P: ISSN NO.: 2394-0344 RNI No.UPBIL/2016/67980 VOL-3* ISSUE-12* (Part-1) March- 2019
E: ISSN NO.: 2455-0817 *Remarking An Analisation*

DFT Analysis of Temparature Depent Micro Raman Spectroscopy and a Calamitic Crystalline System 4-Undecyloxy Benzoic Acid

Wakil Ray
Assistant Professor,
Deptt. of Physics,
D.B.S.D. Degree College,
Kadna, Saran
Chapra, Bihar

Abstract

We have recorded temperature dependent micro-Raman spectra from room temperature to 140®c of a calamitic crystalline system 4-undexyloxy benzoic acid (UDBA). The 4- decyloxy benzoic acid (4DBA) molecule has a long alkoxy chain. The phase transition temperatures of UDBA were reported by differential scanning calorimetry (DSC) study. [1] J.D Bunning et al [2] has earlier proposed the possible dimer structure in crystal phase of 4DBA.

Keywords: Micro Raman Spectroscopy, DFT Calculation and Benzoic Acid.

Introduction

Liquid crystals have optical and electrical anisotropy like crystalline state and molecular mobility and fluidity like liquid state [1]. The LC molecules contain standard structural elements called rigid core, spacers, leteral groups and flexible terminals. [2]

The LC phase transition in liquid crystalline system is associated with the changes in molecular arrangement as well as in the molecular geometry. Raman spectra result from molecular vibration and contain structural as well as dynamical information The structural changes often cause changes in the symmetry and polarizability of the molecule, which are reflected in the measurable parameters of the Raman Marker bands.] However, subtitle changes in the line width, peak position and intensity of Raman marker bands are also useful to study the molecular dynamics during the transition.

Objective of the Study

In this work our main objective is to characterized crystal phase trasition more precisely at molecular level through temperature dependent micro –Raman study DFT calculation.

In this work we have recorded temperature dependent micro Raman spectra from room temperature to 140°C of a calamitic liquid crystalline system 4-undecyloxy benzoic acid (UDBA). The 4 decyloxy benzoic acid (4DBA) molecule has a Phenyl ring with a long alkoxy chain. The phase transition temparatures of UDBA were reported by differential scanning calorimetry (DSC) study [3]. J.D. Bunning et al [4] has dimer proposed the possible climer structure in crystal phase of 4DBA.In this work our main objective is to characterize this liquid crystal Phase transition more precisely at molecular level through temperature dependent micro –Raman study DFT calculation. We have optimized monommer as well as dimer of UDBA by density function theory.The interpretation of the temperature. Dependent Raman Spectra needs accurate vibrational assignments which were done with the help of calculated Raman spectra and potential energy distribution (PED)[5]. The change at low wave number modes, C-H in plane deformation and C-O modes belonging to the alkoxy Chain and modes phenyl groups and CO OH group are explained in terms of change in intra and inter-molecular intractions at phase transitions.

Experimentals Details

Raman spectra of UDBA were recorded on a micro Raman setup from Renishaw,UK equipped with a grating of 2400 lines /mm and a peltier cooled CCD.

The accumulation time for one window was selected as 60 seconds and five spectra were accumulated in each window. In one window approximately 800 cm^{-1}range was covered. The 514.5mm line of

Ar+ laser was used as an excitation source. The laser power was kept very low (10 mW) to avoid laser heating. The stage containing the sample was placed on an automated X-Y stage below the Olympus long distance 50x microscope objective. The reported accuracy in the measurement of temperature is #0.1k.

Theoretical

The quantum chemical calculations were performed DFT with technique Gaussian 03 program package. The method used for this DFT that the mixes the Becke three hybrid functional for exchange part and Lee Yang and parr hybrid functional for correlation part (B3LYP)[6]. with appropriate level basic set 6-31G (d). The Gaussion-03 out put gives the Raman activity which comes from the second derivative of the polarizability with respect to the normal coordinate [7]. Raman intensity is propertional to the Raman Scattering Cross section $d\sigma / d\Omega$, witch is given by the expression

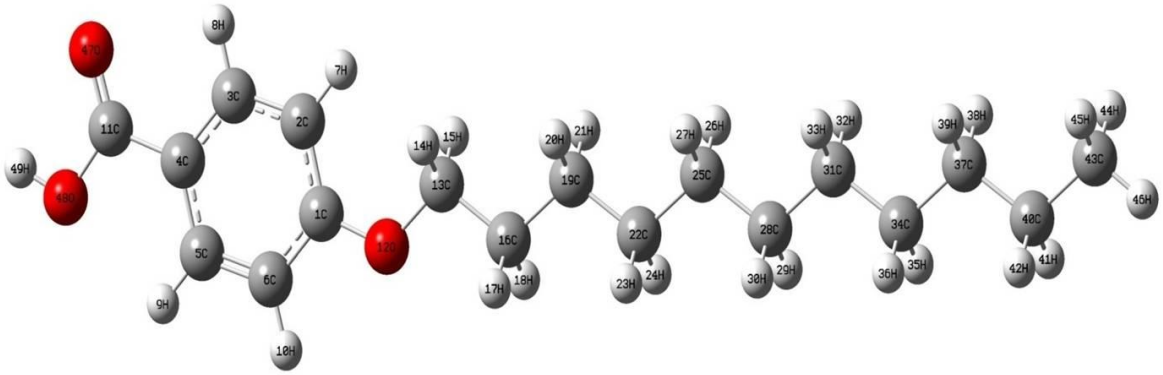
$$\frac{d\sigma}{d\omega} = \frac{2^4\pi^4}{45}\left[\frac{(v_0 - v_j)^4}{1-\exp\left(\frac{-hcv_j}{kT}\right)}\right]\frac{h}{8\pi^2 c v_j}S_j$$ whore Vo is the excitation frequency. Vj is the harmonic vibrational wavenumber.

Result and Discussion

The crystalline arrangement of UDBA is triclinic and with point group P_1[8]. The XRD studies of UBDA have suggested that the molecules are paired by hydrogen bonding between carboxyl groups. The optimized structures of monomer have been calculated and shown in fig.- (I)

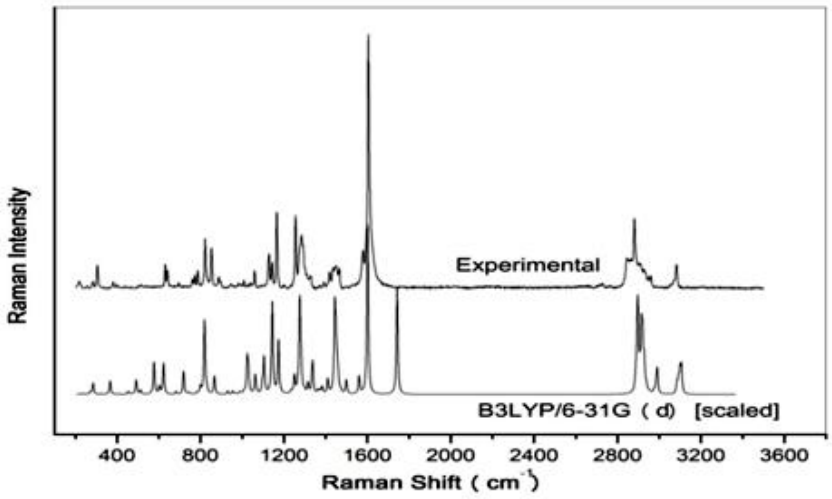
Figure 1

Optimized Structure of UDBA Calculated Using DFT Method Employing B3LYP/6-31(D) Functional.



The calculated Raman spetra of monomer along with the experimental spectra at room temperature in the region 300-3300cm^{-1} are shown in fig.(2).

Figure 2 The Experimental and DFT /B3LYP Derived Raman Spectra at Room Temperature.



The disagreement in the calculated and experimental is due to the fact that the calculated spectra are for single unit. The Vibration assignment has been done for further meaningful discussion in temperature dependent Raman study in next section. The vibrational assignment of experimentally observed Raman bands has been shown in table-1.

Table 1
Vibrational assignments of some Raman marker modes of UDBA

Scaled Harmonic wavenumber (cm^{-1})	Observed Raman wavenumber (cm^{-1})	Assignment[a]
718	786	β (O_{47}–C_{11}–O_{48}) + v(C_4–C_{11}) + β_{IN} (C–C of ring)
798	822	W(C_2–H_7) -W(C_3–H_8) + W(C_6–H_{10})
819	852	β(ring) + v(ring) + v(C_1–O_{12})
866	886	δ(R(C–C)) + v(C_1–O_{12}) + v(C_1–C_2) + v(C_1–C_6) + v(C_3–C_4) + v(C_4–C_5)
1104	1128	S(CH_2 groups of alkoxy chain) + v(C–C of the alkoxy chain)
1144	1143	β_{IN} (C–H of ring) + β(C_{11}–O_{48}–H_{49})+ v(C–C of ring)
1174	1165	β_{IN} (C–H of ring) +β (C_{11}–O_{48}–H_{49})+ v (C–C of ring)
1560	1578	v(C-C of ring) + β_{IN} (C–H of ring)
1601	1604	v(C-C of ring) + β_{IN} (C–H of ring)

[a]β: bending, v: stretching, W: wagging, δ: deformation, S: scissoring, ring: ring($C_1C_2C_3C_4C_5C_6$)

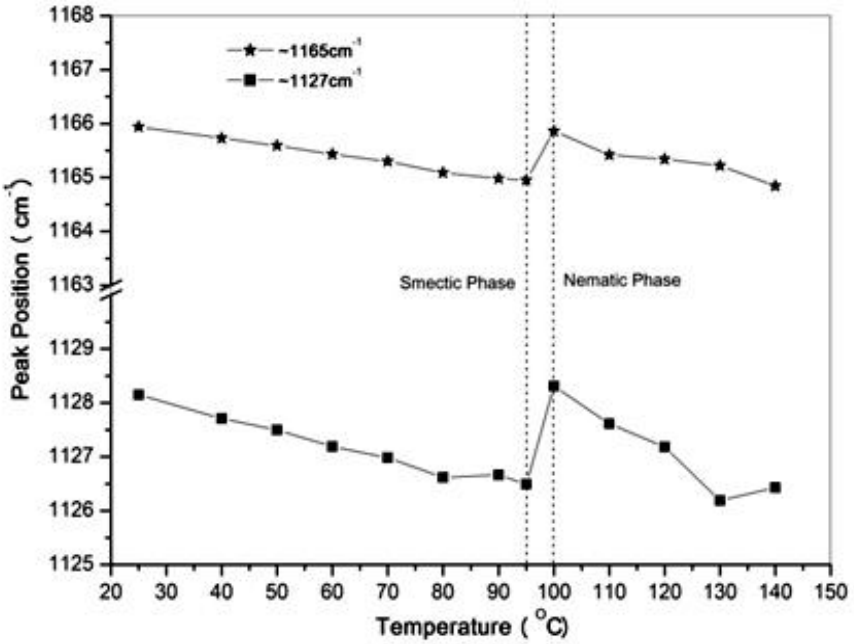
The DSC study of UDBA have revealed Semitic (s) mimetic N and nimetic (H) isotropic (1) in the temperature ranges 94-121°C and 121-143°C respectively. The temperature dependent Raman spectra were recorded experimentally in the region 300- 2000cm^{-1}. but for clear presentation and systematic discussion we have divided the spectra into three regions 730-925cm^{-1},1080-1220$cm^{-1}$and 1500-1720cm^{-1}

The temperature dependent Raman spectra of UDBA in the region 730-925cm^{-1} at thirteen different temperature in shown in fig-(3).

The vibrational assignment of major band at 786,822 ,852 and 886cm^{-1} are given in table (1).

The Raman spectra in region 1080-1220cm^{-1} at different temperature is shown in fig-(4). The band of 1128cm^{-1} is due to scissoring motion of CH2 groups of alkoxy chain, and c-c stretching aloxy chain, variation of peak position of the 1128cm^{-1} band with temperature is shown in fig-(5).

Figure 5
Variation of Peak Position of The 1128 And1165 Cm^{-1} Bands with Temperature.



The shift of the band ot 1128cm¯1 is forwards the higher wave number side between 95-100°C is due to decrease in the inter molecular interaction of the alkoxy chain of UDBA.

The Raman spectra of UDBA in the region 1500-1700cm^{-1} as shown in fig-(6) . The 1578 and 1604cm^{-1}bands both shifted lower ot transition due to decrease in intermolecular interaction.

This bands is due to C-O stretchin band. This may be due to change co-planarity of the phenyl group of smectic-Nematic transition , the C=O bond becomes more symmetrical and polarized on increasing the temperature results increase in Raman Intensity.

Conclusions

The phase transitions of calamitic liquid crystalline system UDBA are characterized by temperature dependent Raman Spectrascopy and able to gain in an idea about the intermolecular interaction changes in smectic liquid and nematic

liquied. The monommer structure are optimized with the help of DFT method.

References

1. *D. Demus, J. Goodby, G.W. Gray, H.W. Spiess, V. Vill, Physical properties of liquid crystals, Wiley-Vch Weinheim, 1999, pp. 44-46.*
2. *P.J. Collings, M. Hird, Introduction to liquid crystals chemistry and Physics, Taylor and Francis, London, 1998.*
3. *N.A. Clark, D. Coleman, J.K. Maclennan, Liq Cryst. 27 (2000) 985-990.*
4. *K.H. Kim, K. Ishikawa, H. Takezoe, A. Fukuda, Phys. Rev. E 51 (1995) 2166-2175.*
5. *S.K. Dash, R.K. Singh, P.R. Alapati, A.L. Verma, J. Phys. Condens Matter. 9 (1997) 7809-7815.*
6. *M. Nollmann, P. Etchegoin, Phys. Rev. E 61 (2000) 5345-5348.*
7. *K. Vikram, P.R. Alapati, R.K. Singh, Spectrochim. Acta Part A 75 (2010) 1480-1485.(2010) 54–62.*
8. *K. Vikram, N. Tarcea, J. Popp, R.K. Singh, Appl. Spectrosc. 64 (2010) 187-194.*
9. *K. Druzbicki, E. Mikuli, M. D. Ossowska-Chrusciel, Vib. Spectrosc. 52 (2010) 54–62.*
10. *Sigma Aldrich on line catalogue, webpage: http://www.sigmaaldrich.com/india.html.*
11. *J.D. Bunning, J.E. Lydon, JCS Perkin II. 22594 (1979) 1621-1626.*
12. *R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W.L. Hovell, R. Gilliland, Gauss View 03, R. Gilliland, Semichem, Inc.: Shawnee Mission, 2003.*
13. *J. M. L. Martin, C. Van Alsenoy,*