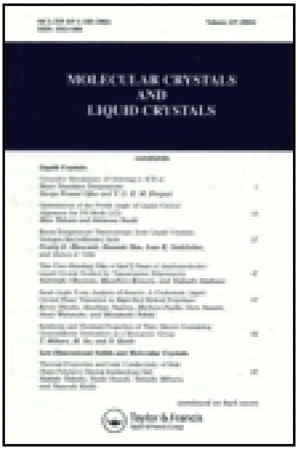

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The Structural Peculiarities of a Chiral Liquid Crystal in Raman Spectra Contours

Shimei Jiang [a] , Weiqing Xu [a] , Yanqing Tian [b] , Ying Wu [a] & Bofu Li [a]

[a] Key Laboratory of Supramolecular Structure and Spectroscopy, Jilin University, ChangChun, 130023, P.R. China

[b] Department of Chemistry, Jilin University, ChangChun, 130023, P.R. China

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THE STRUCTURAL PECULIARITIES OF A CHIRAL LIQUID CRYSTAL IN RAMAN SPECTRA CONTOURS

SHIMEI JIANG [1] , WEIQING XU [1] , YANQING TIAN [2], YING WU [1],
BOFU Li [1]
[1] Key Laboratory of Supramolecular Structure and Spectroscopy,
Jilin University , ChangChun , 130023 , P.R.China
[2] Department of Chemistry , Jilin University , ChangChun , 130023, P.R.China

Abstract Fourier transform (FT) Raman spectroscopy is shown to be a very powerful and valuable technique for the analysis of liquid crystal materials. By temperature-variable FT-Raman spectroscopy , we found a new crystalline phase of a chiral liquid crystal compound and studied the intermolecular interaction of the compound in its smectic phases (S_A,S_C* ,S_B) .

INTRODUCTION

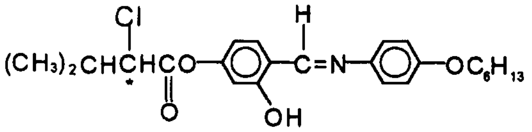
Generally speaking , the properties of liquid crystals depend on the structure of liquid crystal molecules, so the study of the relationship between molecular structure and the properties of liquid crystals is very important and interesting .Vibrational spectroscopy has proved to be useful for studying the structure and physical properties of liquid crystals.Temperature-Variable FT-Raman Spectroscopy is one of the most powerful tools for studying the molecular environment of liquid crystals . [1,2]

In our previous paper , [3] we presented the synthesis of this new chiral liquid crystal compound. And the differential scanning calorimetry (DSC) , optical polarizing microscopy and X-ray diffraction measurements were used to study the phase transition temperatures and behaviour. The results reveal that this compound shows the following transition[3] :

$$\mathrm{Cr} \xrightarrow{76^\circ\mathrm{C}} S_C^* \xrightarrow{90^\circ\mathrm{C}} S_A \xrightarrow{103^\circ\mathrm{C}} \mathrm{I} \quad \text{(upon heating)}$$

$$\mathrm{I} \xrightarrow{102^\circ\mathrm{C}} S_A \xrightarrow{90^\circ\mathrm{C}} S_C^* \xrightarrow{59^\circ\mathrm{C}} S_B \xrightarrow{51^\circ\mathrm{C}} \mathrm{Cr} \quad \text{(un cooling)}$$

In this paper, we reported the structural studies of this compound by temperature-variable FT-Raman spectroscopy . Its chemical structure is :



On cooling, the results obtained by Raman spectroscopy is corresponding well with the conclutions of DSC and optical polarizing microscopy[3] , the investigated compound exhibited S_A , S_C^* and S_B phases . But upon heating , we observed two crystalline phases by Raman spectroscopy .

EXPERIMENTAL

The sample was analysed in the solid state using a Bruker RFS-100 FT-Raman instrument. The sample was scanned 500 times in order to obtain a good signal-to-noise. The output laser power is 50mw. Sample was mounted as powder in a hot stage. The rate of temperature changing is 2°C/min in both heating and cooling processes. In this cycle before Raman spectra registration the sample was kept at each temperature point for 15 minutes.

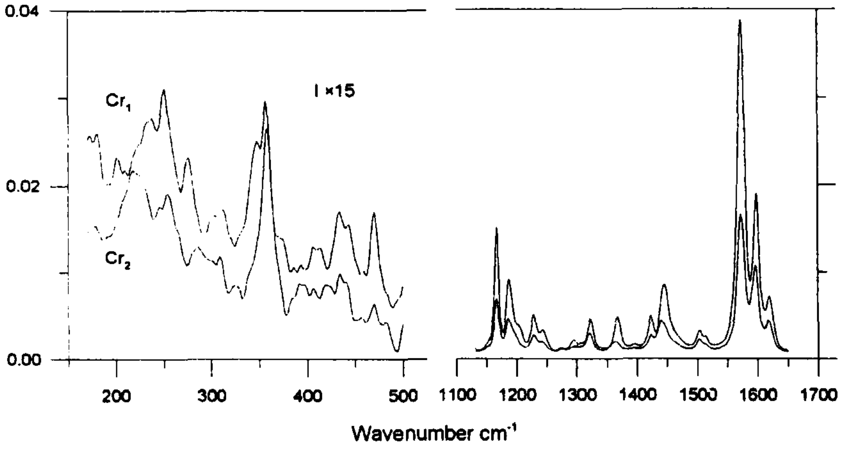


FIGURE 1 FT-Raman spectra of Cr_1 phase (above curve) and Cr_2 phase (below curve) in 150-500 cm^{-1} and 1130-1650 cm^{-1} regions .

RESULTS AND DISCUSSION

When heating the new sample , below the Cr-Sc* transition temperature we observed a clearly change in Raman spectra, see Figure 1. The most obvious changes are the two bands at 1446cm^{-1} and 1367cm^{-1}. The band 1446cm^{-1} which is assigned to the asymmetric CH_3 deformation and the CH_2 scissors deformation shifted to 1441cm^{-1} , the band 1367cm^{-1} the symmetric CH_3 deformation shifted to 1362cm^{-1} and became broad in shape and decreasing in intensity. [4] These changes indicate that the molecule vibrations and the interactions between molecules are all changed . But in the studies of phase behaviour by DSC and optical polarizing microscopy [3], we don't find this kind of phase transition. So we think it does not a crystalline-liquid crystal phase transition , this transition occurs between two crystalline phases, i.e. $Cr_1 \rightarrow Cr_2$ .Continuing heating , one after another we observed the structure peculiarities of the S_C* , S_A and isotropic (I) , respectively . So now the compound shows the following transition upon heating: $Cr_1 \rightarrow Cr_2 \rightarrow S_C{}^* \rightarrow S_A \rightarrow I$.

When cooling the compound from the isotropic phase , by Raman spectroscopy we obtained the structure peculiarities of the following phases transitions: $I \rightarrow S_A \rightarrow S_C{}^* \rightarrow S_B \rightarrow Cr_2$. Generally speaking ,in smectic A phase the lateral distribution of the molecules within each layer is however random , and the molecules in the S_A layers are able to rotate freely about their long axes.[5] In Sc phase there is no long range correlation between the layers, the constituent molecules are randomly packed within the layers but the long axes of the molecules are tilted with respect to the layer normal[5] (For this compound the tilt angle in the S_C* phase is in the range of 2° to 30°).[3] The molecules rotate about their long axes. In S_B phase the molecules are still arranged in layers, but the molecular long axes are shown in a hexagonally close-packed array. So the rotation of a individual molecule is confined, thus the molecular rotation must be completely cooperatively. [5] That is to say, un cooling from S_A to S_C* then to S_B and Cr_2 , the intermolecular interaction of molecules is becoming stronger and stronger and the freedom degree of molecular motions is becoming smaller and smaller.

Now let us look at the Raman spectra of the investigated compound in the 200-450cm^{-1} region, see Figure 2. The bands in this region are associated with a group motions of the hexyl side groups, most probably the all trans accordian band .[6] These bands originated from the CCC deformations containing some C-C stretching, it may lead to chain stretch out and draw back.[4] Following the decreasing of the freedom degree of the molecular motions , we observed the changes in the intensities of these bands . Figure 3 illustrated the temperature dependencies of integral values of bands 218cm^{-1} and 418cm^{-1} . In the whole thermal circulation the band at 639cm^{-1} which we assigned to C-Cl stretching model [6] remains no change .We use this band as a internal sign , so the integral values in Figure 3 are not the absolute values of those bands , there are only the relative values , i.e. I_{218} / I_{639} and I_{418} /I_{639} . From Figure 3 we can say that the bands at 218cm^{-1} and 418cm^{-1} are the signs for the freedom degree of the molecular motions . The shifts and the appearances of new bands at the liquid crystal-crystal transition indicate that the enviroment of the molecule is changed, i.e.the intermolecular interaction is modified.

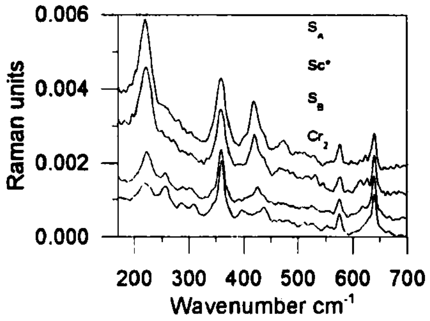


FIGURE 2 FT-Raman spectra of S_A , Sc*, S_B and Cr_2 phases in region 170-700cm^{-1} .

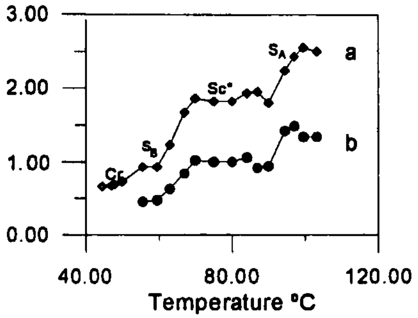


FIGURE 3 Temperature dependencies of relative integral value : $a = I_{218}/I_{639}$, $b = I_{418}/I_{639}$.

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