Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Vibrational Spectroscopy of Liquid Crystals. 3. Very Low Frequency Raman Spectra of Some Polycrystalline Cholesteryl Esters

Gerard Vergoten [a] & Guy Fleury [b]

[a] Service Spectrochimie Infra-Rouge et Raman, C.N.R.S., C5, Universite des Sciences et Techniques de Lille, B.P. 36, 59650, Villeneuve d'Ascq, France

[b] Centre de Technologie Biomedicale I.N.S.E.R.M., Laboratoire de Physique, Faculte de Pharmacie, Rue du Professeur Laguesse, 59045, Lille, Cedex, France

Version of record first published: 21 Mar 2007.

To cite this article: Gerard Vergoten & Guy Fleury (1975): Vibrational Spectroscopy of Liquid Crystals. 3. Very Low Frequency Raman Spectra of Some Polycrystalline Cholesteryl Esters, Molecular Crystals and Liquid Crystals, 30:3-4, 223-232

To link to this article: http://dx.doi.org/10.1080/15421407508083434

Mol. Cryst. Liq. Cryst., 1975, Vol. 30, pp. 223–232

Printed in Holland

Vibrational Spectroscopy of Liquid Crystals. 3. Very Low Frequency Raman Spectra of Some Polycrystalline Cholesteryl Esters

GERARD VERGOTEN†

Service Spectrochimie Infra-Rouge et Raman, C.N.R.S., C5, Universite des Sciences et Techniques de Lille, B.P. 36, 59650, Villeneuve d'Ascq, France

and

GUY FLEURY

Centre de Technologie Biomedicale I.N.S.E.R.M., Laboratoire de Physique, Faculte de Pharmacie, Rue du Professeur Laguesse, 59045, Lille, Cedex, France

(*Received February 4; 1975*)

The very low frequency Stokes and anti-Stokes Raman spectra of polycrystalline cholesteryl chloride, benzoate, palmitate and stearate are reported. Contrary to some previous observations,[1,2] significant variations in the observed frequencies between the various esters were found. It must be pointed out that vibrations of the molecule as a whole have to appear in addition to the lattice vibrations.

INTRODUCTION

It is of current interest to investigate the nature of the ordering forces responsible for the liquid crystalline behavior of a great number of organic compounds.

Vibrational spectroscopy can be used as a probe of these forces.

The present work reports a study by low frequency Raman scattering of polycrystalline cholesteryl chloride, benzoate, palmitate and stearate in the spectral range 0–60 cm^{-1}.

---

† To whom correspondence should be addressed.

Despite several reports of vibrational spectra of liquid crystals which have been recently reviewed,[3,4] to our knowledge only four papers on Raman and Infra-red spectra of substances exhibiting a cholesteric mesophase have appeared.[1, 5–7]

EXPERIMENTAL SECTION

The cholesteryl chloride and benzoate used in this study were purchased from E. MERCK (Darmstadt, GERMANY).

The cholesteryl stearate and palmitate were supplied by KOCH-LIGHT (Colnbrook, Bucks, ENGLAND). All the chemicals were used without further purification.

The Raman spectra were recorded using the RAMANOR HG2 spectrometer manufactured by LIRINORD INSTRUMENTS. This spectrometer consists of the first commercially available double monochromator equipped with two concave aberration corrected holographic gratings of 2000 grooves per mm and one meter focal length. Spectra of the same quality were obtained using a home-built triple monochromator[8] with three 1800 lines/mm plane ruled gratings used in the first order.

The monochromators are characterized by a very low stray-light level and a total absence of "ghosts" which lead to the observation of very small Raman shifts without adjunction of "tricks" to the monochromator (such as an iodine filter).

The use of holographically recorded concave gratings in designing monochromators represents a real progress in the field of low-frequency Raman spectroscopy.[9]

A Spectra-Physics model 165-03 Argon ion laser (514,5 nm) delivered 800 mW at the sample which was put in a spinning cell to prevent local heating.[10]

Raman spectra were recorded at 1 cm^{-1}/mn with a spectral slit width of approximately 0.8 cm^{-1} and were reproducible.

The uncertainty in the Raman shifts measurements was estimated as better than $\pm 0.5\ cm^{-1}$.

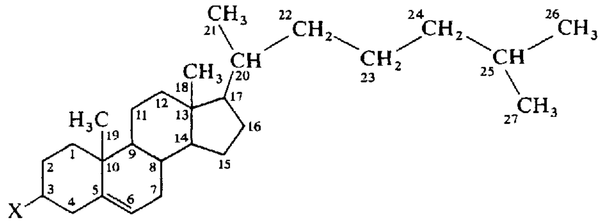
RESULTS AND DISCUSSION

The structural formulae of cholesteryl chloride, benzoate, palmitate and stearate are given in Table I.

For these compounds the low frequency Raman spectra recorded at room temperature are shown in figures 1–4.

TABLE I

Structural formulae of the cholesterol esters



Cholesteryl Chloride: $X = Cl$
Cholesteryl Benzoate: $X = C_6H_5COO—$
Cholesteryl Palmitate: $X = CH_3—(CH_2)_{14}—COO—$
Cholesteryl Stearate: $X = CH_3—(CH_2)_{16}—COO—$

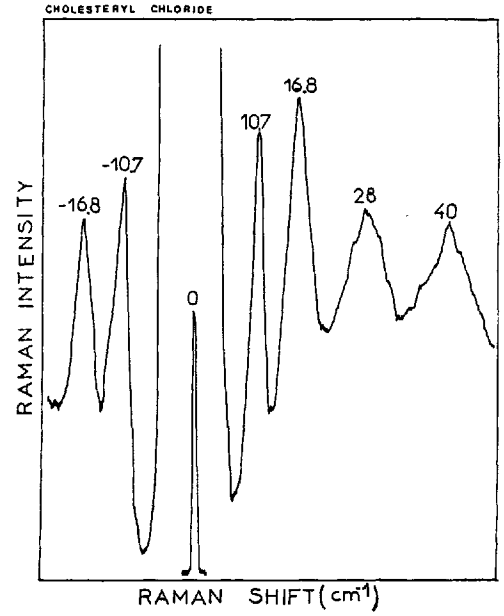


FIGURE 1 Low frequency RAMAN spectrum of cholesteryl chloride in the range 0–60 cm^{-1}

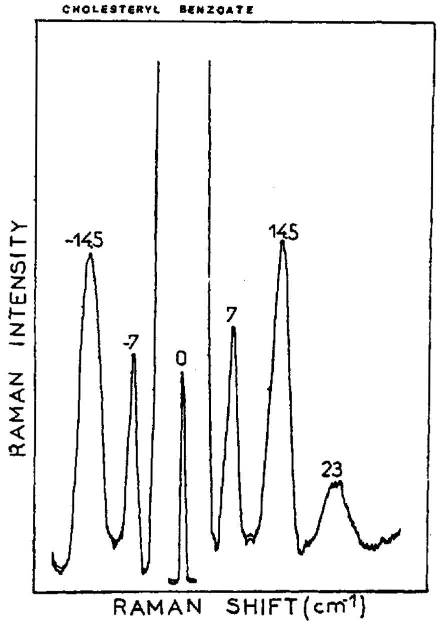


FIGURE 2 Low frequency RAMAN spectrum of cholesteryl benzoate in the range 0–30 cm^{-1}.

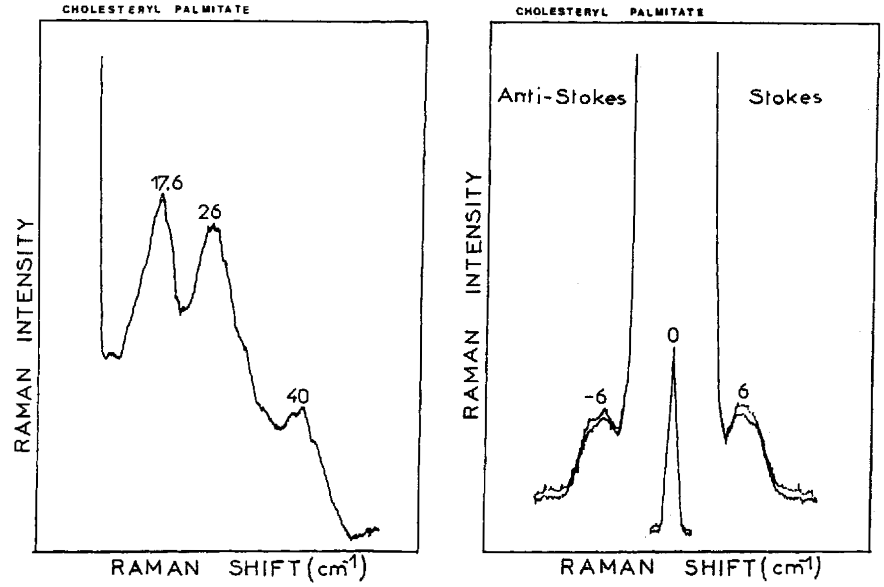


FIGURE 3 Low frequency RAMAN spectrum of cholesteryl palmitate
a) in the range 10–50 cm^{-1}
b) in the range 0–10 cm^{-1}

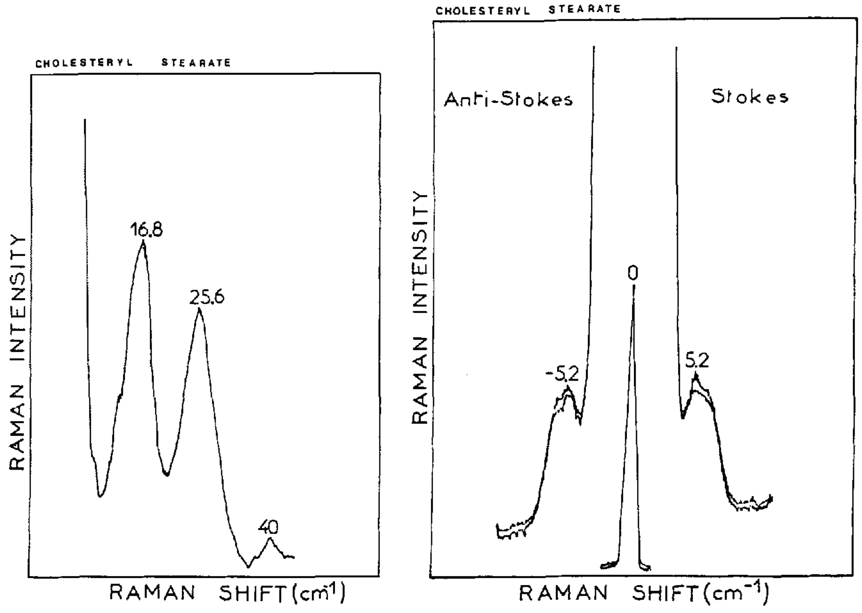


FIGURE 4 Low frequency RAMAN spectrum of cholesteryl stearate
a) in the range 0–50 cm^{-1}
b) in the range 0–10 cm^{-1}

We sketch here the most important experimental features. A more complete description, including infra-red and Raman spectra of thirty cholesterol esters, will be given elsewhere.

To our knowledge, this is the first study of low frequency vibrations of cholesteryl chloride, benzoate and stearate. The low frequency Raman scattering of cholesteryl propionate, nonanoate and palmitate has been published previously.[1] For these three compounds, two sharp bands were observed at 18 cm^{-1} and 26 cm^{-1} in the crystalline phase without any changes in frequency with the substitution in position 3 of the hydroxyl group of the cholesterol skeleton.

Although this result seems to indicate that these bands are spurious in origin, such an explanation was ruled out on the basis of other measurements. The two bands were assigned respectively to the longitudinal optical and transverse optical lattice vibrations of the crystal with the conclusion that the intermolecular vibrations depend principally on the cholesteryl part of the molecule and are independent of the side chain length.

Meanwhile, as noticed by Bulkin,[3] one might expect some change in the lattice vibration frequencies between the various esters, depending on molecular mass and moment of inertia.

TABLE II

Correlation diagram

Isolated molecule	Site	Unit cell	
C_1	C_1	C_2^2	
A	A	A	T_z R_z XX YY ZZ XY
		B	T_x T_y R_x R_y YZ XZ

acoustical modes: $\Gamma = 2B \oplus A$
rotatory lattice modes: $\Gamma_R = 3B \oplus 3A$
translatory lattice modes: $\Gamma_T = B \oplus 2A$

To our knowledge, the crystal structures of the cholesteryl esters used in this study are not established. Cholesteryl iodide was reported[11] to crystallize in the monoclinic system (space group $P2_1/C_2^2$) with two molecules per unit cell. Under this assumption, nine infra-red and Raman active optical external modes of vibration as shown in the correlation diagram (Table II) are expected.

The low frequency Raman spectrum of cholesteryl stearate recorded at liquid nitrogen temperature is shown in figure 5. Seven Raman bands are clearly observed in the spectral range 0–110 cm^{-1}. This indicates that the approximation found in reference[1] and assignments included therein are not reasonable. Such assignments will be possible when Raman polarization measurements on single crystal and far infra-red spectra become available.

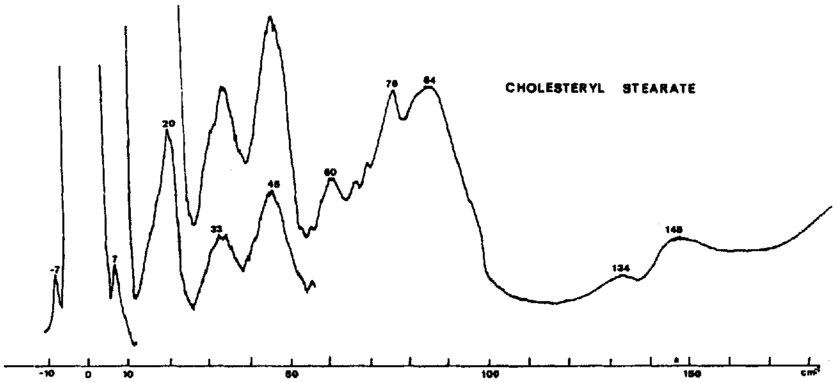


FIGURE 5 Low frequency RAMAN spectra of cholesteryl stearate obtained at liquid N_2 temperature.

TABLE III

Observed low frequency (cm^{-1}) in the RAMAN spectrum of cholesterol esters

Cholesteryl chloride	Cholesteryl benzoate	Cholesteryl palmitate	Cholesteryl stearate
10.7	7	6	5.2
16.8	14.5	17.6	16.8
28	23	26	25.6
40	40	40	40

We have reported in Table III the observed Raman shifts in the range 0–60 cm^{-1}. It is most probable that the fairly intense band of lowest frequency arises from the in-phase rotatory lattice vibrations of the two long molecules in the unit cell about an axis perpendicular to the direction of elongation.

Figure 6 shows the low frequency Raman spectrum of cholesteryl benzoate

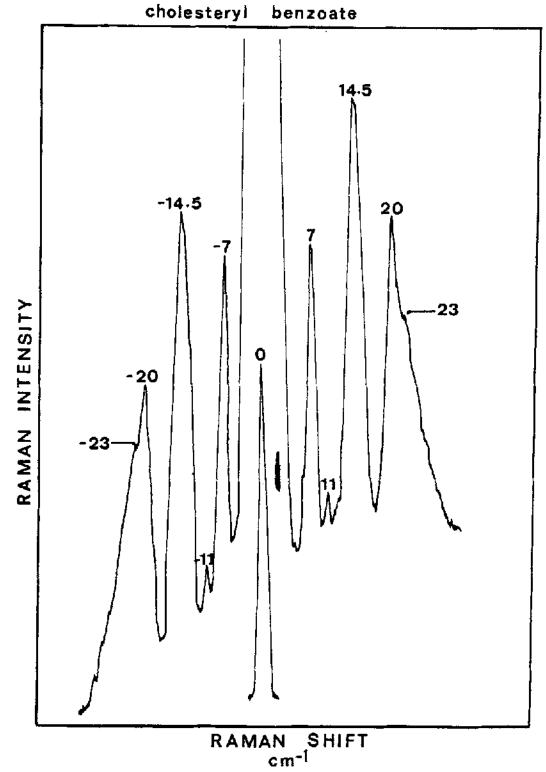


FIGURE 6 Low frequency RAMAN spectrum of cholesteryl benzoate after a rapid cooling.

rapidly cooled from its isotropic liquid phase. It must be pointed out that some new bands at 11 cm^{-1} and 21–23 cm^{-1} appear. Among all Raman bands observed in the low frequency range, some of them have certainly an intramolecular origin, especially in the case of cholesteryl fatty esters. These bands, particularly those associated with transverse acoustical modes of vibration, will be of special interest since they are closely related to the molecular environment as shown for the normal paraffins.[12-13]

LOW FREQUENCY RAMAN SPECTRUM AS A FUNCTION OF TEMPERATURE

The Raman spectra of cholesteryl benzoate and stearate have been investigated in their different phases.

Figure 7 shows the spectra obtained for cholesteryl benzoate in the polycrystalline solid, cholesteric and isotropic liquid states. The transition tem-

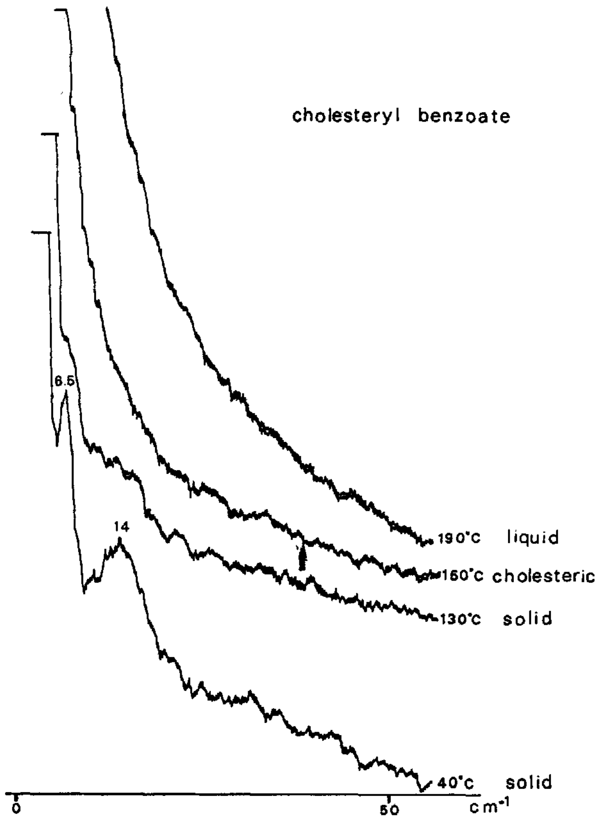


FIGURE 7 Low frequency RAMAN spectrum of cholesteryl benzoate in its different phases.

peratures have been found to be 146°C (solid-cholesteric) and 181°C (cholesteric-isotropic liquid). No spectral differences are observed between the cholesteric and the liquid phases except for the increase of the Rayleigh wing scattering. It must be pointed out that, even in the solid phase (130°C) the low frequency bands rapidly broaden and hence disappear, owing to the weakness of intermolecular interactions due to the increased spacing between the molecules.

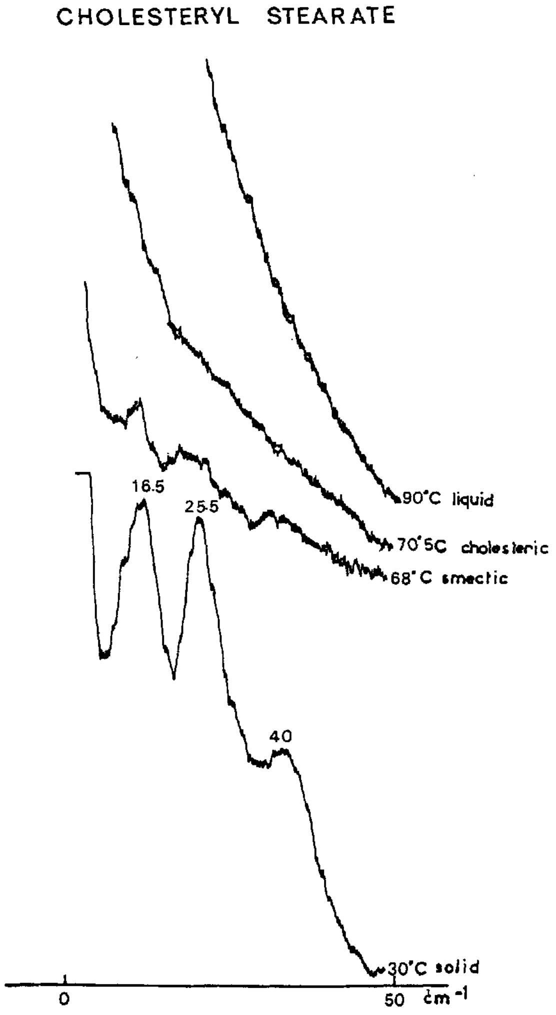


FIGURE 8 Low frequency RAMAN spectrum of cholesteryl stearate in its different phases.

In cholesteryl stearate, all the mesophases are monotropic. The solid-isotropic transformation temperature is 82°C, the isotropic-cholesteric transition is observed at 71.5°C, the cholesteric-smectic transition at 70°C and the smectic-solid one at 67°C.

Figure 8 reports typical spectra obtained in the different phases for this compound. In the cholesteric and isotropic liquid states, the intermolecular interactions seem to be quite similar, like the smectic mesophase which is more closely related to the solid phase.

A rigorous understanding of the presence of low frequency Raman bands in the smectic phase will be possible when theoretical studies of the dynamics of intra- and intermolecular vibrations in such compounds become available.

References

1. R. Chang, *Mol. Cryst. Liq. Cryst.*, **12**, 105 (1971).
2. V. Dimic and M. Osredkar, *Mol. Cryst. Liq. Cryst.*, **19**, 189 (1973).
3. B. J. Bulkin, to be published.
4. G. Vergoten and G. Fleury, to be published.
5. A. S. L'Vora and M. M. Sushchinskii, *Opt. Spektr.*, **2**, 266 (1963).
6. B. J. Bulkin and K. Krishnan, *J. Am. Chem. Soc.*, **93**, (23), 5998 (1971).
7. B. J. Bulkin, J. O. Lephardt and K. Krishnan, *Mol. Cryst. Liq. Cryst.*, **19**, 295 (1973).
8. R. Demol, Diplôme d'Etudes Supérieures, 21 mars 1974, Lille, France.
9. G. Vergoten, to be published.
10. W. Kiefer and H. J. Bernstein, *Appl. Spectrosc.*, **25**, 500 (1971).
11. C. H. Carlisle and D. Crawfoot, *Proc. Roy. Soc.*, **A184**, 64 (1945).
12. G. Vergoten, G. Fleury, M. Tasumi, and T. Shimanouchi, *Chem. Phys. Lett.*, **19**, (2), 191 (1973).
13. H. Takeuchi, T. Shimanouchi, M. Tasumi, G. Vergoten, and G. Fleury, *Chem. Phys. Lett.*, **28**, (3), 449 (1974).