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Photographic and photopyroelectric measurements of aligned octylcyano-biphenyl (8CB) liquid crystal samples

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Abstract: Thermal properties of homogeneously aligned 8CB samples have been derived from photoacoustic and photopyroelectric measurements. Special attention is given to the heat transport parallel and perpendicular to the long molecular axes. A new accurate technique for measuring high optical absorption coefficients is also presented.

1. INTRODUCTION

Liquid crystals are organic anisotropic molecules which do not melt in a single stage from the crystalline solid to an isotropic liquid [1,2]. The different liquid crystalline phases are characterized by the orientational order of the long molecular axis (for rod-like molecules) and the positional order of the molecules. In the nematic phase the centers of mass of the molecules are randomly distributed, but there is a long-range orientational order. The more ordered smectic phase has a typical layered structure. Within the layers there is no long-range positional order but all the molecules are oriented parallel.

Thermal measurements play an important role for characterization and for distinguishing between different liquid crystalline phases. Photoacoustic and photothermal techniques have proven to be capable of studying static and dynamic thermal parameters [3-8]. Thermal transport properties, e.g. the thermal conductivity, show anisotropic behavior in homogeneously aligned liquid crystals. Alignment can be imposed by an external (magnetic or electric) field, or can be surface induced. In the homeotropic case the long molecular axis is perpendicular to the orienting surface, while in the planar alignment these axes are parallel to the surface. By using these orienting possibilities in a photoacoustic or photopyroelectric setup it is possible to investigate heat transport parallel or perpendicular to the long molecular axis.

2. EXPERIMENTAL SETUP

In order to probe heat transport parallel to the long molecular axis a completely automatic, PC controlled gas-microphone photoacoustic (PA) setup [3,5,7] was used for measurements on free-surfaces homeotropic aligned 8CB samples in an external magnetic field of about 0.1 T perpendicular to the free surface. We used a 5 mW He–Ne laser operating at a wavelength $\lambda = 3.39 \mu m$ because it coincides with the strong absorption band of the C–H groups of the liquid crystal compounds. In order to be able to calculate the heat capacity $C$ and thermal conductivity $\kappa$ from the photoacoustic amplitude and phase data one needs to know the optical absorption coefficient $\beta$. In literature we have found $\beta$ values ranging from 90000 m$^{-1}$ [3] to 627000 m$^{-1}$ [9]. Fitting of photoacoustic data with $\beta$ adjustable gave the best $C$ and $\kappa$ results for $\beta$ values between 50000 m$^{-1}$ and 100000 m$^{-1}$ [7]. In an effort to solve this problem we developed a new accurate technique for measuring high optical absorption coefficients. The liquid crystalline sample is placed between two quartz pieces, a flat and a rounded one with known
radius of curvature (see figure 1a). The modulated light intensity, transmitted through the sample, is measured by a pyroelectric transducer as a function of horizontal displacement, thus as a function of sample thickness. A stepmotor moves the two quartz pieces. With the law of Lambert-Beer we can find an equation for the transmitted light intensity $I$ as a function of the incident light intensity $I_0$, absorption coefficient $\beta$, the radius $R$ of the rounded quartz piece and the distances $x$ from the position $x_0$ where the two pieces are touching (see figure 1b). In that figure the applicable expressions are also given.

\[
I = I_0 \exp(-\beta d) \quad \text{with} \quad d = R[1 - \cos(\theta \sin((x-x_0)/R))] \\
\text{so that} \quad \ln(I) = \ln(I_0) - \beta R[1 - \cos(\theta \sin((x-x_0)/R))] 
\]

**Fig. 1**: Setup for accurately measuring high optical absorption coefficients in liquid crystals.

**Fig. 2**: Photopyroelectric measuring cell for measurements on small liquid crystal samples.
Due to the strong homeotropic free surface alignment of the liquid crystalline molecules it was not possible to obtain a homogeneous planar sample with the photoacoustic configuration [4-6]. Even a magnetic field of 0.6 T was not strong enough to reorient the homeotropic free surface layers. By using a photopyroelectric (PE) setup, shown in figure 2, we have the possibility to put the sample between two plates: at one side the pyroelectric transducer and on the other side a coated quartz piece that absorbs the incident modulated laser light operating in the visible with a wavelength of 640 nm. The heat diffuses through this very thin Ni–Cr–Au coating to the sample and reaches the gold coated LiTaO₃ pyroelectric transducer. The surfaces of both pieces were treated with a rubbed polyvinyl alcohol film, which orients the molecules in a planar configuration. In order to enforce further planar alignment of the bulk of the sample a magnetic field of 0.2 T parallel with the surface was applied.

3. RESULTS AND DISCUSSION

Figure 3 shows results of a measurement of the absorption coefficient of a 6CB liquid crystal sample. The best least square fit with free parameters $x_0$, $I_0$ and $\beta$ for a 6CB sample in the isotropic phase is shown. Averaging over more then ten measurements gave us a $\beta$ value of $\beta=81000 \, \text{m}^{-1} \pm 3\%$. Within this accuracy the absorption coefficient is nearly temperature independent (see the inset in figure 3).

![Figure 3](image-url)

*Fig. 3 : The logarithm of the pyroelectric signal amplitude (proportional to the transmitted light intensity) as a function of the lateral displacement $x$ in the setup of figure 1. The inset gives resulting absorption coefficients as a function of temperature for the 6CB liquid crystal.*

Although small samples (about 15 mg) and small sample thicknesses (of about 0.3 mm) were used in the PA and PE experiments, the conditions for thermal and optical thickness were still largely satisfied. In this case it was possible to derive the thermal conductivity parallel with the thermal wave $\kappa_{//}$ (see figure 4b) from the PA signal.

Figure 4a and 4b show the heat capacity $C$ and the different thermal conductivities in homogeneously aligned 8CB samples. $\kappa_{IS}$ is for the isotropic phase, $\kappa_{//}$ and $\kappa_\perp$ are respectively, for the heat transport parallel and perpendicular to the long molecular axes. In the nematic phase (between $T_{NI}$ and $T_{NA}$) and in the smectic phase (below $T_{NA}$) a large anisotropy is, indeed, observed. The differences between the nematic and the smectic phase are small, thus additional layering in the smectic phase has not a large impact on the thermal conductivities.
At the nematic–isotropic (NI) transition we can observe a two phase region. The photoacoustic results for $\kappa_{//}$ show a small peak at the second order smectic A–nematic (NA) phase transition. The dip we observe in these preliminary pyroelectric results for $\kappa_\perp$ at this transition point is probably an artifact. These measurements have been carried out at rather fast scanning rates (0.03 K/min) and, moreover, the sample thickness could not very well be determined. Accurate measurements at slow scanning rates near the AN transition are in progress.

**Fig.4**: Temperature dependence of the heat capacity and the thermal conductivity of 8CB, from the smectic A to the isotropic phase. $\kappa_{//}$ results have been obtained from gas–microphone photoacoustic measurements and $\kappa_\perp$ results have been measured with the photopyroelectric cell of figure 2.

**REFERENCES**