Orientation of discotic and ferroelectric liquid crystals in macroporous silicon matrix

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Macroporous silicon with deep regular channels $3-4.5\,\mu$m in diameter was infiltrated with discotic and ferroelectric liquid crystals (LCs) at the temperatute of the isotropic phase and then the system was slowly cooled down to room temperature, with the liquid crystalline mesophase formed. The orientation of the LC molecules in the porous matrix was studied by FTIR spectroscopy. The alignment of LCs was ascertained by comparing the behavior of various vibrational bands of a liquid crystal introduced into the porous matrix with that for LC inside the bulk cells of planar and homeotropic alignment. The molecules of the discotic LC show a planar orientation of their column's axis with respect to the surface of the macroporous silicon wafer, i. e., are perpendicular to the channel axis. The long molecular axis of the ferroelectric LC is aligned with the pore walls, having homeotropic orientation with respect to the wafer surface. In a macroporous silicon matrix, both kinds of LCs show unexpected enhancement of the low-frequency vibrational bands.

Over the last decade, considerable scientific effort has been focused on studying liquid crystals within a confined geometry. Liquid crystals are a crucially important enabling technology for the manufacture of displays. The understanding of the layer structure, phase transitions, order parameter fluctuations, liquid-solid interface, and dynamics of collective modes and molecular motions will be significantly advanced if results on samples restricted to confined geometries are compared with those in the bulk [1–4].

Porous systems are suitable hosts for the liquid crystal molecules. These systems are characterized by a ligh surface-to-volume ratio, and therefore are very sensitive to any interactions between the infiltrated molecules and the surrounding walls. A possible interaction of this kind is the aligning power of the walls [5], which can give rise to such sub-phases as a quasi-nematic layer [6].

Polarized infrared spectroscopy with normal and oblique incidence of light is one of the most powerful techniques that can be used to investigate the orientation of liquid crystal (LC) molecules with respect to a substrate [7,8]. The application of this technique to confined LCs is frequently restricted by the nature of the host material (e. g., Vocor glass), which is usually opaque to light in the IR region. However, this problem can be overcomed by using porous silicon for LC infiltration. In this case, the size and depth of pores and the porosity can be varied widely.

Regular porous structures, such as microporous superlattices and macroporous silicon have attracted considerable scientific interest because of their having a photonic band gap [9–11]. Infiltration of porous systems of this kind with liquid crystals allows the control over the position of their photonic band gap, relying upon the fact that the refractive index of LC changes with temperature [12] or external electric field [13]. It is important to find out how different kinds of liquid crystal molecules will behave in a macro-porous silicon (*ma*-PS) matrix. In this study, Fourier Transform Infrared Spectroscopy (FTIR) was used as a tool to investigate the alignment of liquid crystals, both discotic and ferroelectric, infiltrated into *ma*-PS.

1. Experimental

Two different types of liquid crystal materials were used in this study: (i) commercial ferroelectric liquid crystal (FLC) mixture SCE-8; (ii) triphenylene-based discotic liquid crystal (DLC) H5T–NO$_2$ [14]. These LCs were chosen for experimental convenience, both having a mesophase at room temperature. The structural formulae and phase sequences of these compounds are shown in Fig. 1, *a*. These liquid crystals were infiltrated into macroporous silicon (shown in Fig. 1, *b*) by means of the capillary effect at temperatures approximately 10°C above the temperature of transition to the isotropic phase.

The macroporous silicon used in this study (Fig. 1, *b*) has a system of regular cylindrical pores of micrometer diameter and high aspect ratio. The starting material was a single-crystal (100)-oriented Czochralski-grown *n*-type silicon with resistivity $\rho = 15\,\Omega \cdot$ cm. A standard photolithographic process was employed to form pits spaced $12\,\mu$m apart
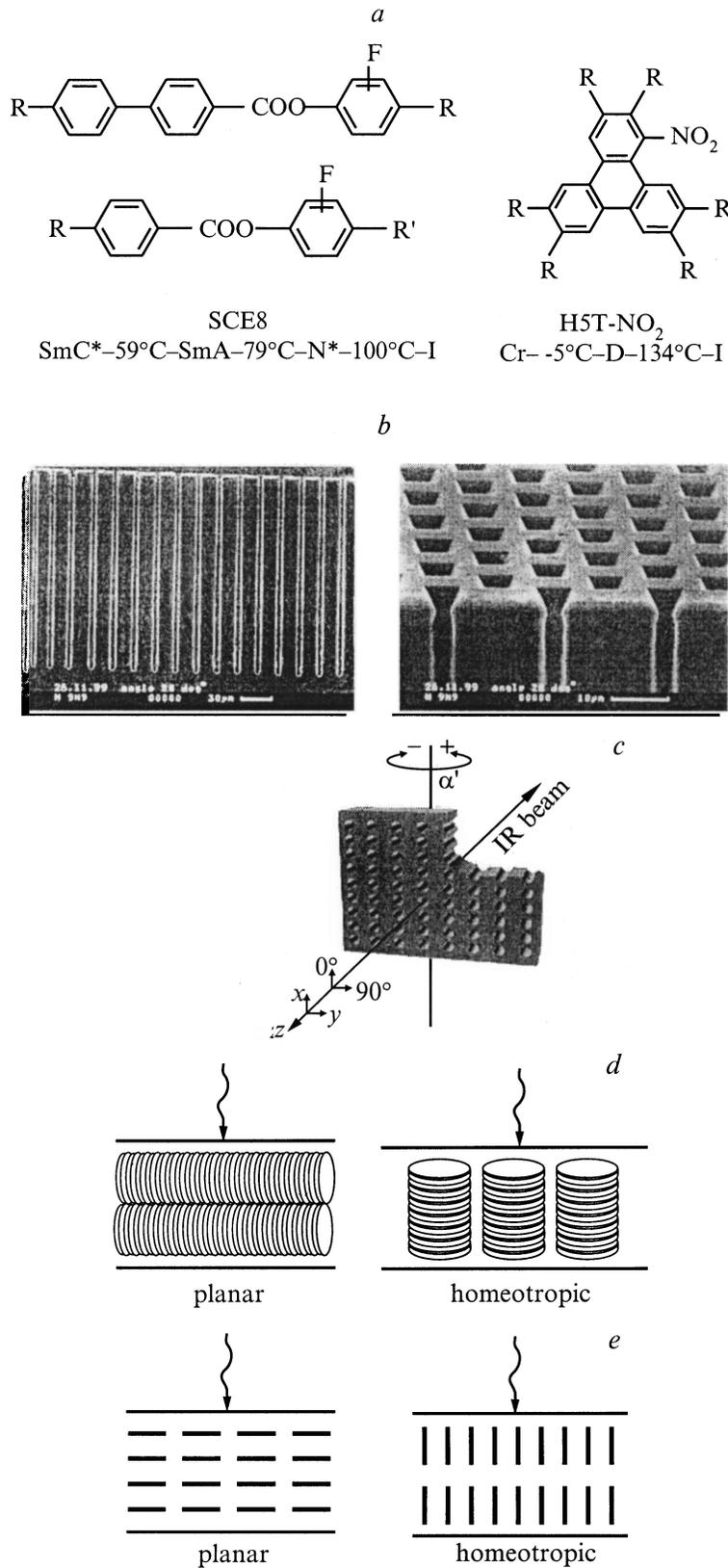
Figure 1. Material properties and experimental setup. a — structural formulas and phase sequences of ferroelectric liquid crystalline mixture SCE8 and tryphenylene-based discotic liquid crystal H5T–NO$_2$ ($R = $ OC$_5$H$_{11}$); b — SEM image of macroporous silicon matrix (cross section side and top view) used to infiltrate with the liquid crystals; c — schematic view of FTIR experiment shows the sample rotation angle α' and macroporous Si sample coordinate frame; d — planar and homeotropic alignment of discotic liquid crystal in ZnSe sell; e — planar and homeotropic alignment of ferroelectric liquid crystal in ZnSe cell.

on the polished surface of the silicon wafer. Deep pores were etched electrochemically in a 2.5% aqueous-ethanol solution of HF for 300 to 450 min under backside illumination [15] at a voltage of 5 V and a constant current density $j = 3$ mA/cm^2. The pore depth and diameter d were, respectively, $200-250$ and $d = 3-4.5\,\mu$m, with these parameters corresponding to a porosity of $5.7-12.8\%$ for our triangular lattice.

FTIR measurements were performed using a Biorad FTS60A spectrometer fitted with a liquid-nitrogen-cooled MCT detector. A schematic of the FTIR experiment is shown in Fig. 1, c. Scans were performed between $450-4000$ cm^{-1} with a resolution ranging from 2 to 8 cm^{-1}. A total of 64 scans were co-added to improve the signal-to-noise ratio. IR spectra were initially recorded for an empty macroporous silicon wafer and then for a matrix infiltrated with the liquid crystal. The difference between these two spectra was taken to be the spectrum of a liquid crystal infiltrated into the porous matrix. The alignment of the LCs within the porous silicon matrix was deduced from a comparison of the relative intensities and positions of the different vibrational bands in the obtained spectra with those of the bulk liquid crystal. For this purpose, a number of liquid-crystal sells with different types of alignment (homeotropic and planar, Fig. 1, d, e) were prepared as follows.

A planar cell with H5T–NO$_2$ was fabricated with ZnSe windows (with a spacer of thickness $\sim 12\,\mu$m). A homeotropic cell was obtained when two ZnSe windows were coated with nylon 6/6 (see [7] for more details). A planarly aligned cell with SCE8 was obtained using two ZnSe windows coated with the commercial (Nissan Chemical Industries, Ltd.) orientant RN-1266 (a 0.4% solution in a mixture of 10% butyl cellosolve and 90% N-methyl pyrrolidone) and rubbed with velvet in a one direction. The thickness of this cell, found from infrared fringes, was $\sim 9\,\mu$m. A homeotropically aligned SCE8 cell, of aproximate thickness $9\,\mu$m, was prepared using ZnSe windows coated with a carboxylato chromium complex (chromolane) (see Ref. [16] for more details). All these cells were filled by means of the capillary effect at a temperature of $\sim 10°$C above the transition to the isotropic phase.

2. Results and discussion

Complete information of the structure and orientation of LC molecules can be obtained by studying a combination of polarized and oblique infrared transmission [7,8]. However, our investigations show that additional interference effects appear in the frequency range $700-1500$ cm^{-1} for tilted macroporous silicon samples. This makes the analysis of the IR spectra of the liquid crystal itself impossible at oblique incidence of light. Therefore, the alignment of LCs was founded by comparing the behavior of various vibrational bands in the spectra obtained at normal incidence of the infrared beam on luquid crystals contained in porous matrix

Assignment of infrared vibrational bands

Band assignment and orientation of the transition dipole moment with respect to the core			H5T–NO$_2$	SCE8
CH$_2$	symmetric stretching	$\perp$	2861	2856
	asymmetric stretching		2934	2926
CH$_3$	symmetric stretching	$\perp$	2873	2873
	asymmetric stretching		2957	2955
N=O	asymmetric stretching	$\perp$	1530	–
C–C	aromatic stretching	$\parallel$	1507	1513
			1521	
			1616	1606
NO	bending	$\perp$	845	–
C–H	aromatic out-of-plane deformation	$\perp$	890	846
			831	829
			818	
			791	
C–C	aromatic out-of-plane deformation	$\perp$		765
NO$_2$	wagging	$\parallel$	750	–
C–H	rocking	$\perp$	733	722

with that in spectra of planar and homeotropic bulk LC cells.

The alignment of liquid crystals is usually considered with respect to the orientation of the long molecular axis (in the case of rod-like molecules) and with respect to the column axis **n** (which is, in general, perpendicular to the core plane) for discotic liquid crystals. Alignment will be planar if the long molecular axis (column axis) is oriented parallel to the substrate plane and homeotropic in the case of perpendicular orientation. Therefore, conclusions about the alignment can be drawn from the behavior of bands associated with vibrations having the transition dipole moment parallel ($\parallel$) and perpendicular ($\perp$) to the rigid part or core of molecules. These bands are listed in Table for both kinds of liquid crystals under study. It should be noted that the spectral position of the majority of the vibrational bands of liquid crystals in a porous matrix is the same as that in the bulk LC cells.

2.1. D i s c o t i c l i q u i d c r y s t a l. There are two methods for determining the type and the extent of alignment for discotic liquid crystals: (i) from the ratio of the peak intensities for a particular vibrational band in isotropic and in the discotic phase ($R_{DI} = A_{iD}/A_{iI}$) and (ii) from the ratio of the peak intensities for the same band in the discotic phase at normal and oblique incidence of light ($R = A_{i\parallel}/A_{i\perp}$), which allows the intensity of the vibrational band to be determined for vibrations with transition dipole moments parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the substrate plane (see Ref. [7] for more details). Neither of these techniques is suitable for our purposes for the technical reasons described above.
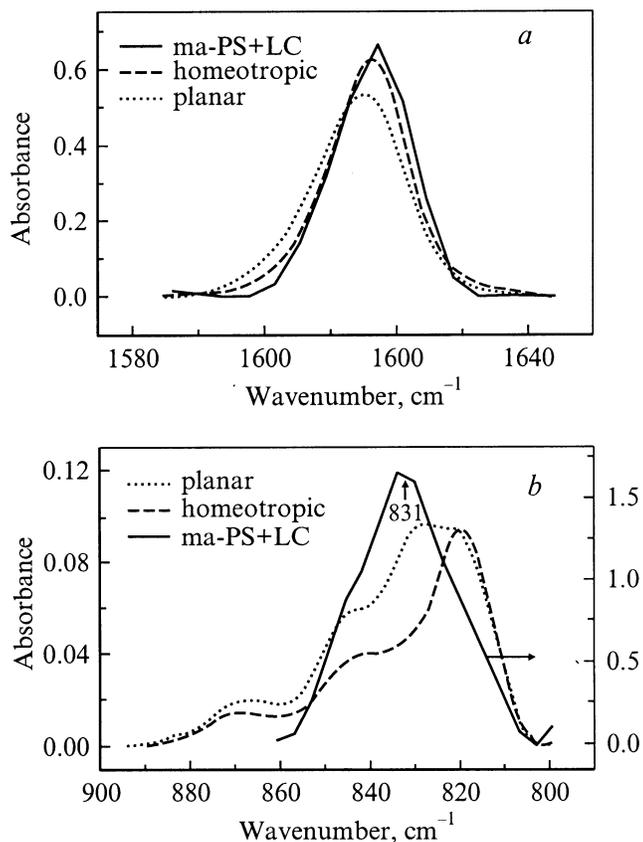
Figure 2. FTIR spectra of H5T–NO$_2$ discotic liquid crystal infiltrated into porous silicon (solid line) and embedded in ZnSe cells with planar (dotted line) and homeotropic (dashed line) alignments. a — C–C streching band, parallel to the core, b — C–H aromatic out-of-plane deformation band, perpendicular to the core. (Note the different scales for the heavy line in (b) and the fact that the absorption of all the samples is reduced in accordance with the intensity of the alkyl chain vibrations in the region 2800–3200 cm^{-1}).

We introduce here a third method for determining the type of alignment by measuring the ratio intensities of two different vibrational bands, i and j, observed in the mesophase (a type of dichroic ratio)

$$R_{ij} = A_i/A_j, \tag{1}$$

where A_i is the intensity of the band associated with vibrations parallel to the LC molecule core and A_j is that associated with vibrations perpendicular to the core. Particular care should be taken in choosing the appropriate set of bands for calculating the dichroic ratio by means of Eq. (1). These bands should correspond to vibrations with transition dipole moments at a right angle ($\sim 90°$) with respect to each other. Our previous investigation [7] performed for a number of triphenylene derivatives (H5T, H7T and H7T–NO$_2$ discotic liquid crystals) demonstrated that the aromatic C–C stretching vibrations at ~ 1510 and ~ 1610 cm^{-1} are parallel to the core (i-band) while the
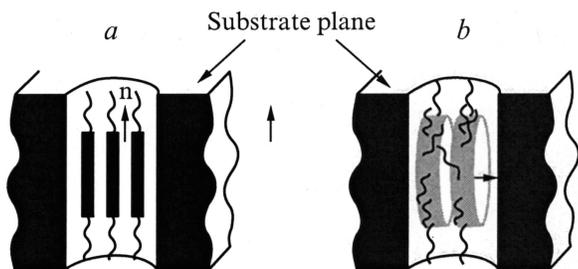
C–H aromatic out-of-plane deformation at ~ 830 cm^{-1} is purely perpendicular to the core (j-band). These vibrational bands are shown in Figs. 2, a and b for the H5T–NO$_2$ discotic liquid crystal in the porous matrix and for both homeotropic and planar alignment of molecules in a liquid-crystal cell.

Qualitative information of the type of alignment in the porous matrix can be obtained by comparing the spectra of different samples in the region 800–890 cm^{-1}. Although the vibrational band in this region is rather complicated, it can be clearly seen that the main maximum of this band is shifted to ~ 830 cm^{-1} for the cell with planar alignment and for the porous matrix, whereas for the cell with homeotropic alignment the peak lies at ~ 820 cm^{-1}.

In order to obtain more precise information on the alignment of H5T–NO$_2$ molecules in a porous silicon matrix, we estimated the dichroic ratio for three samples, using Eq. (1). For this purpose, we fitted the composite band in the region 800–890 cm^{-1} with four (for the bulk planar cell) or five (for the bulk homeotropic cell) Voight functions in order to determine the intensity of the band at ~ 830 cm^{-1}. The results of this fit are shown in
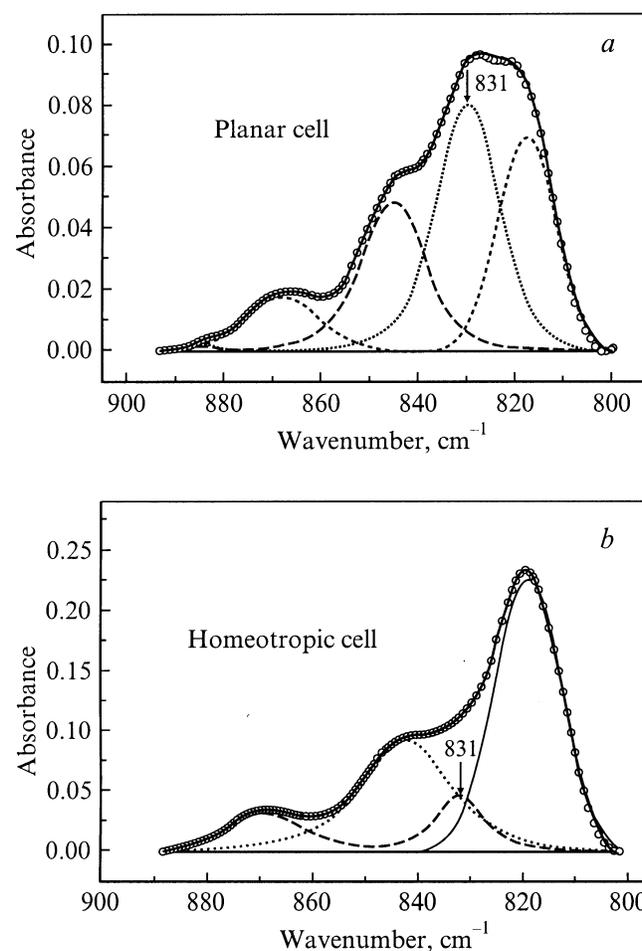
Figure 3. Example of the fitting procedure for the low-frequency band for H5T–NO$_2$ contained in planar (a) and homeotropic (b) cells. Note that the thickness of the homeotropic cell is 2.45 times that of the planar cell.

Figure 4. Side view of the orientation of ferroelectric (*a*) and descotic (*b*) liquid crystals in the macroporous silicon matrix.

Fig. 3, *a, b*. It can be seen that the C–H aromatic out-of-plane deformation occurs at $831\,cm^{-1}$ for both liquid crystal cells and for the porous matrix. The dichroic ratio R_{ij} is 31 for the cell with homeotropic alignment, 7 for the cell with the planar alignment, and is only 0.4 for H5T–NO$_2$ infiltrated into the porous matrix. At first glance, it seems that the alignment in the porous matrix is even better than for the bulk cell with planar alignment, but a more detailed analysis of both types of alignment for a number of triphenylene derivatives shows that this is not the case. The best planar alignment is observed for hexapentyltryphenylene (H5T) [7]. R_{ij} was found to be in the range from 3 to 5 for H5T.

We conclude that the obtained small value of the dichroic ratio is due either to the enhancement of the intensity of the low-frequency vibrational bands or to the dampening of the intensity of the high-frequency vibrational band. In order to obtain more precise data on this issue we compared the results obtained with all the three samples in terms of the absorption per unit volume. This was particularly important for the porous matrix, in which the liquid crystal occupied only a part (V_{LC}) of the volume probed by the IR

beam. This fraction was evaluated by multiplying the total volume (V) by the porosity ($p = 9.5\%$). The comparison enabled us to conclude that strong intensity enhancement is observed for the low-frequency vibrational bands. This conclusion is further supported by a comparison of the intensities of the vibrational bands for the alkyl chain in the region $2800-3200\,cm^{-1}$. It is accepted that the alkyl chain is rather disordered for discotic liquid crystals, and its absorption intensity in this range for different cells depends only on thickness, being independent of the alignment.

Therefore, we compared the spectra of different samples by reducing their intensity in the range $2600\,cm^{-1}$ to the same value. This normalization procedure allowed us to conclude that there is a strong intensity enhancement (~ 15 times) for the low-frequency vibrational bands.

Finally, it is obvious from our results that the alignment of H5T–NO$_2$ in *ma*-PS is planar with respect to the wafer surface. However, as seen from Fig. 4, *b*, the alignment of discotic LCs is homeotropic with respect to the pore walls. This is in agreement with the results of previously published work [7], where the high stability of homeotropic alignment has been found for discotic liquid crystals deposited on untreated substrates.

2.2. Ferroelectric liquid crystals. It should be noted that for this type of molecelar shape, we have to take into account the polarization of light when measuring the spectrum of the cell with planar alignment. We use the following notation: $P = 0°$ for the electric vector of the incident light coinciding with the long molecular axis, and $P = 90°$ otherwise. The IR spectra of SCE-8 introduced into a porous silicon matrix show that the relative intensities of „parallel" (*i*) and „perpendicular" (*j*) bands are in this case close to that observed for the bulk LC cell with homeotropic alignment (Fig. 5). In particular, as seen
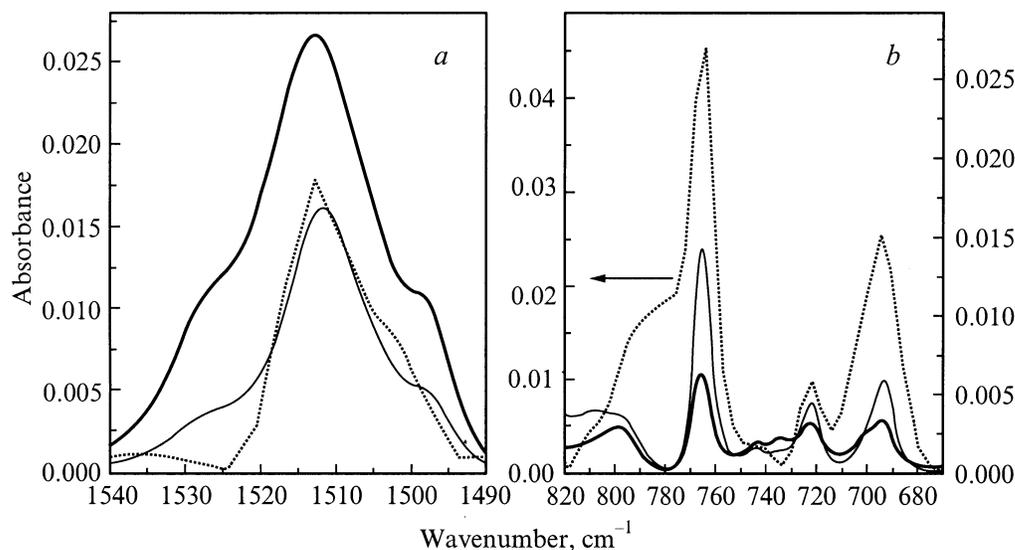
Figure 5. FTIR spectra of SCE8 ferroelectric liquid crystal infiltrated into porous silicon (short dotted line) and contained in ZnSe cells with planar (heavy solid line) and homeotropic (thin solid line) alignments. (Note the different scales for the heavy line in (*b*) and the fact that the absorption of the FLC cells is decreases by a factor of 20 for both cells).

from Fig. 5, *a, b*, the intensity of the C–C aromatic stretching vibration (*i*-band at $\sim 1513\,cm^{-1}$) in the case of the planar cell is much higher with polarizer angle $0°$ (II polarization), when the electric vector of the incident light coincides with the orientation of the transition dipole moment for this molecular unit. At the same time, the intensity of the *j*-bands, perpendicular to the core vibrations (e. g. C–H out-of-plane deformation at ~ 828; C–C aromatic out-of-plane deformation at ~ 765 and CH_2 rocking vibrations at $\sim 722\,cm^{-1}$) is smaller. The intensity ratio found for these bands in the case of a planar cell at a polarizer angle of $0°$ $R_{ij} = A_{1513}/A_{765} = 4.3$. For the homeotropic LC cell, the intensity of the perpendicular bands becomes higher, or at least comparable with the intensity of the parallel bands, owing to the difference in oscillator strength. In this case, the intensity ratio $R_{ij} = A_{1513}/A_{765} = 1.1$. For the SCE8 infiltrated into the porous matrix this ratio of $R_{ij} = A_{1513}/A_{765} = 0.4$ is even smaller than that obtained for the homeotropic LC cell and indicates that the alignment of ferroelectric liquid crystal in confined porous silicon matrix is definitely homeotropic with respect to the substrate's plane (Fig. 4, *a*). This result coincides with the alignment obtained for nematic LCs deposited on untreated surfaces of Anapore membranes [17] and infiltrated into both microporous [18] and macroporous [12] silicon. Such an orientation is expected if one considers the alignment of rod-like molecules with respect to the surface of the pore, in which case the alignment is planar. The planar alignment is typically observed for rod-like molecules on various untreated surfaces, including crystalline silicon [19]. Only a special surface treatment or coating of the substrate surface by a surfactant may give a homeotropic alignment of LCs formed from rod-like molecules.

In the course of these investigations, we found strong intensity enhancement of the low-frequency vibrational bands in the region $600-900\,cm^{-1}$ for both types of liquid crystals in *ma*-PS. This enhancement becomes noticeable when comparing the intensity ratios for the parallel and perpendicular bands. As already mentioned, the intensity ratio is much smaller than that obtained for both LC cells with homeotropic alignment. Moreover, this enhancement is observed for both parallel and perpendicular vibrational bands shown in the low-frequency region. A similar effect has been observed by Alieva et al. [20] for the species in the microcavity of a $1D$ photonic structure. It is worth noting that the enhancement takes place as soon as the light wavelength becomes close to the period of the artificial lattice ($12\,\mu$m). Although the frequency range is in our case outside the main photonic band gap, which is expected in the lower frequency range, this observation seems to be related to the properties of holey wave guides [21].

Thus, we conclude that traditional IR methods cannot establish the alignment of liquid crystals infiltrated into a macroporous silicon matrix. We propose a new technique for determining the alignment, which is based on FTIR investigation of LC in the mesophase, and implies a comparison of the intensity of different vibrational bands, namely, those with transition dipole moment parallel and perpendicular to the core. This method is of particular interest for discotic liquid crystals, since it allows the alignment to be determined without heating a sample to the temperature of the isotropic phase or using oblique transmission IR spectroscopy.

With this method, the alignments of two kinds of liquid crystals infiltrated into a macroporous silicon matrix have been determined. The channel walls of macroporous silicon affect the orientation of LC molecules so that the column axis of the discotic LC is perpendicular to the walls. The long molecular axis of the rod-like molecules of the ferroelectric LC is aligned along the channel walls. A strong intensity enhancement of the low-frequency vibrational bands was detected for the both kinds of LCs infiltrated into the porous silicon matrix.

References

[1] T.Bellini, N.A. Clark, C.D. Muzny, Lei Wu, C.W. Garland, D.W. Schaefer, B.J. Olivier. Phys. Rev. Lett. **69**, *5*, 788 (1992).

[2] N.A. Clark, T. Bellini, R.M. Malzbender, B.N. Thomas, A.G. Rappaport, C.D. Muzny, D.W. Schaefer, L. Hrubesh. Phys. Rev. Lett. **71**, *21*, 3505 (1993).

[3] G.S. Iannacchione, G.P. Crawford, S. Zumer, J.W. Doane, D. Finotello. Phys. Rev. Lett. **71**, *16*, 2595 (1993).

[4] H. Xu, J.K. Vij, A. Rappaport, N. Clark. Phys. Rev. Lett. **79**, *2*, 249 (1997).

[5] P. Ziherl, A. Sarlah, S. Žumer. Phys. Rev. **E58**, *1*, 602 (1998).

[6] P. Ziherl, S. Žumer. Phys. Rev. Lett. **78**, *4*, 682 (1997).

[7] T.S. Perova, J.K. Vij, A. Kocot. Adv. Chem. Phys. **113**, 341 (2000).

[8] A. Kocot, J.K. Vij, T.S. Perova. Adv. Chem. Phys. **113**, 203 (2000).

[9] O. Bisi, S. Ossicino, L. Pavesi. Surface Science Reports **38**, *1–3*, 1 (2000).

[10] U. Gruning, V. Lehmann. Appl. Phys. Lett. **68**, *6*, 747 (1996).

[11] A. Chelnokov, K. Wang, S. Rowson, P. Garoche, J.-M. Lourtioz. Appl. Phys. Lett. **77**, *19*, 2943 (2000).

[12] S.W. Leonard, J.P. Mondia, H.M. van Driel, O. Toader, S. John, K. Busch, A. Birner, U. Gosele, V. Lehmann. Phys. Rev. **B61**, *4*, R2389 (2000).

[13] M. Thonissen, M. Marso, R. Arens-Fisher, D. Hunkel, M. Kruger, V. Ganse, H. Luth, W. Theiss. J. Porous Materials **7**, *1/3*, 205 (2000).

[14] S. Kumar, M. Manickam, V.S.K. Balagurusamy, H. Schonherr. Liquid Crystals **26**, *10*, 1455 (1999).

[15] V. Lehmann, H. Foll. J. Electrochem. Soc. **137**, *2*, 653 (1990).

[16] N.M. Shtykov, J.K. Vij, M.I. Barnik, H.T. Nguyen. Crystallography Reports **45**, *4*, 682 (2000).

[17] H. Binder, H. Schmiedel, G. Lantzsch. C. Cramer, G. Klose. Liquid Crystals **21**, *3*, 415 (1996).

[18] M.V. Wolkin, S. Chan, P.M. Fauchet. Phys. Stat. Sol. (a) **182**, *1*, 573 (2000).

[19] A. Sonin. The Surface Physics of Liquid Crystals. Gordon&Breach Science Publishers, Amsterdam (1995). 180 p.

[20] E.V. Alieva, L.A. Kuzik, G. Mattei, J.E. Petrov, V.A. Yakovlev. Phys. Stat. Sol. (a) **175**, *1*, 115 (1999).

[21] A.M. Zheltikov. Uspehi Fizicheskih Nauk **170**, *11*, 1203 (2000) (in Russian).