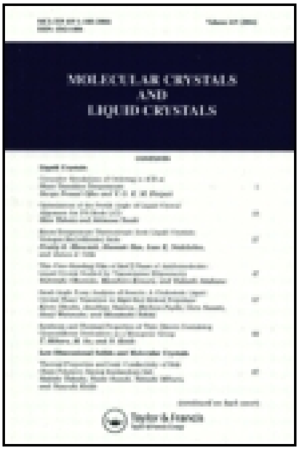

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Roger Chang [a]
[a] Science Center, North American Rockwell Corporation, Thousand Oaks, California, 91360

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Characterization of Liquid Crystals: The Low Frequency Raman Scattering of Cholesteryl Propionate Nonanoate and Palmitate

ROGER CHANG

Science Center
North American Rockwell Corporation
Thousand Oaks, California 91360

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Abstract—The low frequency Stokes Raman spectra of polycrystalline cholesteryl propionate, nonanoate and palmitate at room temperature are reported. Two high intensity peaks (18 and 26 cm^{-1}) and two lower intensity peaks (52 and 60 cm^{-1}) were found in all three materials. The bands were shown to be very sensitive to the degree of short range ordering. It is tempting to associate the 18 cm^{-1} band with the LO mode and the 26 cm^{-1} band with the TO mode of the intermolecular vibrations.

1. Introduction

Raman spectroscopy of molecular solids is concerned with the phenomenon of a change of frequency when light is scattered by the solid, the shift corresponding to vibrational and/or rotational transitions of the scattering molecule. Such frequencies, particularly associated with those transitions arising from molecule–molecule interactions, lie in the far-infrared and microwave spectral region. In Raman spectroscopy they can be observed (as frequency shifts) in the more convenient visible region. With the advent of lasers and modern spectrometer techniques, the sensitivity of detection and resolution are much improved. The more recent work of Amer *et al.*⁽¹⁾ on *p*-azoxydianisole is a good example.

There are several reasons to do Raman work on liquid crystalline materials. As has already been discussed by Amer and coworkers, Raman scattering can be used conveniently to probe phase transitions and short range ordering, and combination of Raman studies with other methods of investigation, such as NMR, etc., may yield a better picture of intermolecular interactions in liquid crystalline materials. More important, analogous to the relationships between the elastic constants and lattice frequency modes in inorganic crystalline solid,(2) there must exist similar relationships between the Frank(3) *elastic coefficients* and the low frequency Raman modes corresponding to intermolecular vibrations in liquid crystalline materials. Although theories concerning the latter have not yet been developed, such development in light of the dynamics of intermolecular vibrations should be straightforward. It is with this motivation in mind that we have pursued the low frequency Raman studies of the cholesteryl esters, which hopefully may turn out to be one of the most powerful methods in direct evaluation of the material parameters needed for the prediction and understanding of the mechanism of light scattering(4) and electro-optic properties of liquid crystalline materials.

2. Experimental Method

The experimental setup was the same as that described by Landon and Porto,(5) with an argon laser (model 52, Coherent Radiation Laboratories) as the light source and a cooled ITT FW130 photomultiplier as the detector. Three sister compounds, cholesteryl propionate, nonanoate and palmitate,† were studied. They were purchased from the Eastman Kodak Company without further purification. It will be shown later that the low frequency Raman spectra in the 10 to 100 cm^{-1} region for the three esters studied were, within the limits of experimental error (± 1 cm^{-1}), *identical in respect to the frequency shifts*. This suggests that, in as much as the identification of the frequencies of the low energy Raman bands is concerned, the presence of small amounts of impurities does not seem to be critical. All the measurements were made at room temperature of the virgin material except in a few cases, where the spectra were searched after the material was heated to the isotropic liquid phase and cooled rapidly at room temperature to the smectic and disordered crystalline states.

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† Their chemical formulae are, respectively, $CH_3CH_2COOC_{27}H_{45}$, $CH_3(CH_2)_7$-$COOC_{27}G_{45}$ and $CH_3(CH_2)_{14}COOC_{27}H_{45}$.

3. Data and Results

Figure 1 is an actual trace of the low frequency Stokes bands (marked *A*, *B*, *C* and *D*) for cholesteryl nonanoate. The bands have frequency shifts of 18(± 1), 26, 52 and 60 cm^{-1} and intensity ratios of 1, 1.8, 0.4 and 0.2, respectively, when excited at room temperature

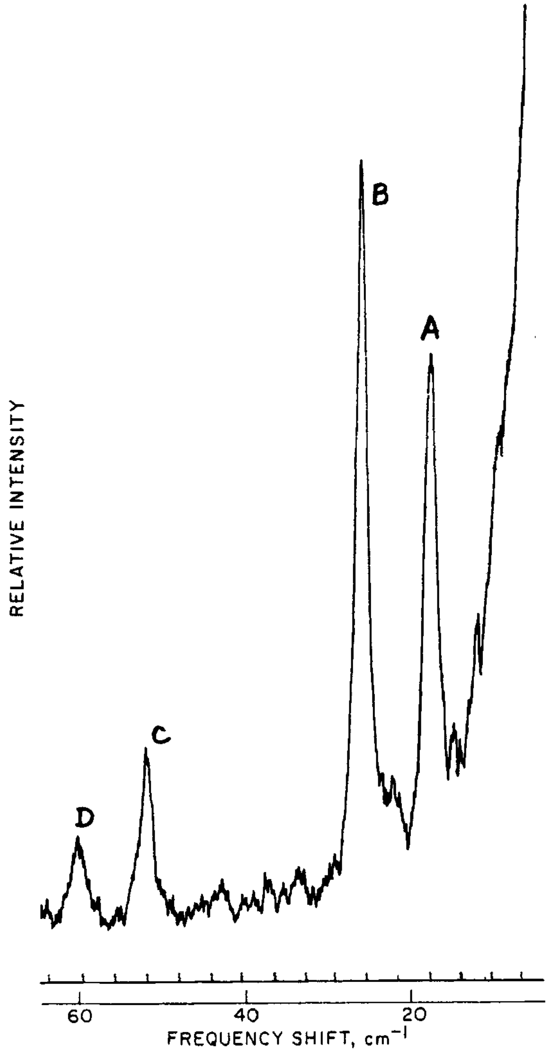

Figure 1. Low frequency Raman spectra (Stokes) of cholesteryl nonanoate at room temperature (excitation wave length 5145 Å).

with the 5145 Å beam. In order to show that the bands seen in Fig. 1 are not ghosts, measurements were repeated with the 4965 Å and the 4880 Å beams. The 4965 Å and 4880 Å beams yielded the same Stokes bands having, within the limits of experimental error, identical frequency shifts.

The frequency shifts and intensity ratios of the low frequency Stokes bands at room temperature for the three sister compounds studied, cholesteryl propionate, nonanoate and palmitate, are summarized in Table 1.

TABLE 1 Low Frequency Room Temperature Raman Scattering of Cholesteryl Propionate, Nonanoate and Palmitate (Excitation Wave Length 5145 Å)

	PROPIONATE		NONANOATE		PALMITATE	
Band Identification	Freq. Shift cm^{-1}	Intensity Ratio	Freq. Shift cm^{-1}	Intensity Ratio	Freq. Shift cm^{-1}	Intensity Ratio
A	18 ± 1	1.0	18 ± 1	1.0	18 ± 1	1.0
B	26	2.2	26	1.8	26	1.5
C	52	0.5	52	0.4	52	0.3
D	60	0.2	60	0.2	60	0.15

It is interesting to note from Table 1 that the frequency shifts for the three materials (differing slightly in the sidechain length) are, within the limits of experimental error, identical. This suggests that the low frequency bands are most likely associated with intermolecular vibrations dependent principally on the cholesteryl part of the molecule which is identical for the three materials studied and is independent of the side chain length $CH_3(CH_2)_n-$, where n equals 1, 7 and 14, respectively, for proportionate, nonanoate and palmitate.

Figure 2 reproduces the low-frequency Raman scattering traces for cholesteryl nonanoate when it was rapidly cooled from the isotropic liquid phase and measured immediately at room temperature (Fig. 2a) and after standing at room temperature for 15 minutes (Fig. 2b) and 30 minutes (Fig. 2c). The peaks have practically disappeared immediately after quench from the isotropic liquid phase. The peaks A and B returned after standing at room temperature for 15 to 30 minutes but are of much lower intensity in comparison with the same peaks A and B shown in Fig. 1. A comparison of the results

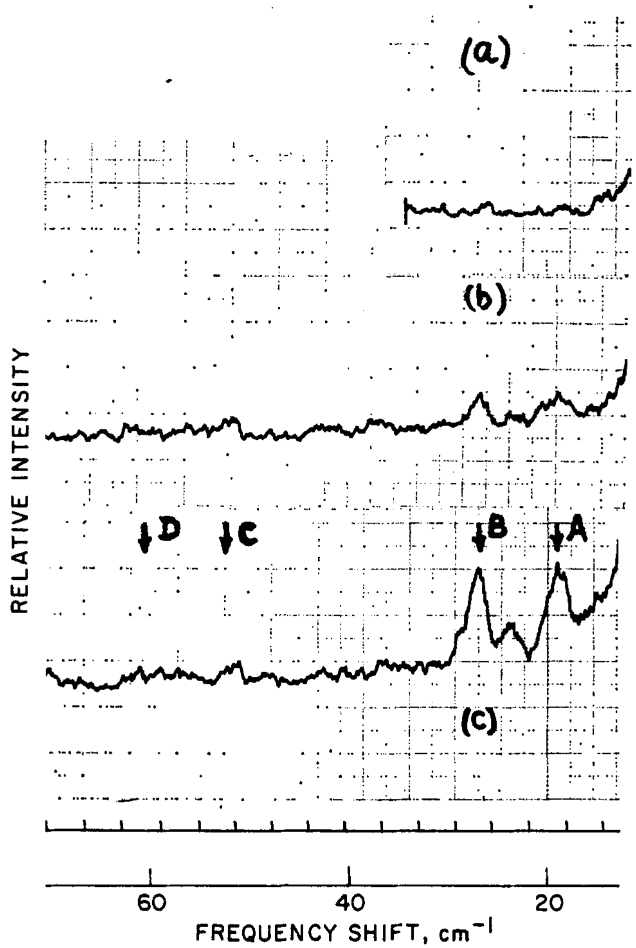

Figure 2. Same as Fig. 1, after rapid cooling to room temperature from the isotropic liquid state and measured (a) immediately (b) after standing 15 minutes (c) after standing 30 minutes at room temperature.

shown in Figs. 1 and 2 suggests that the low frequency Raman bands are very sensitive to the degree of short range ordering of the material.

4. Discussion

The association of the low-frequency Raman modes of complex organic crystals with intermolecular vibrations has been mentioned briefly in literature.(1,6,7) As a first order approximation, one may treat the molecules as if they behave as atoms. The crystal structure of cholesteryl iodide (a sister compound of the cholesteryl esters used in this study) was reported by Carlisle and Crawfoot(8) to be monoclinic, space group P_{2_1}/C_2^2, and containing two molecules per unit cell. Assuming that the cholesteryl esters crystallize in the same monoclinic form as the iodide, one may simply treat the low-frequency Raman modes observed in this study as if they were originated from lattice vibrations of a monoclinic crystal containing two atoms per unit cell: There are three allowed Raman modes, one LO and two TO, the latter degenerate. Therefore, two Raman bands are expected which may well correspond to the A and B bands shown in Fig. 1. Since in cholesteryl esters the electrostatic forces are expected to predominate over the anisotropy in interatomic forces, it is further anticipated according to the argument put forward by Loudon(9) that band A is probably associated with the LO mode and band B with the TO mode (see Fig. 2b, p. 431 reference 9). The assignments are tentative and are in need of verification when single crystal Raman and polarization data become available.

Cholesteryl nonanoate supercooled from the isotropic liquid state becomes smectic(10) which transforms slowly at room temperature to the crystalline state. We have obtained also the low frequency Stokes traces of cholesteryl nonanoate in the isotropic liquid state at about 100 °C and in the smectic state (cooled from 100 °C to and maintained at about 60 °C); the traces are almost identical to those shown in, respectively, Figs. 2a and 2b and are not reproduced here for the sake of space. The Raman bands shown in Fig. 2b, characteristic of the smectic state, correspond in frequency shifts identically to the A and B bands shown in Fig. 1. According to Frank(3) and Osen,(11) there are only two elastic coefficients k_{22} and k_{33} associated with the smectic liquid crystalline phases and corresponding to, respectively, the twist and the bend mode of distortions. It is therefore very tempting to identify the LO mode (band A) with k_{33} and the TO mode (band B) with k_{22}. Theoretical studies of the dynamics of intermolecular vibrations of these materials are in need, which, combined with more refined single crystal low frequency Raman data, may pave the way for a rigorous understanding of the relationships between intermolecular structures and the various physical properties of organic solids for liquid crystal applications.

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