Gyrotropy in vibrational transitions

Yu. V. Denisov, V. A. Kizel', V. V. Mnev, E. P. Sukhenko, and V. G. Tishchenko

Moscow Physico-technical Institute
(Submitted July 15, 1975)
ZhETF Pis. Red. **22**, No. 4, 242–245 (August 20, 1975)

Gyrotropy (rotation of the plane of polarization) was observed in the region of vibrational transitions in cholesteric liquid crystals. It is proposed that the possibility of observing the phenomenon is connected with the ordered disposition of the molecules.

PACS numbers: 78.50., 61.30.

Spatial dispersion of first order (gyrotropy) can occur in all regions of the spectrum; its easiest-to-observe manifestation is the rotation of the plane of polarization. However, in the region of vibrational transitions, its observation is more difficult than in the region of electronic transitions, since the oscillator strengths of the vibrational transitions are smaller by three or four orders of magnitude. Therefore, in spite of numerous attempts, rotation in inordered molecular systems has not been observed.

Gyrotropy in vibrational transitions was first observed in[1] on the bands of the water of crystallization in dithionate crystals. The authors have attributed the appearance of gyrotropy to the ordered disposition of the molecules in a spiral structure, which increases the value of gyrotropy after summing the contributions of the individual molecules.[2] Gyrotropy on the same bands was observed later[3] in another object. Indications of gyrotropy of impurities in nematic liquid crystals were recently published,[4] but the theoretical interpretation of the results has not been sufficiently well developed.

In this paper we establish gyrotropy in vibrational transitions in cholesteric liquid crystals (CLC).

We measured the rotation of the plane in the mesophase under careful thermostatic control (±0.03°); the substances were placed in flat quartz cells 5 to 15 μ thick, previously tested for the absence of birefringence. The measurements were performed with the infrared polarimeter of our institute[1] with an improved analyzer; the measurement accuracy in the ~4 μ region was not less than 0.1°, the spectral width of the slit was of the order of 0.03 μ. A planar texture was established in the samples, with layers parallel to the surface of the cell; it was obtained by melting to the liquid phase followed by cooling to the mesophase while moving a cover glass. The presence of this structure and its single-domain character were verified *in situ* with the aid of a polarization microscope with large magnification. In such a texture, as is well known, the optical axis is perpendicular to the surface of the cell. The measurement results are shown in Figs. a–c.

The electronic absorption bands of the given substances lie[5] in the region $\lambda < \sim 2200$ Å, and the selec-

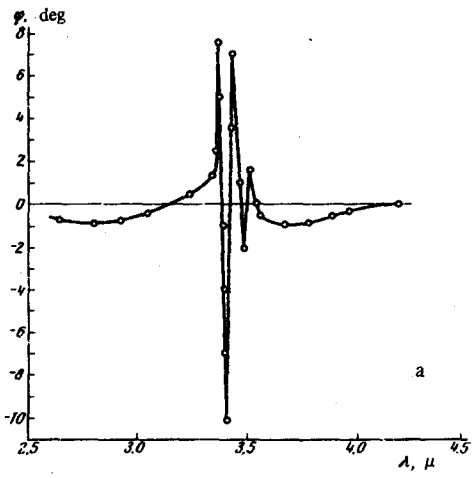

FIG. a. Dispersion of optical rotation of chlosteryl perlargonate; cell 10 μ thick, $T = 80$°C.

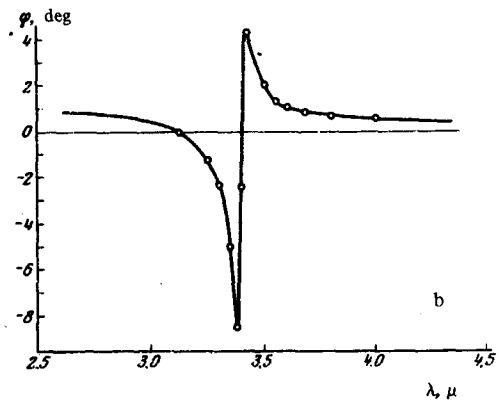

FIG. b. The same for cholesteryl chloride, $T = 62$°C.

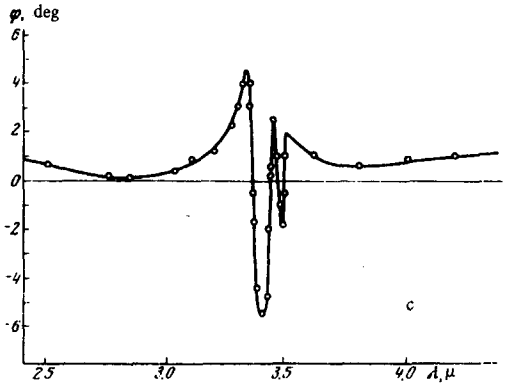

FIG. c. The same for the compound "Licrystal-Merck 10217", $T = 20°C$.

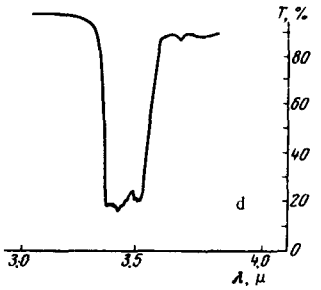

FIG. d. Absorption spectra of cholesteryl pelargonate at the same temperature (the spectra of the other compounds are similar).

tive-transmission bands typical of CLC, and the associated region of normal dispersion of the rotation, lies at 3300–6300 Å.[5] The absorption spectra in the investigated region were obtained with an IKS-14 spectrometer (Fig. d). Bands of this type with insignificant changes of the structure were observed for all the investigated substances and are typical of cholesterin and all its derivatives[6]; they are connected with valence oscillations of the C–H bonds (CH_3 and CH_2 groups). Deferring a detailed analysis of the shapes of the curves to a later study (the differences are due to the different environment of the cholesterin base), we indicate only that their vibrational origin is subject to no doubts.

Existing theoretical considerations[2] show that when the molecules are ordered the total rotation may increase by several orders of magnitude, especially when spiral-like CLC structures, which favor gyrotropy, are produced. Even within the framework of the primitive model of "oriented gas," this holds true, let alone the possibility of exciton effects and lowering of the symmetry of the molecules in the asymmetrical internal field of the crystal.

Indeed, as shown by our measurements,[5] near the electronic transitions, the rotation in our substances reaches $(4–5)\times10^4$ deg, so that the rotation on vibrational transitions, while remaining smaller by three or four orders of magnitude, becomes perfectly observable in this case; we see that the order of magnitude is precisely as expected.

Outside the vicinity of this transition, there remains only a rather small rotation, which represents the far wing of the strong bands of anomalous rotation due to selective reflection and to electron resonance. On going over to the isotropic phase, the rotation decreases monotonically from 4–5° near the electronic absorption (3000 Å) to several minutes at 2 μ; in the considered region it is already difficult to measure (although the absorption band changes little), as is the case also for other disordered molecular systems.

Thus, the large rotation in the region of the given vibrational transition is due precisely to the structure of the mesophase—cholesteric spiral structure—and to the indicated influence of the ordering.

[1]V. I. Burkov, V. A. Kizel', M. F. Kostenko, and Z. B. Perekalina, Dokl. Akad. Nauk SSSR **199**, 806 (1968) [Sov. Phys.-Dokl. **16**, 663 (1969)].
[2]V. A. Kizel', Yu. I. Krasilov, and V. I. Burkov, Usp. Fiz. Nauk **114**, 295 (1974) [Sov. Phys.-Usp. **17**, 745 (1975)].
[3]E. Hsu and G. Halzwarth, J. of Chem. Phys. **59**, 4678 (1973).
[4]J. Chabay, J. Chem. Phys. **58**, 4816 (1973).
[5]Yu. V. Denisov, V. A. Kizel', E. P. Sukhenko, and V. G. Tishenko, Trudy MFTI, Fizika, No. 6, 102 (1975).
[6]J. Lecomte, *Infrared Radiation* (Russian translation), GIFML, 1958, p. 337.