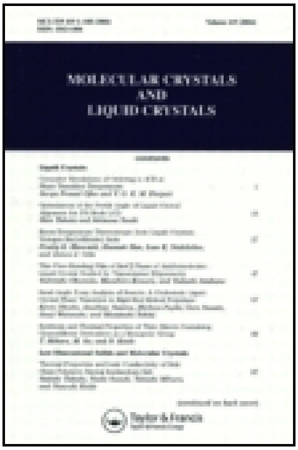

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Vibrational Spectra of Liquid Crystals VI. Relative Intensities in Raman Spectra of Cholesteric and Nematic Solutions(1)

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Vibrational Spectra of Liquid Crystals VI. Relative Intensities in Raman Spectra of Cholesteric and Nematic Solutions(1)

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Abstract—The Raman spectra of solutes in cholesteric solvents show differences in relative intensity from those in isotropic liquids. These are discussed in terms of a polarization scrambling model. Similar effects should be seen for solutes in some nematic phases. The intensity perturbations may occur for liquid crystal modes as well as for solute modes.

1. Introduction

Vibrational spectra of liquid crystals can yield information about intermolecular interactions in anisotropic phases, but with regard to certain aspects considerable caution is needed. Recently, in this laboratory, spectra of a number of solutes have been examined in nematic and cholesteric solvents, in an effort to understand the nature of the interaction between solutes and mesomorphic solvents. These studies represent an extension of earlier work on spectra of the liquid crystals themselves.

One observation in the solution studies is that large changes in relative intensity of solute Raman lines occurs in certain cholesteric solvents. These relative intensity changes are not present in the isotropic liquid phase. It is the purpose of this paper to show that a simple polarization scrambling model can be used to explain the observed intensities. Carbon tetrachloride in a cholesteric solvent is used as an example. The model may also explain some changes in relative intensities of solvent molecules observed at phase transitions (crystal–liquid crystal as well as liquid crystal–isotropic). It must certainly be considered in addition to other possible causes such as intermolecular interactions and conformational changes.

2. Experimental

Measurements were carried out using a Spex Model 1401 double monochromator, Helium–Neon laser delivering approx. 50 mw of power (632.8 nm) at the sample, and photon counting amplification.

The samples were contained in glass capillaries mounted in the transverse-transverse geometry shown in Fig. 3. The laser beam was brought to a focus at the sample. Because no special attempts were made to align the samples, many ordered regions of different orientation were certainly present. For quantitative measurements on nematics this would not be adequate; a well-defined orientation is required. For cholesterics, however, if one is only looking for the effects of complete scrambling, an oriented sample is not necessary. That this is indeed true is verified by making measurements in both positions of a polarization analyzer in the cholesteric phase. The intensity of all bands is identical indicating complete scrambling.

Cholesteric compounds were purchased from Vari-light, Inc. and were used without further purification.

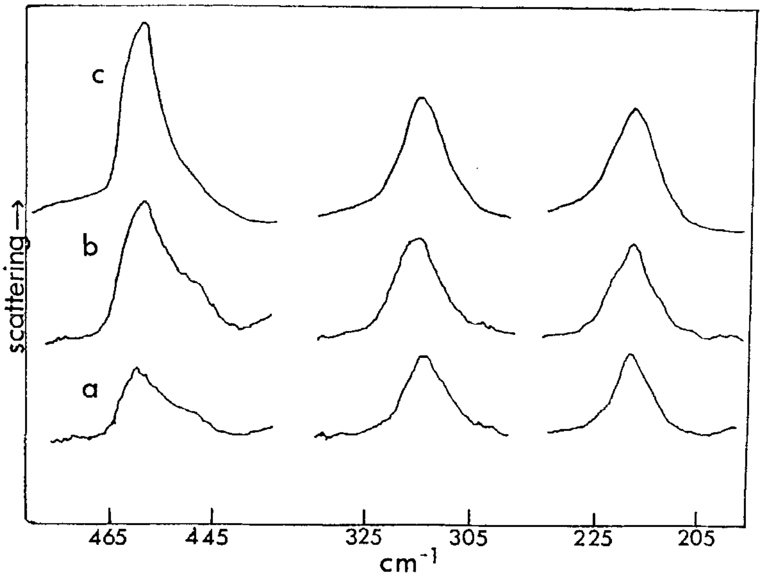

Figure 1. (a) Raman spectrum of CCl_4 in a cholesteric solvent; (b) same sample in the isotropic phase; (c) pure liquid CCl_4. The solvent has no Raman bands in these spectral regions.

3. Example of the Effect

Figure 1(a) shows the Raman spectrum of CCl_4 in the cholesteric solvent 75% cholesteryl nonanoate–25% cholesteryl chloride. In pure CCl_4 liquid (Fig. 1(c)) the two bands at 218 and 314 cm^{-1} are depolarized ($\rho = 0.75$) modes while the 459 cm^{-1} band is an almost completely polarized ($\rho = 0.005$) mode. As seen in Fig. 1(c), the A_1 mode is ordinarily about twice as intense as the degenerate modes, but in the cholesteric phase it decreased in relative intensity. When the temperature is raised above the cholesteric–isotropic transition temperature the CCl_4 relative intensities return to those of the pure liquid.

Similar variations in relative intensity have also been observed in a

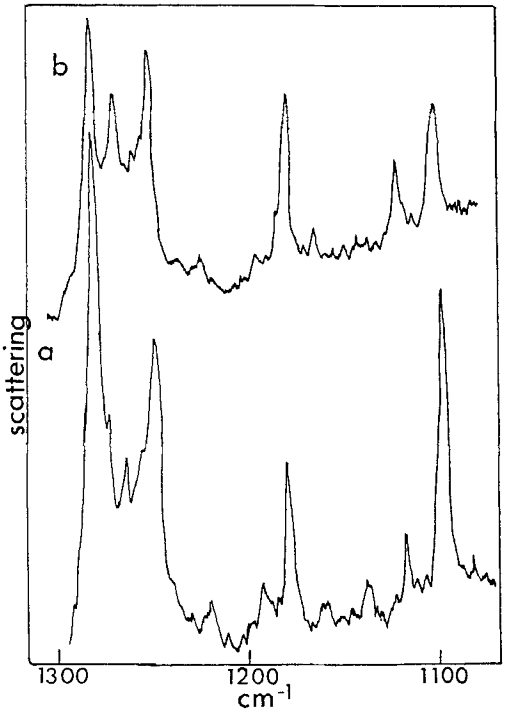

Figure 2. (a) Raman spectrum of PAA in cholesteryl propionate which has been rapidly quenched; (b) same sample cooled slowly. All strong bands in this region come from the PAA. Spectrum *b* is identical with spectra of pure polycrystalline PAA in this region.

number of other solutions with different cholesteric solvents and a variety of solutes. In all cases there is no variation in frequency of the solute vibrations, only an intensity change.

Another example of a slightly different system is shown in Fig. 2a. Here one sees a variation in the relative intensities of bands in the spectrum of *p*-azoxyanisole (PAA) when it is in a rapidly frozen cholesteric phase. When the cholesteric solution is allowed to crystallize slowly (Fig. 2(b)) the usual PAA crystalline intensities are observed.

In the next section we show how the change in relative intensities of solute molecules in cholesteric phases can be explained. A succeeding section discusses the problem of Raman intensities in nematic phases.

4. Cholesterics

The relative intensities of Raman bands of solute molecules in liquid crystals depend upon their depolarization ratios. Note that this ratio cannot be measured in the cholesteric phase, but must be obtained in an isotropic liquid or solution. In the cholesteric phase all polarization information is lost, as bands are observed to have identical intensity in either position of a polarization analyzer.

The highly polarized incident radiation used in a laser excited Raman spectrometer undergoes complete scrambling of its **E** vector in propagating through a cholesteric sample. This may occur by two mechanisms, and both are almost certainly operative here. First, the optical activity of the helical regions rotates the polarization. Second, refractive index discontinuities cause scattering of the incident beam which results in depolarization. Both these mechanisms are known to Raman spectroscopists. The first occurs in spectra of optically active materials, such as quartz, the second in spectra of powders. In any case, independent of the mechanism of depolarization, to determine the scattered intensity one has an equivalent situation to that which is obtained if an unpolarized source is used.

Suppose, as shown in Fig. 3, the laser beam is incident along the z direction with **E** along x. Scattered light propagating along y is

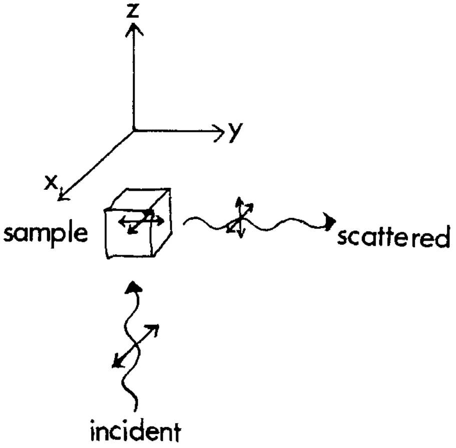

Figure 3. Geometry used for the experiments shown in Figs. 1 and 2.

observed without an analyzer. This is the geometry for the experiments in Figs. 1 and 2.

After the incident beam centers the cholesteric phase we assume that its intensity is evenly distributed with **E** along x and y. Thus if I_0 is the initial laser intensity, in the cholesteric sample

$$I_x^{\mathrm{Ch}} = I_y^{\mathrm{Ch}} = 0.5 I_0$$

For a completely polarized band such as the CCl_4 459 cm^{-1} line in an isotropic solvent the scattered intensity polarized along y is zero so that in the cholesteric phase the intensity observed for this band is half that observed in the isotropic phase.

For a completely depolarized band $I_y = 0.87 I_x$. In the cholesteric phase the depolarized light intensity is $0.5 + 0.5(0.87) = 0.94$ that in the isotropic phase.

In general, for this experiment one can show that the relative intensity of a band will be attenuated by a factor

$$(1 + 3\rho)/[2(1 + \rho)]$$

in the cholesteric phase, where ρ is the depolarization ratio defined in the usual way. We thus see that the relative intensity of a highly polarized band is considerably reduced relative to that of a depolarized band in the cholesteric phase.

5. Nematics

The analysis of nematic liquid crystal spectra may not be as direct as the analysis of cholesteric liquid spectra. For nematic liquid crystals, the long range order of the sample must also be considered. As with uniaxial single crystals, the uniaxial single liquid crystal will split the incident radiation into two components and the scattered intensity will be related to the orientation of the polarizability ellipsoid with respect to the two components. If the sample is polyliquid crystalline, the orientations may be distributed uniformly and the analysis becomes the same as for cholesterics. If the sample size viewed is small or the sample has long range order, all sample orientations may not be present and the intensities will not be as for a cholesteric. In such a case, the scattered intensity may vary with the orientation of the polarizer and/or analyzer.

The intensities which one can predict for polarized and unpolarized light will provide the limits for the intensities in nematic solutions but exact prediction of intensities would require knowledge of the order of the liquid crystal, its dispersion, and several other optical parameters. For practical purposes, awareness of the limits on intensity should suffice.

6. Conclusions

This work points up several things to watch for in vibrational spectroscopic studies of liquid crystals and mesomorphic solutions. The optical activity and refractive index discontinuities of the mesophases give rise to a polarization scrambling which affects the intensity of polarized and depolarized solute bands unequally. One may expect a variation in solute relative intensities as a rule, particularly in high symmetry solutes where complete polarization is possible. An exception to this is predicted if the optical activity of the cholesteric pitch band falls well outside the wavelength of the laser exciting line.

Nematic materials may show similar effects, particularly in the case of short range order relative to the observation element size. For a sample which appears truly uniaxial, one should be able to predict the intensities from the classic works of Saksena(2) or Mathieu.(3) A highly oriented sample will be needed, however.

It is necessary to make two further points quite clearly: First, one can make these observations without using a polarization analyzer or rotating a half-wave plate. Second, the effects may appear in the spectra of the solvent molecules as well. This is not commonly seen because all Raman bands in these low symmetry molecules are partially polarized and the relative-intensity variations are probably within experimental error. A possible example of polarization scrambling causing intensity variations in the solvent is seen in some recently published spectra from this laboratory.(4) It should be clear that even if the solvent molecules are of low overall symmetry, there may be locally " hidden " degeneracy which gives rise to more extreme polarizations.(5)

Finally, it should be pointed out that infrared spectra, when compared with Raman spectra, can provide unambigious confirmation of the role of polarization scrambling in observed changes in Raman spectra of liquid crystals.

Acknowledgement

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REFERENCES

1. Part V of this series: B. J. Bulkin and W. B. Lok, *J. Phys., Chem.* in press.
2. Saksena, B. D., *Proc. Indian Acad. Sci.* **11A**, 229 (1940).
3. Mathieu, J. P., " Spectres de Vibration ", Hermann, Paris, 1945.
4. Bulkin, B. J. and Krishnan, K., *J. Amer. Chem. Soc.* **93**, 5998 (1971).
5. Edgell, W. F., *J. Phys. Chem.* **75**, 1343 (1971).