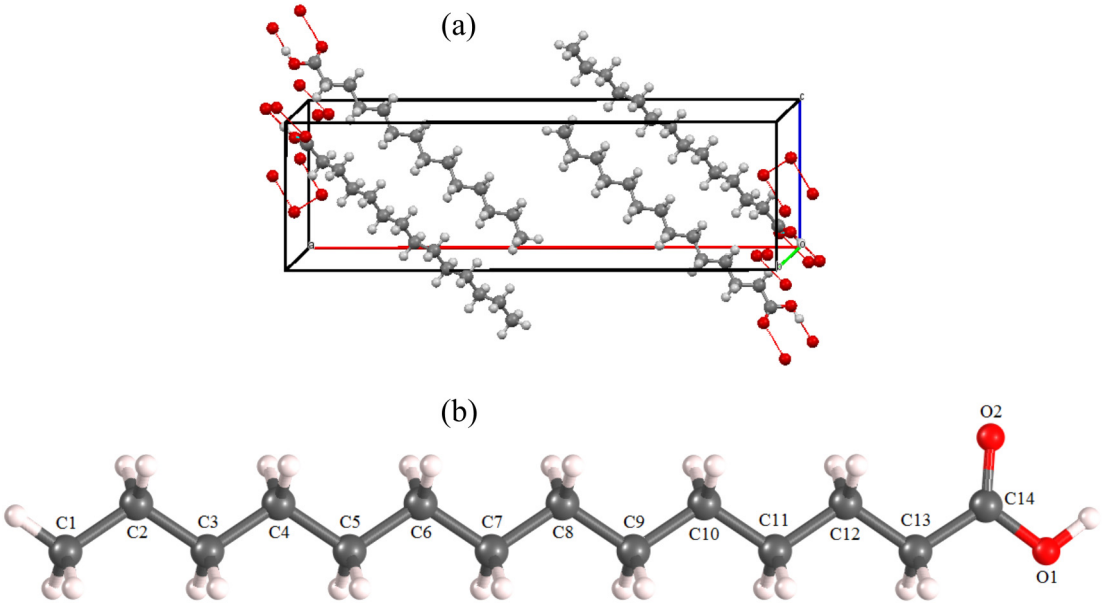

Fig. 1. (a) Molecules of myristic acid in the unit cell, (b) isolated molecule with atom numbering used in the vibrational assignments.

detailed assignment of the normal modes of MA. Additionally, our study investigates the thermal stability of MA crystals via low-temperature differential scanning calorimetry (DSC), X-ray diffraction (XRD), and unpolarized Raman scattering. Thermal analysis exhibited an enthalpy anomaly in the DSC thermogram, while the XRD patterns and Raman spectra of powder crystals presented slight changes on cooling. The results discussed below provide important evidence that all these techniques corroborate a conformational change in MA molecules in the unit cell.

2. Experimental Section

MA (>99%) was purchased from Merck (USA), and its powder crystals were recrystallized by heat treatment at 389 K and cooled naturally at room temperature. In-situ powder XRD was performed on a Philips diffractometer (PW1170), using Bragg-Brentano geometry, with an Anton-Paar TTK450 temperature chamber from 298 to 110 K. Cu–Kα radiation (λ = 1.54056 Å) was used, with the diffractometer operating at 40 kV/30 mA. Diffraction patterns were obtained in the 2θ range 3°–42°

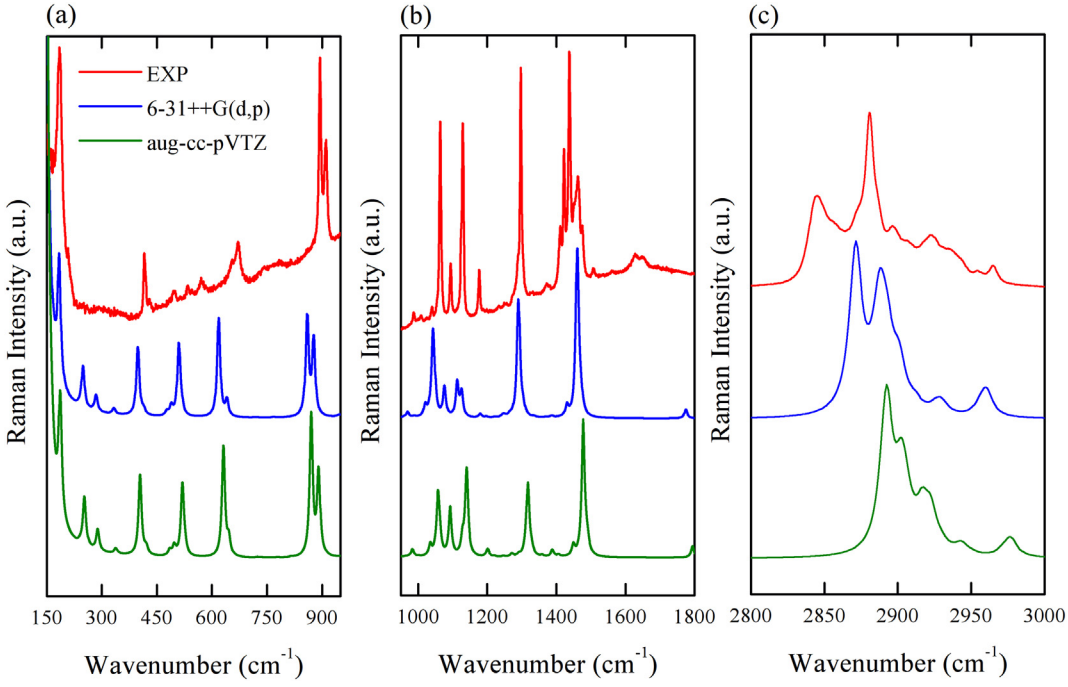

Fig. 2. Experimental and calculated (scaled) Raman scattering spectra of myristic acid under atmospheric conditions in the regions: (a) 150–950 cm^{-1}, (b) 950–1800 cm^{-1}, and (c) 2800–3000 cm^{-1} for the unpolarized scattering geometry.