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An *ab initio* and DFT study of structure and vibrational spectra of γ form of Oleic acid: Comparison to experimental data

Soni Mishra[a], Deepika Chaturvedi[a], Naresh Kumar[a], Poonam Tandon[a,*], H.W. Siesler[b]

[a] *Department of Physics, University of Lucknow, Lucknow 226007, India*
[b] *Department of Physical Chemistry, University of Duisburg-Essen, Essen D45117, Germany*

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ABSTRACT

Oleic acid (cis-9-octadecenoic acid) is the most abundant cis-unsaturated fatty acid in nature; it is distributed in almost all organisms. In this work, we present a detailed vibrational spectroscopy investigation of Oleic acid by using infrared and Raman spectroscopies. These data are supported by quantum mechanical calculations, which allow us to characterize completely the vibrational spectra of this compound. The equilibrium geometry, harmonic vibrational frequencies, infrared intensities and activities of Raman scattering were calculated by *ab initio* Hartree-Fock (HF) and density functional theory (DFT) employing B3LYP with complete relaxation in the potential energy surface using 6-311G(d, p) basis set. After a proper scaling the calculated wavenumbers show a very good agreement with the observed values. A complete vibrational assignment is provided for the observed Raman and infrared spectra of Oleic acid. In this work, we also investigate the deviation of vibrational wavenumbers computed with two quantum chemical methods (HF and B3LYP).

1. Introduction

Oleic acid (cis-9-octadecenoic acid: OA Fig. 1) is a monounsaturated omega-9 fatty acid, which means it has only one double bond between the carbons. It is a common fatty acid found in most animal and vegetable fats. The saturated form of this acid is stearic acid. Fatty acids are a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. OA is organic, monobasic acids derived from hydrocarbons. The number, geometry, and position of this double bond and the degree of unsaturation determine its physical properties. OA is one of the major components of membrane phospholipids. It contributes about 17% of the total fatty acids esterified to phosphatidylcholine, the major phospholipid class in porcine platelets. OA occurs naturally in greater quantities than any other fatty acid. It is present as glycerides in most fats and oils. High concentrations of OA can lower cholesterol levels in blood. OA is known as an efficient penetration enhancer; particularly for lipophilic drugs (Franceur et al., 1990). OA is also the major unsaturated fatty acid of stratum corneum (SC), the outermost layer of human skin. SC lipids bilayers consist mainly of three fractions namely, ceramides, free fatty acids and cholesterol and its derivatives. It is known that the degree of unsaturation of fatty acid chains in membrane lipids has profound effect on membrane fluidity. Thus, OA, a relatively abundant component of SC has been proposed to modulate the properties of the stratum corneum lipid bilayer (Barry, 1987; Lieckfeldt et al., 1994). It is assumed that OA 'fluidizes' the close packing of the bilayer due to the kink structure of its hydrocarbon chain residue (Walker and Hadgraft, 1991). Generally, it is known that OA acts as an efficient penetration enhancer for percutaneous drug delivery (Franceur et al., 1990; Naik et al., 1995; Kalbitz et al., 1996; Schneider et al., 1997).

OA crystallizes in three forms called α, β and γ (Kaneko et al., 1998). The crystal structures of the γ and β phases have been reported (Abrahamsson and Ryderstedt-Nahringbauer, 1962; Kaneko et al., 1997) and vibrational spectra of all the three known phases of crystalline OA are reported in the literature (Kobayashi et al., 1986; Kim et al., 1988). It was found that the solid–solid phase transition between γ and α is of an order–disorder type accompanied by a conformational disorder in the methyl-sided alkyl chain segment (Kobayashi et al., 1986).

In the γ phase the unit cell is pseudo-orthorhombic (space group $P2_1/a$) with four molecules (or two hydrogen bonded dimers) per unit cell. The C=C bond assumes the *cis* form and the hydrocarbon type chains on both sides of the C=C bond take the all-tans conformations. The molecules are bent at the *cis*-double bond. The internal rotation angles of the C—C bonds linked to the C=C bond are +133° and −133° respectively. The γ phase transforms to the α phase reversibly at −2.2 °C on heating, accompanying a selective conformational disordering in the methyl terminal chains. Tandon et al. (2000) studied the γ to α transition in OA using X-ray diffrac-

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* Corresponding author. Tel.: +91 522 2782653; fax: +91 522 2740840.
E-mail address: poonam_tandon@hotmail.com (P. Tandon).

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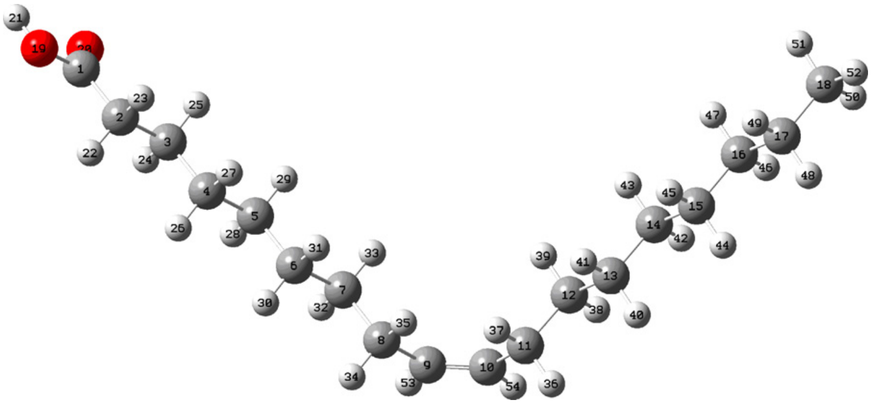

Fig. 1. Optimized structure of Oleic acid.

tion and FT-Raman spectroscopy. They reported that during this transition, the conformation of the olefin group changes from skew-*cis*-skew' to skew-*cis*-trans and this change results in the different orientation and subcell packing of the methyl-sided fragments, whereas the orientation and packing of the carboxyl-sided chain fragments remains the same. In the γ phase the methylene chains on both sides of double bond form a modified $O'_{||}$ subcell. During the γ to α transition only the subcell of methyl-sided chain transforms to the $M_{\perp}$ one, while the carboxyl-terminal chain keep the modified $O'_{||}$ subcell.

OA is one of the major components of oils (olive, castor and peanut oil) used in pharmacy and medicine. OA is widely used in pharmaceutics as an ingredient of semisolid formulation, e.g. ointments, lotions, emulsions and gels. OA is also known as Red Oil, with the quite different and moderately toxic, “Turkey Red Oil”. It is a component of many edible foods. However, ingestion of large amounts of OA would produce unpleasant gastrointestinal disorders.

Lipids are the important class of biomolecules and are responsible for the stability of several biological systems. They are hydrophobic in nature, the major source of cellular energy and function in living organism in many specific fields such as antigen, receptors, sensors, electrical insulators and biological detergents. Many hormones are lipids, e.g. steroid hormones. They are the important constituents of bio-membranes. They also play an important role in human afflictions such as atherosclerosis, obesity, gallstone disease, etc. In industries they are used as lubricant in cosmetics and pharmaceutic.

Spectroscopic techniques are one of the most powerful tools to study the dynamical behavior of biological systems at microscopic level. Biological system, no doubt are dynamical in nature and the characterization of dynamical changes is best done through correlation function which are related to inverse Fourier transform of spectral features. In this context the Raman spectroscopy provides very rich data. Even characterization of polymorphic form can be conveniently done by polarized Raman study. Infrared and Raman techniques have been widely used to study the dynamical behavior of large number of biomolecules in studying energetic and thermal behavior apart from vibrational dynamics.

For complete understanding of the vibrational spectra, in the present communication, we report a normal mode analysis of the γ form of OA using density functional theory. Reduction in the computed harmonic vibrations, though basis set sensitive are only marginal as observed in the DFT values using 6-311G (d, p). In continuation to our work on spectroscopic studies of OA (Tandon et al., 2000; Misra, 2006) in the present communication we have calculated the equilibrium geometry, harmonic vibrational wavenumbers, electrostatic potential surfaces, absolute Raman scattering activities and infrared absorption intensities by HF and DFT with B3LYP functionals having extended basis set 6-311G (d, p). The present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with a better wavenumber accuracy, *ab initio* HF and density functional theory (DFT) calculations have been performed to support our wavenumber assignments. On comparing the results of both methods we see that the predicted wavenumbers by HF are larger than those by B3LYP. The molecular structure of the γ form of OA is shown in Fig. 1. The optimized structure of OA is very close to the crystalline structure reported by Abrahamsson and Ryderstedt-Nahringbauer (1962). The total number of atoms in this molecule is 54; hence it gives 156(3N-6) normal modes. The calculated vibrational spectra were analyzed on the basis of the potential energy distribution (PED) of each vibrational mode, which allowed us to obtain a quantitative as well as qualitative interpretation of the infrared and Raman spectra. We have also used these results to interpret the changes that take place during γ to α transitions in OA.

2. Experimental details

2.1. Fourier transform infrared spectroscopy

OA with purity above 99% was purchased from Sigma Chemical Co. (St. Louis, MO, USA). The FT-IR spectra are recorded at Bruker IFS 88 FT-IR spectrometer, with a spectral resolution of 4 cm^{-1}. Typical spectra were recorded at −10 °C (γ phase) and 0 °C (α phase) with 16 scans. The observed FT-IR spectra are shown in Fig. 2.

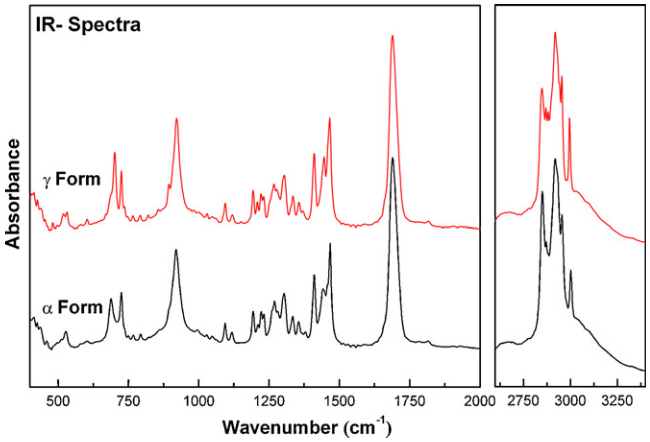

Fig. 2. Comparison of infrared spectra of α and γ form of Oleic acid.