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Photoacoustic Detection of Phase Transitions in 4-Octyl-4'-Cyanobiphenyl†

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Phase transitions in a thermotropic liquid crystal are investigated by means of photoacoustic detection with an infrared laser excitation. With samples as small as 0.2 mg the technique is shown to be sensitive for the analysis of second order or weak first order phase transitions.

1. INTRODUCTION

In recent years, the photoacoustic technique has proved to be a powerful tool to study optical and thermal properties of materials. When the sample, placed in a gas filled cell, is illuminated by a chopped monochromatic light beam, the absorption of photons by the sample produces a periodic heat flow from the sample to the gas. The subsequent gas pressure variations may be detected by means of a microphone. Thermal expansion can also induce mechanical vibra-

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tions of the sample which may strongly perturb the signal.[1] Therefore, the photoacoustic (PA) effect should be sensitive to density, thermal conductivity and specific heat capacity of the sample and consequently phase transitions can be observed. First measurements were performed by Pelzl,[2] Boccara[3] and Korpium.[4,5]

In this paper we report our work on photoacoustic effects in liquid crystal samples, and experiments to investigate second order or weak first order phase changes in a thermotropic mesogen are described.

2. EXPERIMENTAL

The experimental set up is shown in Figure 1. The light source is a 15 mw helium-neon laser. Two radiations at 0.633 μm and 3.39 μm are used. The laser beam is intensity modulated by an acousto-optic modulator (Soro IM 20) or by a mechanical chopper. The frequency modulation range is 15 Hz–200 Hz. Two kinds of experimental arrangements can be used: the front surface excitation and the rear surface excitation (Figure 2).

The sample is contained in a thermostatted photoacoustic cell described elsewhere in full detail.[6] For the 3.39 μm excitation the windows of the cell are of calcium fluoride glass. The pressure oscillations of the gas surrounding the sample are detected by means of an electret microphone (Sennheiser KE4), the sensitivity being 8

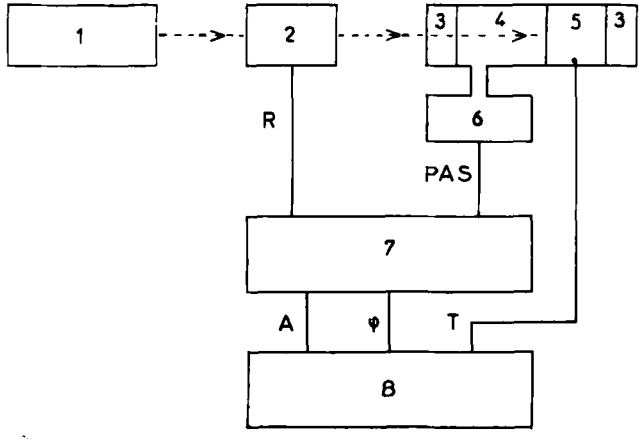

FIGURE 1 Experimental set up: 1. He Ne laser, 2. mechanical or acoustooptical light modulator, 3. backing, 4. Gass cell, 5. Sample, 6. Microphone, 7. Lock-in-amplifier, 8. Recorder; R = reference signal, PAS = photoacoustic signal, A = PAS amplitude, ϕ-PAS phase shift, T = sample temperature.

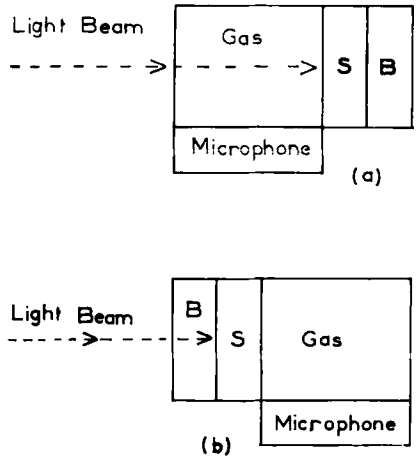

FIGURE 2 Scheme of rear and front surface excitations.

mV/Pa. The photoacoustic signal is analyzed by a lock-in amplifier (PAR 5206) and an analogue recorder (Bryans BS 314).

Experiments to observe phase transitions are performed such that the amplitude of the overpressure and the phase angle between the incident chopped light and the overpressure can be measured as function of the temperature.

3. RESULTS

The PA signal has been measured on 4-octyl-4'-cyanobiphenyl (8 CB) samples (British Drug House). In our preliminary experiments[6] we have used the front surface excitation method and we have added to the liquid crystal sample a small amount of dye (chloro-aluminum phthalocyanin). In that configuration, as in the experimental results of Scudieri and Papa[7] on COOB, the sample is optically opaque for the wavelength radiation excitation (0.633 μm). With the analysis of only the amplitude of the PA signal we have observed the two phase transitions smectic A (S_A)—nematic (N) and nematic (N)—liquid (L). Let us notice that there is no notable variation of the phase angle versus the sample temperature.

In the literature the values of transitional molar enthalpy changes are 0.030 to 0.0729 kcal/mole for the S_A–N transition and 0.20 to 0.2944 kcal/mole for the N–L phase transition.[8] With ac calorimetric investigations, Kasting, Garland and Lushington[9] have measured the

critical heat capacity in 8 CB and their results are consistent with a second order N–S_A phase transition.

In order to avoid disturbances due to the dye, such as photodecomposition of these molecules, we have used infrared radiation excitation, strongly absorbed by the studied material. We have measured the transmittance spectrum (Figure 3) of the sample using a Beckman spectrophotometer and the optical absorption coefficient at $\lambda = 3.39$ μm is about 900 cm^{-1}. The corresponding value of optical absorption length is about 11 μm. Experiments on pure samples that undergo phase transitions are now performed by the rear surface excitation method.

Using only 0.2 mg sample and a sample thickness $l_s = 100$ μm, experimental amplitude and phase angle signals are plotted in Figure 4 versus the temperature. Several remarks must be made about these curves:

i) the phase angle temperature dependence shows an important variation near transition points,

ii) the magnitude of the peaks is sensitive to the frequency modulation, increasing as f^{-1},

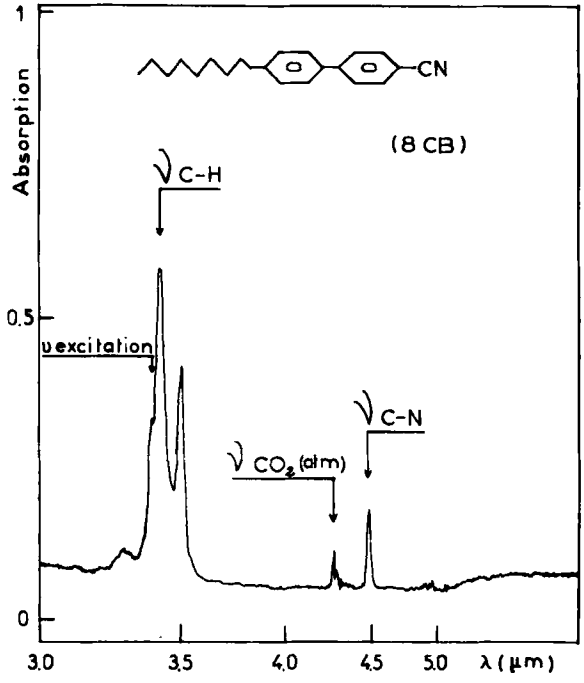

FIGURE 3 Infra-red absorption spectrum of 8 CB in smectic A mesophase.

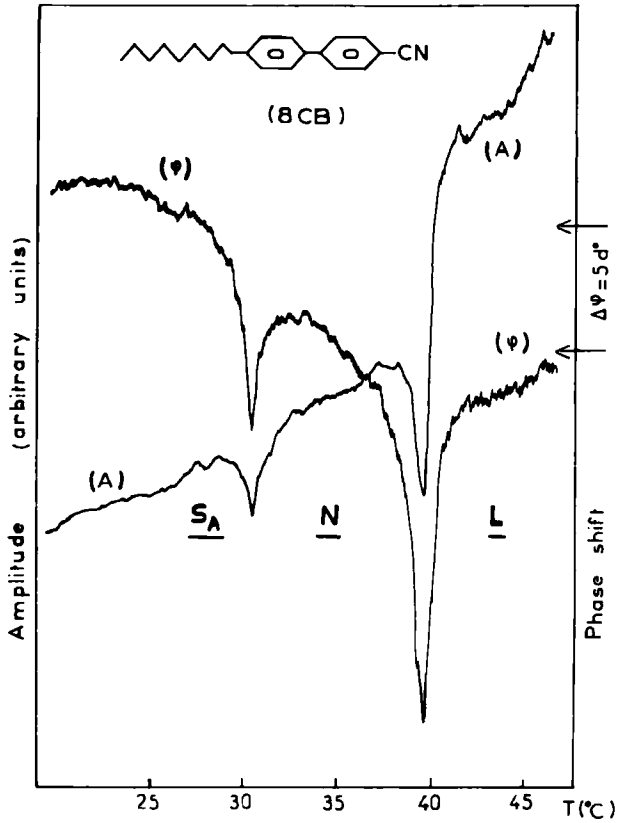

FIGURE 4 Amplitude (A) and phase angle shift (ϕ) temperature dependence. The modulation frequency is $f = 25$ Hz.

iii) the halfwidth of these transition peaks is reduced to a third of that of our preliminary results.

According to the theoretical results of Lepoutre and co-workers[10,11] it seems that, in the case of rear surface excitation, thermoelastic forced motions of the sample surface (acoustic piston) can yield the preponderant contribution to the photoacoustic signal. For that hypothesis, at modulation frequencies greater than the characteristic frequency f_c, the amplitude of the thermoelastic bending must decrease as f^{-1}. Assuming that the sample thermal diffusivity α_s is about $10^{-7}m^2S^{-1}$, the characteristic frequency $f_c = \alpha_s/l_s^2$ is about 10 Hz. In our case $f > f_c$ and the experimental results (Figure 5) are in agreement with this amplitude behavior. Furthermore the acoustic piston model is confirmed by the fact that the ratio Q_F/Q_R between

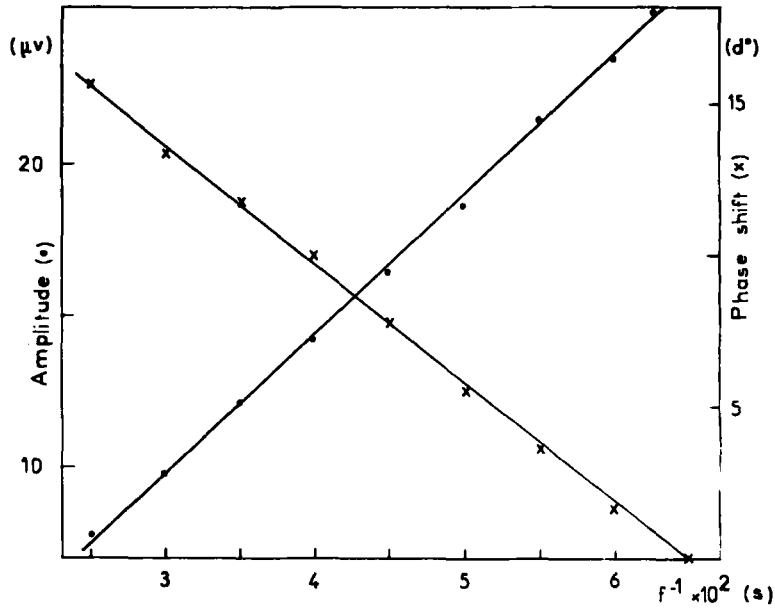

FIGURE 5 Amplitude (o) and phase angle shift dependence (x) as a function of the reciprocal frequency at 29° C.

the amplitudes of front surface (Q_F) and rear surface excitation (Q_R) is only 0.3 at $f = 20$ Hz. If the thermal piston was preponderant the ratio value would be expected to be about 0.01.[10]

4. CONCLUSION

We have shown that the photoacoustic detection method is a powerful technique to observe first and second order phase transitions of mesogens with a very small amount of sample. The use of infrared laser excitation and rear surface excitation allow us to obtain a better resolution by the phase angle/temperature dependence analysis.

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