SECOND-HARMONIC GENERATION IN LIQUID CRYSTALS

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The unusual properties of liquid crystals[1] suggest interesting applications to nonlinear optics. The unparalleled optical activity of the cholesteric mesophase may be important in optical frequency mixing[2] and in demonstrating phase matching using optical rotatory dispersion.[3] The large, controllable birefringence of nematic liquid crystals in magnetic fields of only a few kilogauss, and the reported ferroelectric behavior[4] of this mesophase, suggest the use of nematic materials in tunable parametric optical oscillators and amplifiers.[5] We report here what we believe to be the first observations of second-harmonic generation in a liquid crystal, the first experimental demonstration that second-harmonic scattering measurements can yield information on angular correlations in fluids,[6] and the first direct determination of the range of angular correlations in a liquid crystal.

The material we have studied is cholesteryl 2-(2-ethoxyethoxy) ethyl carbonate,[7] a liquid crystal at room temperature.[8] We have observed second-harmonic generation in ordered films[9] and in bulk samples, but we report here only our results on bulk samples. A Q-switched ruby laser and conventional associated equipment were employed. Variations in laser power and mode structure were compensated for by simultaneous measurement of the second harmonic produced in a quartz wedge.[10] The observed emission from the liquid crystal was demonstrated to be due to second-harmonic generation as follows: (a) The emission from the liquid crystal was found to have the same dependence on laser power as the second harmonic from crystalline quartz over a 30-fold range of intensities.[11] (b) The frequency of the liquid-crystal emission was observed to be within 0.05 Å (the instrumental uncertainty) of the second harmonic frequency of quartz. (c) The emission from the liquid crystal was collimated along the direction of the laser beam. (d) The emission disappeared above the liquid crystal—isotropic liquid transition temperature.

Liquid crystals are believed to consist of random ensembles of ordered regions known as swarms.[1] It is also believed that within each swarm there eixsts a high degree of molecular angular correlation. The range of this angular correlation was determined from measurements of the angular dependence of the second-harmonic intensity, by the method suggested by Bersohn, Pao, and Frisch.[6] The experimental second-harmonic intensity versus scattering angle is shown in Fig. 1. A least-squares procedure was used to smooth the data, and the broadening due to the laser divergence and finite instrumental resolution (obtained from measurements on quartz) was removed using standard procedures.[12] The relevant portion of the resulting curve was effectively a Gaussian, and had a half-width of 8 mrad. Bersohn, Pao, and Frisch[6] have shown that this curve is described by

$$\text{S.H.}(\kappa) \propto \int \frac{\sin \kappa r}{\kappa r} r^2 dr \int d\Omega_1 \int d\Omega_2 g(r, \Omega_1, \Omega_2) \times \beta_{JLM}(1)\beta_{JLM}(2), \qquad (1)$$

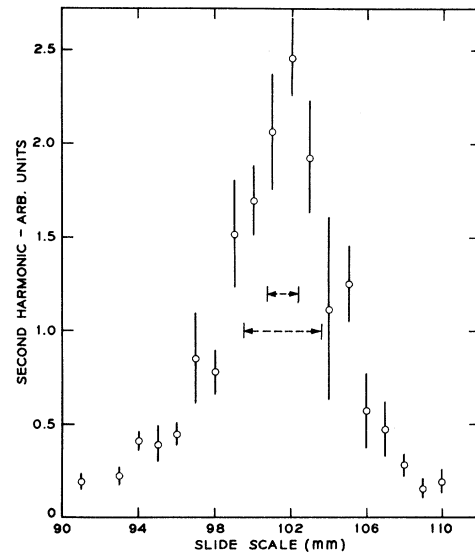where κ is the difference in wave vector between

FIG. 1. Second-harmonic scattering intensity versus detector position. A least-squares fit to the data yields a curve with a half-width of 11 mrad. The larger dashed arrow is the half-width of a similar curve for crystalline quartz (half-width of 7 mrad). The smaller arrow is the detector resolution.

the incoming laser and outgoing second harmonic photons, and is given by Bersohn,[13] the β's are the molecular nonlinear susceptabilities, and $g(r, \Omega_1, \Omega_2)$ is the two-particle angular correlation function for molecules separated by distance r; it measures not only the loss of angular correlation with distance, but also, in the usual way, the decreasing contributions to the structure factor of increasing interparticle separations. In writing (1) we have neglected incoherent contributions since these are much too weak to be measured in our experiment. The quantity we obtain experimentally is the intensity relative to zero angle. The Gaussian shape of the experimental scattering curve suggests as the simplest choice that the angle-averaged correlation function also be chosen as Gaussian.[14] Using our data and recently measured refractive indices,[15] we obtain a value of 13 ± 6 μ for the average distance over which this angle-averaged correlation function falls to $1/e$ times its initial value.[16]

The assumption that the liquid crystal is composed of an ensemble of randomly oriented swarms, a necessary condition for the applicability of (1), leads directly to the prediction that the second-harmonic intensity is a linear function of sample thickness.[17] When absorption at the second-harmonic frequency is accounted for, the second-harmonic intensity is found to be proportional to $1-T$, where T is the fractional transmission of the sample. A confirming experimental plot of second-harmonic intensity versus measured sample transmission is shown in Fig. 2.
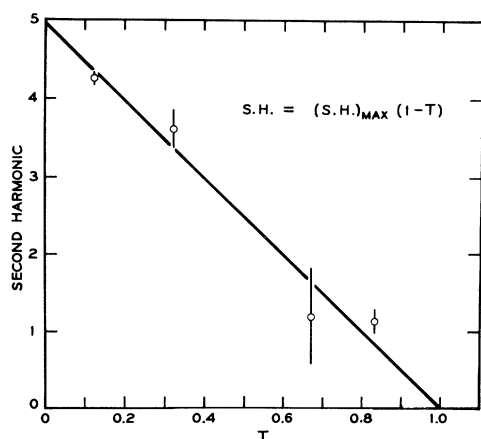
Our experiments support the conventional

view of a liquid crystal; demonstrate that the molecular arrangement within the swarms of the liquid crystals we have studied is such that an effective center of symmetry does not exist, as shown by the generation of second harmonics; and lead to the first direct measurement of the range of angular correlations in a liquid crystal.

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FIG. 2. Second-harmonic intensity versus fractional transmission of sample. The points are for sample thicknesses of 10, 5, 2, and 1 mm.

[1]G. W. Gray, Molecular Structure and the Properties of Liquid Crystals (Academic Press, Inc., New York, 1962).

[2]P. M. Rentzepis, J. A. Giordmaine, and K. W. Wecht, Phys. Rev. Letters 16, 792 (1966).

[3]H. Rabin and P. P. Bey, Bull. Am. Phys. Soc. 12, 81 (1967).

[4]R. Williams and G. Heilmeier, J. Chem. Phys. 44, 638 (1966); E. F. Carr, J. Chem. Phys. 43, 3905 (1965).

[5]J. A. Giordmaine and R. C. Miller, Phys. Rev. Letters 14, 973 (1965).

[6]R. Bersohn, Y. H. Pao, and H. L. Frisch, J. Chem. Phys. 45, 3184 (1966).

[7]Obtained from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York. Two related liquid crystals, cholesteryl 2-(2-methoxyethoxy) ethyl carbonate and cholesteryl 2-(2-butoxyethoxy) ethyl carbonate, also exhibit second harmonic generation.

[8]This material is a clear, isotropic, viscous liquid that does not exhibit measurable optical activity. We believe it exists in the smectic mesophase.

[9]Preliminary results, only on ordered films, were reported by the authors in Bull. Am. Phys. Soc. 12, 81 (1967).

[10]A. Savage, J. Appl. Phys. 36, 1496 (1965).

[11]The second harmonic intensity from the liquid crystal is, for a 1-cm path, approximately 10^{-2} that from d_{11} of quartz.

[12]A. Guinier, X-Ray Diffraction (W. H. Freeman & Co., San Francisco, 1963), pp. 142-149. The total first-order scattering is not more than a few percent and exerts a negligible influence on our results.

[13]R. Bersohn, J. Am. Chem. Soc. 86, 3505 (1964).

[14]We are grateful to Y. H. Pao and H. L. Frisch for pointing this out to us.

[15]L. Kopf, to be published; $l_c = \lambda_1/4(n_2 - n_1) = 5.5$ μ.

[16]Equation (1) is appropriate for a spherically symmetrical correlation function; this is clearly an approximation here. Our data are not sufficiently precise, however, to yield information on the anisotropy of the angular correlation length in the liquid crystal and on its dispersion.

[17]The situation here is analogous to a ferroelectric containing a random array of antiparallel domains. R. C. Miller, Phys. Rev. 134, A1313 (1964).