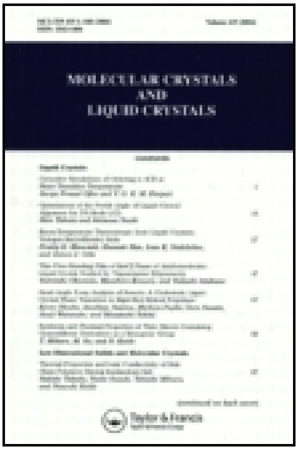

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Probing Liquid Crystals with Nonlinear Optical Processes

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PROBING LIQUID CRYSTALS WITH NONLINEAR OPTICAL PROCESSES

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Abstract Nonlinear optical effects provide some unique opportunities to study certain properties and structures of liquid crystal systems. Examples are presented here to illustrate the potential of such studies.

Liquid crystalline materials are highly nonlinear. Their strong optical nonlinearity arises from a high degree of electron delocalization in the molecules, the large anisotropy of the molecular structure, and the strong correlation of molecular motion under the influence of light.[1] Consequently, nonlinear optical effects in liquid crystals can be easily observed. Many of them have been reported in the literature[1] and some are presented in this issue of the proceedings.

While nonlinear optical effects in liquid crystals (LC) are extremely interesting in their own right, they can also be used as a tool to study liquid crystalline materials. The characteristic features of nonlinear optical probing could provide us with some unique opportunities to obtain information on certain properties of liquid crystalline materials that cannot be studied otherwise. The first attempt in this area was used to study the pretransitional behavior of molecular reorientation in the isotropic phase.[2] Both critical divergence of the molecular reorientation and critical slowing-down of the orientational relaxation as T → T_{NI} were observed and shown to agree quantitatively with predictions from the Landau-de-Gennes theory. The critical pretransitional behavior results from correlated molecular response to the applied field. It was recognized that reorienation of individual molecules can also contribute to the optical Kerr effect,[3] and the corresponding relaxation time should be of the order of picoseconds. This could be probed by using picosecond laser pulses in the Kerr measurements, as has been attempted by LaLanne et al. on LC in the isotropic phase.[4] One expects to see similar individual molecular reorientation in the mesophases. In general, pulsed optical Kerr measurements also allow us to probe the correlated reorientation dynamics in the mesophases as well as transient effects incurred by laser heating.[5] With picosecond pulse excitation, it may even be possible to deduce from the measurements the effective moment of inertia for the director $\hat{n}$. In the literature dealing with the motion of $\hat{n}$, the inertia term has always been neglected.[6]

The examples discussed above to illustrate how nonlinear optical effects can be used to probe LC rely on the optical nonlinearity arising from molecular reorientation. Such a nonlinearity is usually very large because LC molecules are highly anisotropic. It happens that electronic contribution to optical nonlinearities of some LC molecules can also be large. This is because of the existence of delocalized electrons on such molecules that are readily perturbed by the applied field. The second-order optical nonlinearity of these molecules can be very high when charge-transfer asymmetry is present. If only the molecules can be properly aligned in a medium, they can constitute some potentially very useful materials for electro-optics and nonlinear optics applications.

Optical nonlinearities of LC molecules should of course be studied by nonlinear optical processes. It turns out that via the study of optical nonlinearities, one can also obtain information about the molecular arrangement of LC molecules in a system. In the rest of this paper, we shall give an example on how optical second harmonic generation (SHG) can be used to obtain information about the alignment of LC molecules on surfaces and interfaces, as well as in a bulk.

We consider first the measurements of a monolayer of 8CB on water.[8] The molecules tend to have their CN polar group in water and the hydrophobic hydrocarbon tail up in air. An incoming laser beam at ω should induce on each molecule an oscillating dipole at 2ω via the nonlienar response of the molecule. This results in an oscillating dipole layer which radiates at 2ω. Measurements of SHG from the monolayer with various polarization combinations and spot-to-spot probing allow us to deduce the arrangement and orientation of the LC molecules in the monolayer. We found from our measurements that the 8CB molecules spread uniformly as a monolayer on water, and on average, they are tilted at an angle of $\theta \sim 70°$ from the surface normal but randomly oriented in the azimuthal plane. The measurements also yield a value of the second-order nonlinear polarizability for an 8CB molecule: $\alpha^{(2)}_{zxx} = 2.5 \times 10^{-29}$ esu, where z is along the surface normal.

When the SHG measurements were repeated on a monolayer of 8CB molecules on glass, with and without DMOAP surfactants, essentially the same results were found, both in the amplitude and the phase of the output. This immediately suggests that the 8CB molecules in the monolayer should have their CN terminal attached to the glass and the molecular axes tilted at ~ 70° away from the surface normal. The latter result is quite surprising since the glass surface was supposed to align the molecules in a homeotropic geometry. However, it can be easily understood if we realize that the molecular tilt on the surface is necessary in order to minimize the phenyl ring interaction between molecules.

The SH signal was found to decrease as soon as the surface coverage of 8CB molecules was over a monolayer. This indicates that the LC molecules, except those in the first monolayer at the interface, are arranged in the quadrupole-pair configuration, i.e., molecules forming side-by-side pairs with their heads pointing in opposite directions, since the quadrupole layer is expected to radiate 180° out of phase with the dipole layer. To be certain of this picture, we made the following measurements.[9]

An 8CB film with a free surface was prepared on a glass plate coated with DMOAP. The film thickness was much larger than the attenuation length at 2ω in the medium. If the picture presented above is correct, then SHG by reflection from the free surface side should arise only from the induced quadrupole polarization at 2ω in the film. From the SHG measurements, the quadrupole nonlinear susceptibility of 8CB can be deduced. On the other hand, SHG by reflection from the glass side should come from the induced dipole layer at the interface as well as the induced quadrupole polarization in the bulk of the film. The corresponding measurements, in comparison with the SHG measurements from the free surface, can then yield the value for the dipole nonlinear susceptibility of the 8CB dipole layer at the LC/glass interface. The value of the dipole nonlinear susceptibility can be compared with that obtained from the monolayer measurements described earlier. We found in our experiment that the values of the dipole nonlinear susceptiblity from the two measurements were indeed the same within experimental accuracy, thus confirming the picture of molecular alignment of the 8CB film presented above.

As a further check, we could also compare the value of the quadrupole nonlinear susceptibility with the one deduced from SHG from a freely suspended smectic film.[10] In the latter case, it has been shown that the molecular alignment in every smectic layer of the film is of the quadrupole-pair type. Consequently, SHG from such a film comes only from the quadrupole nonlinear polarization induced in the film. We expected the two values of the quadrupole nonlinear susceptibility of 8CB deduced from the two different measurements to agree, and this was indeed the case. We can therefore safely conclude that the 8CB film on glass has all its molecules in the quadrupole-type arrangement except a single monolayer at the LC/glass interface that takes on a dipole-type arrangement.

The above example shows that SHG is a unique technique to investigate possible ferroelectric (dipole-type) ordering of LC molecules on surfaces and in bulk. It can also be extended to many other studies of LC structures. For example, one can imagine the use of this technique to probe the local surface structure of an LC film, the molecular arrangement of ferroelectric LC surface layers, the dipole-dipole interaction between LC molecules, and many others.

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