Infrared and Raman polarization spectroscopy of molecules aligned in nematic liquid crystals: results from cooperation with Bojidar Jordanov

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Dedicated to the memory of Prof. Bojidar Jordanov

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Molecules, dissolved in an anisotropic solvent, tend to adopt the preferred orientation of the host. Probing the aligned molecules with polarized radiation reveals the orientation of their individual vibrational transition moments not only within the sample but also with respect to the molecular axes. The results – whether obtained with infrared (linear dichroism) or Raman spectroscopy – yield insight in the conformation and the symmetry of the molecules.

There is a good choice of different nematic liquid crystals, which offer the desired uniaxial anisotropy within a comfortable temperature range, sufficient solubility for organic molecules and a favourably weak absorption spectrum, which does not impede the precise measurement of most bands of the dissolved (guest) molecules. The experimental procedure and some examples are represented.

When chiral molecules are embedded in a similar way, they twist the nematic order into a cholesteric one, i.e. a screw-like, helical structure whose period (pitch) often equals infrared wavelengths. Enantiomers produce oppositely twisted structures and this effect is used to discriminate between them. For its easy observation with conventional spectrometers several simple experimental set-ups have been developed.

Key words: Infrared spectroscopy, Raman spectroscopy, nematic liquid crystals, anisotropic solvent, molecular symmetry, chirality, induced cholesteric solutions.

1. INTRODUCTION

Typical vibrational spectroscopy – either infrared or Raman – deals with a double averaging of the information. The first averaging is due to the fact that for most samples the observed molecules are randomly orientated (such as gas, liquid, amorphous or polycrystalline solids), the second is due to using unpolarized radiation, so that the orientation of the observed transition moment relative to the propagation direction of the probing beam is not revealed. And vice versa, employing polarized radiation would supply much more information on the molecular structure provided the solute molecules are aligned in a direction perpendicular to the beam. Most compounds cannot be orientated to a sufficient extent by growing single crystals or by applying e.g. an electric field. However a uniform orientation can be achieved by using an anisotropic solvent such as a stretched polymer or a liquid crystal (LC) [1]. Since 1980 for many years our common interest in this field was to employ nematic liquid crystals, whereupon a wide selection of chemically different types became available.

Nematic liquid crystals are characterized by a preferred orientation of the long axis of their molecules, which are usually described as being rod-like [2]. This direction is pointed by a vector, called director and usually denoted by $n$, which coincides with the axis of the uniaxial anisotropy of the liquid crystal. Since there is no short-range order of the positions of the molecules (centers of gravity) and since the molecules can move freely with respect to each other, the 'crystal' is liquid and adopts the shape of its container. Due to the thermal energy of the molecules, they oscillate around the preferred orientation the stronger the higher the temperature is. At the so-called clearing temperature, the alignment is lost and an isotropic liquid state results.

In this state non-mesogenic molecules (i.e. those not forming a liquid crystal on their own) are dissolved preferably. When the temperature is
lowered the anisotropic state is adopted spontaneously and the “guest” molecules are aligned within the nematic liquid crystal. The nematic temperature interval is reduced by the non-mesogenic solute, therefore liquid crystals with a wide interval are preferable. Other favourable aspects are allowing the experiments to be performed at an easily accessible temperature between 30 and 60°C, sufficient solubility of the guest molecules of interest, and a weak solvent absorption spectrum to avoid spectral interferences. While nematics with a core comprising two phenyl rings prevailed during the time of our first studies, later those with bicyclohexyl skeletons became available and promoted the studies. A bulk nematic liquid crystal looks turbid due to the fact that it is not uniformly aligned (this led to the term “clearing temperature”). An uniform orientation of a thin layer is obtained between the windows of a liquid cell when these windows have been rubbed and polished unidirectionally to produce parallel micro grooves on their surface that would guide the flow of liquid filled between them. With such a sample the infrared absorbance will vary with the azimuth of the polarization: for a vibrational transition with its dipole moment parallel to the molecular long axis, it will be maximal when the electric vector of the incident radiation oscillates in parallel to the director. Minimal absorbance is found with radiation polarized under 90° to the former. The fact that any absorbance is observable at all, is due to the thermal motion of the molecules. The absorbance ratio of the two mutually orthogonal polarizations is called “dichroic ratio”, it exceeds unity for a vibration parallel to the long axis and is smaller than unity for a perpendicular vibration. The dichroic ratio depends on the orientation order, i.e. on the amplitude of the thermal oscillations and thus on the temperature. *Vice versa*, the dichroic ratio measured at bands of the guest molecules indicate the orientation of the related transition moment within the anisotropic solvent and further – under the reasonable assumption that the guest molecules are also aligned preferably with their long axis parallel to the director of the anisotropic solvent – the orientation with respect to the molecular skeleton.

In such a way, the symmetry and the conformations of numerous molecules were studied and the assignment of bands confirmed. The specific details and typical examples are outlined in the following text, where section 2 deals with infrared spectroscopic studies, while section 3 addresses the application of Raman spectroscopy. Finally, section 4 is devoted to solutions of chiral molecules in nematic LCs. In such a case a helical structure results, which is oppositely coiled for enantiomers [3]. This in turn allows us to discriminate between enantiomers and some work has been done to develop experimentally simple set-ups and procedures.

## 2. INFRARED LINEAR DICHROIC SPECTRA OF MOLECULES DISSOLVED AND ORIENTED IN NEMATIC LIQUID CRYSTALS

Infrared linear dichroism (IR-LD) of molecules dissolved and orientated in nematic solvents or embedded in stretched polymers is a very convenient tool for determination of the vibrational transition moments directions as well as the symmetry of the vibrational states [1]. Experimental measurements are usually done by recording the absorption of linearly polarized light by a partially orientated sample, setting the polarization plane first parallel to the sample orientation direction and then perpendicular to it. The relations of the observed polarized absorption regarding the orientation distribution of solute molecules in the sample, on one hand, as well as with respect to the orientation of the individual vibrational transition moments within the fixed molecular coordinate system, on the other hand, is the key to determination of the above quantities.

This valuable spectral information can be extracted by means of the so called “stepwise reduction procedure” primarily proposed by Thulstrup and Eggers for polarized electronic spectra [4] and extended by Spanget-Larsen to polarized IR spectra [5]. The method has also been applied by Korte and Lampen for studying nematic solutions [6]. Within this method the IR polarized absorption spectra, measured in directions parallel $A_\parallel(\tilde{ν})$ and perpendicular $A_\perp(\tilde{ν})$ ($\tilde{ν}$ being the wavenumber) with respect to the uniaxial orientation of the nematic solvent or the stretched polyethylene film, are interactively subtracted $A_\parallel(\tilde{ν}) - m A_\perp(\tilde{ν})$, where the constant $m$ is being varied until some specific bands vanish. Using this simple procedure, the bands having one and the same symmetry appurtenance are simultaneously eliminated when the free variable parameter $m$ becomes equal to the dichroic ratio $R = A_\parallel(\tilde{ν})/A_\perp(\tilde{ν})$. $R$ is directly related to the orientation factors $K_\parallel$ that define the average molecular orientation within the solute molecules assembly, and depends on the orientation of the individual vibrational transition moment within the fixed molecular framework. So it was demonstrated that the proposed technique allows easy symmetry band assignments and reliable determination of the vibrational transition moments directions [1, 7–10]. The spectra obtained in this way were designated as reduced IR-LD.
spectra [8]. Their graphical representation is quite simple: the consecutive elimination of each set of bands, polarized along \( x, y \) or \( z \) directions, leads to obtaining of difference spectra which consist of linear combinations of the remaining two other absorptions (\( xz, xz \) or \( xy \) respectively).

In a series of papers [9–13] we extended the method for measuring IR–LD spectra to high- and low-symmetry molecules orientated in the nematic liquid crystals ZLI–1695 and ZLI–1638 (Merck notation for trans-trans-4-alkyl-4’-cyanobicyclohexyl mixtures). The use of these anisotropic solvents offers some practical advantages in comparison with the method in which the molecules are embedded and orientated in stretched polyethylene. Most chemical substances are easily soluble in these liquid crystals and form stable solutions at room temperature. Similarly to polyethylene, ZLI-1695 and ZLI-1638 are largely trans-soluble in these liquid crystals and form stable solutions at room temperature.

If the symmetry of the solute molecule is sufficiently high (\( C_{2v} \) or \( D_{2h} \)), the directions of vibrational transition moments \( M_f \) coincide with the molecular axes \( x, y \) and \( z \) and the orientation tensor \( K \) acquires a diagonal form, whereupon its trace remains equal to unity:

\[
K_x + K_y + K_z = 1.
\]  

For the sake of simplicity the following convention was used: \( K_x = K_{xx}, K_y = K_{yy}, K_z = K_{zz} \). These orientation factors can be easily calculated by the following expression [1]:

\[
K_u = R_u/(R_u + 2)
\]  

where \( R_u (u = x, y, z) \) are the dichroic ratios determined after consecutive band elimination using the stepwise reduction procedure. The applicability of the stepwise reduction is illustrated below. Diphenylacetylene (tolane) was chosen as an example, which belongs to \( D_{2h} \) point group. Its unpolarized and reduced IR spectra in the range 2500–400 cm\(^{-1}\) are displayed in Fig.1. The bands assignment together with the calculated dichroic ratios and orientation factors are listed in Table 1.

### Table 1. Polarization distribution, dichroic ratios \( R_u \) and orientation parameters \( K_u \) of tolane.

<table>
<thead>
<tr>
<th>( x ) polarized</th>
<th>( y ) polarized</th>
<th>( z ) polarized</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_x = 0.330 )</td>
<td>( R_y = 0.625 )</td>
<td>( R_z = 3.26 )</td>
</tr>
<tr>
<td>( K_x = 0.142 )</td>
<td>( K_y = 0.238 )</td>
<td>( K_z = 0.620 )</td>
</tr>
<tr>
<td>985</td>
<td>1572</td>
<td>1602</td>
</tr>
<tr>
<td>913</td>
<td>1443</td>
<td>1498</td>
</tr>
<tr>
<td>758</td>
<td>(1328)(^a)</td>
<td>1310</td>
</tr>
<tr>
<td>689</td>
<td>1281</td>
<td>1158</td>
</tr>
<tr>
<td>511</td>
<td>1179</td>
<td>1027</td>
</tr>
<tr>
<td>1070</td>
<td>997</td>
<td></td>
</tr>
<tr>
<td>540</td>
<td>(620)(^a)</td>
<td>(822)(^a)</td>
</tr>
</tbody>
</table>

\(^a\) Wavenumbers in parentheses mean uncertain polarization feature due to low band intensity

\(^b\) This axis is usually used to define the uniaxial direction in nematic liquid crystals and stretched polymers.
Tolane is a relatively long molecule therefore close values or even equality for \( K_x \) and \( K_y \) were reasonably expected. The reduced spectra showed, however, that there is a distinct difference between the orientation parameters leading to unambiguous bands assignment as \( x \), \( y \) and \( z \) polarized features. This result confirms the previous assignments made by Lunelli [14] and Baranovich [15]. The only peculiarities were observed for the band at 537 cm\(^{-1}\). According to ref. [14] it was expected to be a \( z \) polarized feature. This band, however, appears in all reduced spectra, namely \( xy \), \( xz \) and \( yz \). While in \( xz \) and \( yz \) spectra this band preserves its wavenumber position at 537 cm\(^{-1}\), in \( xy \) reduced spectrum it
appears shifted up to 540 cm\(^{-1}\). It was concluded that two very close bands, one \(z\)-polarized and the other one \(y\)-polarized were hidden in the overall band profile, which could be detected only by their band polarizations.

2.3. Overlapped bands

Spectral bands’ overlapping occurs frequently in the IR spectra of complex molecules. Overlapped or hidden bands can be lying closely or exactly coinciding in frequency. Such close or coinciding bands, pertaining to different symmetry classes, are often found in the spectra of aromatic compounds. Owing to the fact that bands with different polarization and hence belonging to different symmetry classes give rise to positive and negative peaks in the reduced spectra, it becomes possible to distinguish them easily. Moreover overlapped spectral bands of different polarizations hidden under common envelope become obvious in the reduced linear dichroic spectra. This is demonstrated amply by the examples given below [9].

**Diphenylacetylene (tolane).** According to Baranovic et al. [16] five C–H stretching bands were found in the IR spectrum of tolane in the region 3000–3150 cm\(^{-1}\). Reduced polarized spectra, however, show quite a different picture (Fig. 2). The C–H stretching bands can be only \(z\)- and \(y\)-polarized. Therefore, the \(y\)-bands are observed in the \(xy\)-spectrum, while the \(z\)-bands are seen in the \(xz\)-spectrum, the \(xy\)-spectrum being identical with the unpolarized one. Thus four \(z\)- and four \(y\)-bands were found in the reduced spectra. The band at 3063 cm\(^{-1}\) turns out to be degenerated accidentally since it clearly appears in the \(z\)- and in the \(y\)-spectrum, as well. A hidden \(y\)-band at 3042 cm\(^{-1}\) appears in the \(xy\)-spectrum.

**Benzonitrile.** In the vibrational analysis of benzonitrile, carried out by Green [17], an out-of-plane phenyl band at 760 cm\(^{-1}\) was assumed to be accidentally degenerate and was assigned simultaneously to \(A_1\) and \(B_2\) symmetry species. Eighteen years later Csaszar and Fogarasi [18] found by \textit{ab initio} calculations two very close frequencies, assigned to different symmetry species: 752 (\(A_1\)) and 754 (\(B_1\)) cm\(^{-1}\) and this result was reported as a confirmation of Green’s assignment. It was interesting to verify the accuracy of this supposition by means of the reduced spectra. As it is seen in Fig. 3 no \(z\)-band is observed in the 600–800 cm\(^{-1}\) range of the \(yz\)-spectrum.

Conversely, the absorption ratio \(A_{760}/A_{689}\) in the unpolarized spectrum is the same as that in the \(xy\)- and \(xz\)-spectra, confirming once again the absence of a hidden \(z\)-band. Hence, either no accidental degeneracy has to be expected at this frequency or the degenerated band must be of a very low intensity. Referring again to the \textit{ab initio} calculations [18] we found there molar intensities of 4 and 34.2 km·mol\(^{-1}\) for the \(A_1(z)\) and \(B_1(x)\) bands, respectively. If these values were correct the \(z\)-band would have been manifested clearly in the \(yz\)-spectrum.

2.4. Low symmetry molecules

If the symmetry of a molecule is intrinsically low or it is lowered under constraint of the environment so that the molecule does not possess at least two mutually perpendicular planes or rotational axes, the transition moment vectors are not restricted to three mutually perpendicular directions. In this case the orientation tensor \(K\) should have five independent...
unknowns, for each transition \( f \). There are also two unknown independent direction cosines \( \cos \phi^f_u \) for which the following relationship is valid [1]:
\[
\cos \phi^f_x + \cos \phi^f_y + \cos \phi^f_z = 1
\]
In order to reduce the number of the unknown \( K_u \) parameters, we may choose the so-called principal molecular axes system, in which the orientational tensor has a diagonal form \( (K_{uu}=K_{dd}) \). In this frame the molecular axes \( x, y \) and \( z \) coincide with the resulting eigenvectors, while the eigenvalues correspond to the orientational factors \( K_u \) [1]. Although the number of the unknown parameters decreases significantly, the task to determine the \( K_u \) values cannot be solved without any previous knowledge of the transition moment orientation. In principle, this information can be obtained from another experimental or theoretical source [11, 12, 20].

If the solute molecule is planar and has only \( C_s \) symmetry, the task to determine the \( K_u \) values can be simplified considerably. In this case all transition moments can be classified in two types of vibrational modes: \( 2N-3 \) in-plane and \( N-3 \) out-of-plane modes, where \( N \) is the number of atoms in the molecule. This means that one of the principal axes of the orientational tensor, say \( x \), should be perpendicular to the plane, i.e. \( K_{xy} = K_{xz} = 0 \). Thus, only the orientational parameters \( K_{yz} \), \( K_y \), \( K_z \) and the directions of \( y \) and \( z \) axes remain unknown since the \( K_i \) value can be determined immediately based on the dichroic ratio \( R_i \) by interactive subtraction. Certainly, all the bands related to transitions polarized perpendicularly to the plane disappear simultaneously. On the contrary, the in-plane bands may all have individual transition moment direction within the \( yz \) plane, whereas none of them will necessarily coincide with the long axis \( z \), so \( K_z \) may not be determined by experiment. If we use a principal axes system, the off-diagonal element \( K_{yz} \) vanishes. In order to determine the orientational parameters \( K_y \) and \( K_z \), a set of two equations similar to Eqn. (3) has to be solved:
\[
\begin{align*}
K_1 &= K_y \cos^2 \varphi_1 + K_z \sin^2 \varphi_1 \\
K_2 &= K_y \cos^2 \varphi_2 + K_z \sin^2 \varphi_2
\end{align*}
\]
(6) (7)
where \( \varphi_1 \) and \( \varphi_2 \) are two unknown angles that can be calculated from the equation:
\[
\tan(\varphi_f) = \frac{K_x - K_f}{K_f - K_y} \quad f = 1, 2
\]
(8)

The \( K_1 \) and \( K_2 \) values are determined directly from the dichroic ratios. One way to solve this set of equations is based on the knowledge of the angle \( \gamma = \varphi_2 - \varphi_1 \) between the two transition moments \( M_2 \) and \( M_1 \) [7]. If such data are not available experimentally, \( ab \) initio or DFT quantum mechanical calculations can help to evaluate both transition moments \( M_1 \) and \( M_2 \) and hence the angle \( \gamma \) [12]. Then \( K_z \) can be defined by the following trigonometric relationship:
\[
\tan(\gamma) = \tan(\varphi_2 - \varphi_1) = \frac{\tan(\varphi_2) - \tan(\varphi_1)}{1 + \tan(\varphi_2)\tan(\varphi_1)}
\]
(9)

Substituting the corresponding expressions for \( \tan(\varphi_1), f = 1, 2 \) from Eqn. (8) into Eqn. (9) and introducing a notation \( a = 1 - K_y = K_z + K_y \), the following expression is obtained for the angle \( \gamma \):
\[
\tan(\gamma) = \frac{\sqrt{K_z - K_y} - \sqrt{K_z - K_1}}{1 + \sqrt{K_z - K_y}}
\]
(10)

The \( K_z \) value is obtained then from the intersection point of the straight line \( |\tan(\gamma)| = \text{const} \) (from \( ab \) initio calculations) and the curve \( |\tan(\gamma)| = f(K_z) \) given by Eqn. (10). A graphical illustration is presented in Fig.4. For that purpose \( K_z \) should vary within an interval \( \text{max } K_f \leq K_z \leq a - K_z \) determined by the following inequalities: \( K_z \geq K_y \geq K_\gamma > 0; \ K_z \geq \text{max } K_f \); \( a - K_z = K_y \geq K_\gamma \) [5] where \( \text{max } K_f \) is the largest \( K_f \) value obtained by interactive subtraction. Once \( K_z \) is known, then the angle \( \varphi_1 \) can be calculated for each transition moment \( f \) based on Eqn. (8).

![Graphical illustration of the method proposed for determination of the \( K_z \) value.](image)

2.4.1. Examples

The approach represented here has been applied to \( p \)-nitrobenzaldehyde (\( p \)-NBA), furfural (FUR) and 2-chlorobenzaldehyde (2-CBA). The latter two molecules possess two distinct planar conformers at dynamic equilibrium in an anisotropic solvent. The
change in the orientation of their vibrational transition moments as a result of conformational interconversion can be observed by means of their IR-LD spectra, measured in nematic liquid crystal as it is demonstrated below.

\[ p\text{-nitrobenzaldehyde (p-NBA)} \]

\( p\)-NBA is a planar molecule and belongs to the \( C_s \) point group. Computational and experimental data for twenty nine in-plane vibrations were included in this evaluation. The angle \( \gamma \) was calculated from the fundamentals \( \nu_{\text{asNO}_2} \) and \( \nu_{\text{sNO}_2} \), located at 1534 and 1344 cm\(^{-1}\). The orientation parameters in the principal axes system were as follows [12]: \( K_x = 0.177 \), \( K_y = 0.307 \), \( K_z = 0.516 \). The results for the orientation tensor elements were also represented in the molecular coordinate system, chosen for quantum chemical DFT calculations: \( K_{xx} = 0.177 \), \( K_{yy} = 0.310 \), \( K_{zz} = -0.025 \), \( K_{xz} = 0.513 \). The \( K_z \) values determined in [19] and those in the present approach are rather close to each other (0.512 and 0.516, respectively), because of the small angle (7º) between the \( z \) and \( z' \) axes.

![Fig. 5. Orientation of p-NBA molecule and definition of angle \( \phi_{\text{calc}} \) in the coordinate system used for quantum chemical calculations.](image)

In general, this angle could be quite different in different molecules and it also differs from zero, since the long molecular axis may not coincide with the \( z' \) axis of an arbitrarily chosen molecular coordinate system. The orientation of the molecule in the Cartesian coordinate system and the definition of angle \( \phi_{\text{calc}} \) is shown in Fig. 5. The obtained results are plotted in Fig. 6. Apparently, the proposed method provides a substantially better correlation between the calculated and redetermined data (Fig. 6b) than in the case with directly obtained „experimental” values (Fig. 6a) without correction for the orientation of the \( z \) axis.

One restriction of the suggested approach is that it is not applicable to the cases when the angle \( \gamma \) is either 0º or 90º (see Eqn. (10)). The bands chosen for our calculations (\( \nu_9 \) and \( \nu_{13} \)) originated from \( \nu_{\text{asNO}_2} \) and \( \nu_{\text{sNO}_2} \) vibrations and thus were expected to have orthogonal transition moments. Conversely, due to the low molecular symmetry (asymmetric coupling effects) they were not exactly perpendicular to each other (\( \gamma \) was calculated to be 80.6º), which allowed us to use them for evaluation of molecular orientation.

![Fig. 6. Correlation between calculated \( \phi_{\text{calc}} \) and experimentally determined transition moment directions: (a) with the directly obtained experimental values, \( \phi_{\text{exp}} \) and (b) with angle values obtained from the combined determination, \( \phi_{\text{det}} \), obtained by the proposed method. (The numbered data points refer to the rows in Table 1. Note that the points lying far away from the dotted straight line invariably correspond to very weak or weak bands.)](image)

\[ \text{Furfural and 2-chlorobenzaldehyde} \]

In solution, at room temperature, both furfural (FUR) and 2-chlorobenzaldehyde (2-CBA) are known to exist in the form of equilibrium mixtures of two conformers. The experimental and theoretical studies show that the aldehyde group is coplanar with the furan and benzene rings respectively [19, 20]. The cis- and trans-FUR conformers differ by
the position of the carbonyl oxygen atom with respect to the furan ring oxygen (Fig. 7). Similarly, with respect to the chlorine atom, the cis- and trans-
conformers of 2-CBA are defined, displayed in the same figure. Both rotamers of the studied molecules belong to the $C_s$ symmetry. The distribution of the vibrational normal modes of each conformer among the symmetry species is as follows:

FUR, cis and trans: $19\ A'(y, z) + 8\ A''(x)$; 2-
CBA, cis and trans: $25\ A'(y, z) + 11A''(x)$.

Fig. 7. Furfural (a), and 2-chlorobenzaldehyde (b) in the
$s$-trans and $s$-cis conformations. The axes of the
molecular coordinate system were chosen so that
the $z$-axis coincides with the preferable direction of
molecular orientation in the nematic solution.

The notations in the parentheses, $(y, z)$ and $(x)$,
indicate the polarization directions of the infrared
active in-plane and out-of-plane modes, respectively
(Fig. 7). For low symmetry molecules belonging to
the $C_s$ point group, the only way to separate the in-
plane and out-of-plane vibrations is to use their
reduced IR-LD spectra (Figs. 8a and 8b) as it is
demonstrated further.

The DFT (B3LYP/6-311+G**) calculated transi-
tion moments of the following band pairs: 1019,
1013 and 930, 946 cm$^{-1}$ for FUR and 1391, 1395
and 1259, 1268 cm$^{-1}$ for 2-CBA, together with the
respective experimentally determined orientation
parameters $K_z$, were used for the evaluation of the average orientation of each conformer. Two addi-
tional orientation parameters, $K_x$ and $K_{max}$ (see Eqn.
(10)) were necessary for the calculations. $K_x$ was
obtained from the experimentally evaluated dichroic
ratios of the corresponding out-of-plane vibrations
(768 cm$^{-1}$ for FUR and 763 cm$^{-1}$ for 2-CBA), while
$K_{max}$ was obtained from those of furan and benzene
ring stretching vibrations (1470 cm$^{-1}$ for FUR and at
1467 cm$^{-1}$ for 2-CBA). Our reasoning to use
theoretically calculated transition moments to estimate the angle $\gamma$ necessary for the determination
of $K_z$-value, was based on the very successful
prediction of polarization directions. These we have
obtained for $p$-nitrobenzaldehyde [19], particularly
for medium and high intensity IR bands. Although
in the mentioned work the calculations have been
done only at medium level of theory (B3LYP/6-
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observed $\varphi_j$ values was $2.2^\circ$ for the 14 most
intensive bands, whereas none of these differences
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As it is expected, the two conformers of FUR
and 2-CBA showed close orientation parameters in
anisotropic solvent since the internal rotation of the

220
aldehyde group does not change the overall molecular geometry, size and shape drastically. Nevertheless, the small differences in the orientation parameters indicate that the dipole-dipole interactions have definite contribution to the orientation mechanism of solute molecules. The listed \( K_z \) values in Table 2 show that trans-FUR is better orientated than cis-FUR, while the opposite is valid for cis- and trans- counterparts of 2-CBA. This is in accordance with the DFT calculated total dipole moments of FUR (\( \mu_{cis} = 3.601 \text{ D}, \mu_{trans} = 4.101 \text{ D} \)) and 2CBA (\( \mu_{cis} = 4.09 \text{ D}, \mu_{trans} = 3.426 \text{ D} \)) as well as with NMR results [19]. The respective orientations of cis- and trans-conformers of FUR and 2-CBA, as they are determined based on the IR-LD spectra and on the DFT calculations, are displayed in Fig. 9.

Table 2. Orientation parameters of FUR and 2-CBA.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( K_{max} )</th>
<th>( K_1 )</th>
<th>( M_{1y} )</th>
<th>( M_{1z} )</th>
<th>( K_{z} )</th>
<th>( M_{2y} )</th>
<th>( M_{2z} )</th>
<th>( \phi )</th>
<th>( K_{y} )</th>
<th>( K_{x} )</th>
<th>( K_{z} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUR-cis</td>
<td>0.425</td>
<td>0.367</td>
<td>2.461</td>
<td>-3.623</td>
<td>0.421</td>
<td>3.203</td>
<td>0.106</td>
<td>57.7</td>
<td>0.210</td>
<td>0.363</td>
<td>0.427</td>
</tr>
<tr>
<td>FUR-trans</td>
<td>0.436</td>
<td>0.362</td>
<td>-2.296</td>
<td>1.250</td>
<td>0.413</td>
<td>1.654</td>
<td>6.024</td>
<td>32.6</td>
<td>0.210</td>
<td>0.347</td>
<td>0.443</td>
</tr>
<tr>
<td>2-CBA-cis</td>
<td>0.450</td>
<td>0.360</td>
<td>1.102</td>
<td>-3.054</td>
<td>0.440</td>
<td>2.685</td>
<td>-3.254</td>
<td>19.7</td>
<td>0.184</td>
<td>0.289</td>
<td>0.527</td>
</tr>
<tr>
<td>2-CBA-trans</td>
<td>0.432</td>
<td>0.390</td>
<td>5.499</td>
<td>5.188</td>
<td>0.430</td>
<td>-0.833</td>
<td>4.583</td>
<td>57.0</td>
<td>0.184</td>
<td>0.383</td>
<td>0.433</td>
</tr>
</tbody>
</table>

Notation used: \( K_{max} \) is the largest \( K_i \) value obtained by interactive subtraction; \( K_i (i = 1, 2) \) are the experimentally determined orientational parameters of two selected vibrational transition moments \( M_i \), where their y- and z-components are denoted by \( M_{iy} \) and \( M_{iz} \), respectively.

3. FT RAMAN POLARIZATION SPECTROSCOPY OF PHENYLACETYLENE GUEST MOLECULES ORIENTED IN NEMATIC LIQUID CRYSTAL

While the IR-LD studies of solute molecules are more abundant, there is only a limited number of articles considering polarization Raman spectroscopy of molecules embedded and orientated in anisotropic media [22–26]. The Raman spectroscopy of orientation order in liquid crystal phases [27] was applied in this work to studying the non-mesogenic molecule phenylacetylene, dissolved and orientated in the host liquid crystal ZLI-1695 (trans-trans-4-ethyl-4’-cyanobicyclohexyl) in order to perform a symmetry assignment of the observed Raman bands.

3.1. Experimental

The nematic liquid crystals ZLI-1695 with a nematic range 13–72ºC were used as an anisotropic solvent. Phenylacetylene (Aldrich) was used after distillation under vacuum. Its solutions (2–10% w/w) were prepared by raising the temperature above the clearing point of the nematic phase. The cell construction and preparation of the cell windows were described elsewhere [25].

The FT-Raman spectra were recorded at ambient temperature in the 3500–80 cm\(^{-1}\) range on a Bruker FTIR IFS-66 spectrometer supplied with the FTR 106 Raman module. The resolution was 4 cm\(^{-1}\) and 1000 scans were collected for each spectrum; the 180º scattering geometry was applied. A diode-pumped Nd:YAG laser (1064 nm) with a power of 420 mW, unfocused, was used for the excitation; the details were described in [24, 25].

Raman spectroscopic measurements were performed at uniaxial orientation of the samples, i.e. with their long axis (z) preferably parallel to the window as well as to the polishing direction, which defines the Z axis of the coordinate system XYZ as outlined in Fig. 10. Four different Raman spectra were recorded for every sample; the direction (X) of the incident laser beam was always kept normal to the surface of the windows. The recorded Raman band intensities were: I_{ZZ} for X(ZZ)X, I_{YZ} for X(YZ)X, I_{ZX} for X(ZY)X, and I_{YY} for X(YY)X. According to Porto’s nomenclature [28] A(BC)D means irradiation in A direction by radiation polarized in B direction produces scattered radiation, that is polarized in C direction and it is observed in D direction. For a uniaxial sample the
intensity $I_{YZ}$ should be equal to $I_{YZ}$. The recorded corresponding spectra, corrected as it was pointed out in [25], were indeed found to be almost identical.

$$X(ZZ)X \quad X(YZ)Y$$

Fig. 10. Exciting and scattering geometry for recording the polarization Raman spectra of guest molecules oriented in nematic liquid crystals; the ellipses depict the liquid crystal molecules ordered parallelly to the micro grooves of the window surfaces.

3.2. Results and discussion

FT Raman spectral intensities $I_{ZZ}$, $I_{YX}$ of the phenylacetylene guest molecules dissolved and orientated in nematic mesophase ZLI-1695 are shown in Fig. 11. The wavenumber positions, intensity and the intensity ratios $R = I_{YY}/I_{ZZ}$ calculated from the spectra for the observed bands of host and guest molecules are collected in Table 3. The $R$ values are used as a measure for the molecular orientation. It is seen from Figure 11 and Table 3 that the C≡N group stretching band of the nematic liquid crystal molecules of ZLI-1695, located at 2239 cm$^{-1}$ shows a strong polarization; its intensity ratio is 0.31. Several other bands of ZLI-1695 show also a similar polarization, listed in Table 3.

Assuming that in the liquid crystalline state the ZLI-1695 molecules rotate around the $Z$ axis an effective polarizability tensor $\alpha^e$ results in the $C_\infty v$ point group symmetry. According to the character table [28] the Raman active vibrational modes can be classified into two classes: the totally symmetric vibrations of class $A_1$ and the twofold degenerate modes of class $E_1$ and $E_2$.

$$X(ZZ)X \quad X(YY)X$$

Fig. 11. Raman spectra of phenylacetylene dissolved and orientated in ZLI-1695 recorded under two polarization conditions: $X(ZZ)X$ - both scattered and incident beams parallel to the micro grooves; $X(YY)X$ - both scattered and incident beams perpendicular to the micro grooves.

On the basis of these considerations and the obtained intensity ratio data $R$ the vibrational modes of ZLI-1695 molecules are assigned in Table 3 to the corresponding symmetry species: $A_1$ with $R$ values from 0.31 to 0.54, $E_1$ and $E_2$ with $R$ values higher than 0.8. The vibrations of the first group, which modulate a polarizability tensor element $\alpha^e_{zz}$ are assigned to the symmetry species $A_1$. The $R$ values of both stretching vibration bands of ZLI-1695 molecule, $\nu_s(CH_2)$ at about 2850 cm$^{-1}$ and $\nu_{as}(CH_2)$ at 2936 cm$^{-1}$, are larger than unity. In other words, higher band intensity is recorded for these bands with perpendicular polarization of the incident radiation ($I_{YY}$) than that with parallel polarization ($I_{ZZ}$). In analogy to the IR results and their interpretation (see above) we expect a vibration perpendicular to the long molecular axis: indeed C-H stretching vibrations occur almost perpendicularly to the cyclohexane ring plane. Thus, the polarizability tensor element for these vibrations $\alpha^e_{yy}$ is larger than $\alpha^e_{zz}$. The better the molecules are aligned the larger is the difference between $\alpha^e_{yy}$ and $\alpha^e_{zz}$. We assign these vibrations in Table 3 to $E_1$ symmetry species.

In the FT Raman spectra of the phenylacetylene guest molecules, dissolved and orientated in the nematic liquid crystal ZLI-1695 several solute bands were observed (see Fig. 12). The band positions and their intensities are near to the typical positions of this compound, dissolved in nonpolar solvents [27, 30]. This confirms the assumption that the guest
molecules stay relatively unaffected in the nematic liquid crystal environment. The Raman bands at 2111, 1601, 1196, 1157, and 1002 cm\(^{-1}\) show prominent polarization with \(R\) values 0.47, 0.44, 0.43, and 0.54 correspondingly. The observed polarization behaviour of these bands can be explained by the fact that the long axes of the dissolved phenylacetylene molecule, are orientated predominantly parallel to the director of nematic liquid crystal molecules of ZLI-1695 (i.e. parallel to the micro-grooves Z).

Table 3. Polarization Raman spectral data on phenylacetylene, dissolved and oriented in ZLI-1695*, the intensity ratios \(R\), and the symmetry assignment of the bands.

<table>
<thead>
<tr>
<th>Wavenumber, cm(^{-1})</th>
<th>Intensity</th>
<th>(R = I_{yy}/I_{zz})</th>
<th>Assignment**</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perpendicular X(YY)X</td>
<td>Parallel X(ZZ)X</td>
<td>Perpendicular (I_{yy})</td>
<td>Parallel (I_{zz})</td>
<td></td>
</tr>
<tr>
<td>3066.7</td>
<td>3066.7</td>
<td>6.86</td>
<td>8.52</td>
<td>0.80</td>
</tr>
<tr>
<td>2936.3</td>
<td>2936.6</td>
<td>76.69</td>
<td>65.42</td>
<td>1.17</td>
</tr>
<tr>
<td>2850.2</td>
<td>2851.8</td>
<td>97.49</td>
<td>63.31</td>
<td>1.54</td>
</tr>
<tr>
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<td>2241.2</td>
<td>11.46</td>
<td>36.99</td>
<td>0.31</td>
</tr>
<tr>
<td>2112.1</td>
<td>2110.9</td>
<td>21.42</td>
<td>45.74</td>
<td>0.47</td>
</tr>
<tr>
<td>1600.9</td>
<td>1600.8</td>
<td>5.67</td>
<td>12.74</td>
<td>0.44</td>
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<tr>
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<td>1443.6</td>
<td>13.20</td>
<td>11.37</td>
<td>1.16</td>
</tr>
<tr>
<td>1357.0</td>
<td>1361.8</td>
<td>3.32</td>
<td>5.67</td>
<td>0.58</td>
</tr>
<tr>
<td>1303.2</td>
<td>1302.5</td>
<td>2.48</td>
<td>2.30</td>
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</tr>
<tr>
<td>1256.2</td>
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</tr>
<tr>
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<td>1195.8</td>
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<td>5.26</td>
<td>0.43</td>
</tr>
<tr>
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<td>1155.9</td>
<td>1.54</td>
<td>2.87</td>
<td>0.54</td>
</tr>
<tr>
<td>1090.4</td>
<td>1088.5</td>
<td>20.77</td>
<td>13.25</td>
<td>1.57</td>
</tr>
<tr>
<td>1002.3</td>
<td>1002.4</td>
<td>9.85</td>
<td>21.54</td>
<td>0.46</td>
</tr>
<tr>
<td>784.5</td>
<td>784.9</td>
<td>5.12</td>
<td>8.05</td>
<td>0.64</td>
</tr>
<tr>
<td>766.3</td>
<td>766.3</td>
<td>12.27</td>
<td>17.69</td>
<td>0.69</td>
</tr>
<tr>
<td>470.3</td>
<td>469.6</td>
<td>3.92</td>
<td>10.53</td>
<td>0.37</td>
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<tr>
<td>356.7</td>
<td>356.7</td>
<td>2.02</td>
<td>2.10</td>
<td>0.96</td>
</tr>
</tbody>
</table>

* The data of the nematic liquid crystal ZLI-1695 are given in italic; ** The assignment in accordance with refs. [27, 29].

In conclusion, FT Raman spectroscopic polarization measurements of phenylacetylene guest molecules, dissolved in nematic liquid crystals of 4-alkyl-4’-cyanobicyclohexyl type show an obvious ordering along the molecular long axis. The intensity ratios of the observed bands help in the symmetry assignment of the Raman active vibrational bands.

4. INFRARED STUDIES OF INDUCED CHOLESTERIC SOLUTIONS

Even if the guest molecules, dissolved in the nematic host phase, are chiral, they are aligned with their long axis in the direction, preferred by the host molecules, in the same way as the achiral ones. However the chirality of the guests causes a twist of their nematic neighbourhood resulting in an overall helical structure that can be modeled with a pile of anisotropic layers whose director (preferred orientation) rotates at a small angle from one layer to the next. The macroscopic structure, as outlined in Figure 12, is stabilized by the cell windows, which support the molecular alignment of the front and the rear layer and between them the helical
order is spontaneously adopted. For such samples the helix axis is parallel to the probing beam.

Fig. 12. Nematic and cholesteric order.

Solutions of chiral molecules in nematic liquid crystals are known as “induced cholesteric solutions” [3] since this molecular arrangement has been found for cholesteric liquid crystals, whose rod-like molecules tend to align themselves and would produce a nematic phase, provided a racemic mixture is used. However, since these molecules are chiral, the individual enantiomers induce the helical structure. The ability of twisting of a given molecular species is quantified by the ‘helical twisting power’ [31]. This is equal for enantiomers, except for the sign, therefore, limited enantiomeric purity reduces the twisting power. If a nematic host phase is just dotted with a chiral solute, the twist is proportional to the concentration of the solute. The twist is conveniently characterized by the pitch of the resulting structure, i.e. the distance between two layers of equal orientation, measured along the helix axis.

The essential of this effect is that enantiomers cause countercurrent helices (see Figure 12). This can be taken as the so-called chirality observation and be employed to discriminate enantiomers or to determine enantiomeric purity. The macroscopic manifestation of the microscopic molecular structure gives raise to various optical effects, whose features indicate the handedness of the helix and thus discriminate enantiomers [3]. However there is no simple relation between the handedness of the induced helix and the absolute configuration of the molecule, even though some relations can be deduced [3, 32].

4.1 Selective reflection

The most striking optical effect of cholesteric and induced cholesteric phases is the so-called selective reflection; an example is given in Figure 13. If the sample is irradiated with unpolarized radiation it exhibits almost 50% reflection in a band with a flat top. The band position is not related to molecular vibration but it is determined by the helical order of the sample and occurs when the wavelength (within the sample) matches the pitch. Closer inspection shows that the reflected radiation is circularly polarized (see Figure 14) indicating the handedness of the structure [33].

Fig. 13. Spectra of an induced cholesteric solution in the liquid-crystalline state (Ch) and - elevated temperature - in the isotropic liquid state (Is); sample between KBr windows, ca. 25 µm thick [3].

Due to the limited solubility of the chiral guest molecules in the anisotropic solvent, induced cholesteric solutions are often moderately twisted resulting in a pitch equal to the wavelength of infrared radiation. Up to now the application of circular polarization [34] is not standard in infrared spectroscopy and the necessary equipment is not at hand everywhere. Therefore the handedness (left or right) of the circular polarization of the selectively reflected radiation is seldom checked. However, based on the same phenomenon, the azimuth plane of linear polarization is rotated when passing through the sample. Spectrally the rotation displays...
a sigmoidal or dispersion-like curve that is known as Cotton effect in polarimetry [3]. For countercurrent helical structures inverted (with respect to the baseline) shapes are found out and thus the discrimination is provided. Even for a sample as thin as 20 µm or so, the amplitude of the Cotton effects even in the infrared range reaches several tens of degrees and thus they are easily measured.

On the other hand, when focusing on the experimental aspect, the different amplitude of left and right circular polarized radiation is measured in the isotropic as well as in the anisotropic case. In the subsequently addressed effects absorption is involved, nevertheless the features originate primarily from the macroscopic helical structure.

4.2. Features related to molecular vibrations

The spectral position of the selective reflection band of an induced cholesteric solution may vary from the visible to the far infrared region, depending on the particular solute, its concentration and enantiomeric purity as well as on the liquid crystal. If the potential of enantiomeric discrimination is to be exploited, one often strives for application of minimum amounts of the analyte even though the method is neither consuming nor destroying, nor modifying the compound. Depending on the twisting power of the particular compound even sub-microgram amounts are sufficient [3], however the pitch of such a less concentrated solution will equal far-infrared wavelengths.

Even though the selective reflection should be observable, when occurring in the far infrared region, it would be convenient to obtain the desired discrimination from an optical effect in the standard spectral range of a spectrometer – somewhere between 4000 and 400 cm\(^{-1}\). This would also enable us to use well suited and commonly available window materials in adequately spaced sample cells. Actually, extraordinary features occur in this spectral range, related to the vibrational bands of the liquid crystal and – provided sufficiently pronounced – of the chiral solute [36]. An example is given in Figure 15.

Fig. 14. Selective reflection of an induced cholesteric solution; the spectra were taken with (a) unpolarized, (b) left circular and (c) right circular polarized radiation.

The first observation of this phenomenon in the infrared range happened in the context of a feasibility study for infrared rotatory dispersion [35]. Strictly speaking this term refers to circular birefringence of isotropic phases and would correlate it with circular dichroism implying absorption, which is not involved essentially here.

Fig. 15. Spectra of an induced cholesteric solution showing the rotation of the plane of linear polarization (OR) and the circular difference (CD); as described in the text, the logarithm of the ratio of single-beam spectra is given (‘absorbance’ A); the complementary features occur at absorption bands of the solvent and of the solute.
At each individual absorption band of the sample optical rotation occurs and left and right circular polarized radiation is transmitted to a different extent [37]. The signs of these features, i.e. prevailing of left or right circular polarization and the shape of the Cotton effects, depend on the handedness of the helical structure and thus on the configuration of the solute; however, they depend also on whether the selective reflection occurs at longer or shorter wavelengths than the absorption band. Eventually they depend on the direction of the transition moment relative to the director [3]. This latter relation corresponds to the linear dichroism and its implications on the molecular orientation and structure is discussed in a previous section of this review, and could be similarly exploited [38]. Holzwarth [39] calculated the optical response of a twisted pile of anisotropic layers; the results confirm the above mentioned observation. We applied the Stokes-Mueller matrix formalism [40] to study the influence of different optical properties of the sample on the measurement results [41].

4.3. Experimental developments

As it was mentioned before, the experimental basis for observing these effects had to be developed [37, 42]. Unlike the circular dichroism of vibrational bands of isotropic phases, it is not a challenge with respect to the limit of detection and, therefore, we strived for simple modifications of or for accessories of the spectrometers used. In a dispersive spectrometer, the induced cholesteric sample and an analyzer with its vector orientated vertically (azimuth 0°) were placed in this part of the optical path, which is common to sample and reference beam (compare Figure 16), so that their absorption is effectively compensated for. An analyzer was placed in the sample holder at an azimuth of 45°. When the sample rotates the polarization plane of the incident radiation, the azimuth angle is altered and a different transmittance is measured.

With interferometers allowing transmittance values exceeding unity to be processed easily, an improved scheme was realized with two subsequent single-beam measurements with analyzer azimuths of +45° and –45° respectively. This set-up is schematically shown in Figure 16 and its action is described by the expression:

\[ T = \cos(45° + \rho) / \cos(45° - \rho) = (1 - \sin2\rho)(1 + \sin2\rho) \]  \hspace{1cm} (11)

where \( \rho \) is the optical rotation by the sample. \( T \) is centred around unity (\( \rho = 0 \)) with a certain asymmetry in regard to \( \rho \). Therefore conveniently the related “absorbance” \( A \) is favoured [42]:

\[ A = -\lg T \approx \sin2\rho \]  \hspace{1cm} (12)

which conveniently indicates the sign of the rotation.

Fig. 16. Measurement of the optical rotation spectrum with the sample (Sa) between polarizer (P) and analyzer (A) whose vectors form an angle of °/–45°; \( P_\rho \) denotes the orientation of the polarizer for the first single-beam measurement, \( P_\rho \) the one for obtaining the reference spectrum; \( \rho \) indicates the rotation of the polarization plane by the sample.

As it is demonstrated by the well-known Fresnel rhomb, total reflection can be employed to introduce a phase shift between radiation being polarized parallelly and perpendicularly to the plane of reflection. In the infrared region materials are available, whose properties allow one reflection to produce a phase shift of 90° and thus, circularly polarized radiation [33]. The optical lay-out of such an accessory is shown in Figure 17. Depending on the polarization azimuth of the incoming radiation (determined by the polarizer) left and right handed circular polarization is achieved [43]. Using this accessory, single-beam spectra were recorded with pure circular polarization at a ratio to yield \( T = I_+ / I_- \). Similar to the optical rotation the logarithm of the ratio (“absorbance” \( \rho = -\lg T \)) is favoured to obtain a zero result for the vanishing difference and to distinguish directly the positive and negative results. In Figure 15 the complementary spectra of the optical rotation and of the circular difference are represented; the selective reflection of this induced cholesteric solution does not occur in the spectral interval shown.

For more detailed and more sensitive studies, a modulation technique would provide advantages. The potential of different techniques was explored [44]. Most schemes, such as those based on a photoelastic modulator, a rotating polarizer or an interferometer with polarizing beamsplitter, would not enable pure circular polarization for an extended period. A square-wave modulation is the most attractive, and therefore Bojidar Jordanov designed several advanced mechanic-optical devices to switch the polarization. A high frequency realization for
application of synchrotron radiation is still in progress.

Fig. 17. Layout of a circular polarization accessory to be used in a sample compartment with centre focus (F) of a conventional spectrometer; the retarder element (R) is a 32.5° ZnSe prism; S denotes the sample, P the polarizer.

5. SUMMARY

A number of Bojidar Jordanov’s long lasting national and international cooperations dealt with fundamental and experimentally basic considerations, the optimization and the application of aligning molecules in nematic liquid crystals and investigating them with infrared and Raman spectroscopy. The aim of such studies is to confirm or to clarify the assignment of vibrational bands that includes resolving closely overlapping signals. In many cases the results shed new light on the molecular structures and symmetry.

The anisotropic solutions of chiral molecules offer an infrared spectroscopic access to the important discrimination of enantiomers. Additional features related to the absorption bands of the solute give analogous information on the guest molecules as it was previously discussed for the achiral molecules. The newly developed measurement techniques allow the reliable measurement of these features and those related to the solvent. The performance analysis of prism retarders in this spectral range led to improved infrared measurements with circular polarization.

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ИНФРАЧЕРВЕНА И РАМАНОВА ПОЛЯРИЗАЦИОННА СПЕКТРОСКОПИЯ НА МОЛЕКУЛИ ОРИЕНТИРИANI В ТЕЧНИ КРИСТАЛИ: РЕЗУЛТАТИ ОТ СЪТРУДНИЧЕСТВО С БОЖИДАР ЙОРДАНОВ

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Посветена на паметта на проф. Божидар Йорданов

Постъпила на 7 юли 2005 г.

(Резюме)

При разтваряне на молекулите в анизотропен разтворител, те се подреждат така, че ориентацията на техните вибрационни моменти на прехода могат да се изследват с поляризирана инфрачервена или Раманова спектроскопия. Тези резултати внасят допълнителна яснота относно симетрията на техните вибрационни състояния или предпочитаната ориентация на отделните конформери. Налице е добър избор от нематични течни кристали, които осигуряват желаната едносънна анизотропия в рамките на удобен температурен интервал, осигуряващ достатъчна стабилност на органичните молекули. Същевременно, вибрационният спектър на тези течни кристали е достатъчно беден, за да позволи прецизно измерване на повечето вибрации на разтворените молекули.

При разтваряне на хирални молекули в нематичен течен кристал, те завъртят така отделните слоеве в него, че образуват спирална структура, чийто период често съвпада по дължина с дължината на вълната в инфрачервената област. Енантиомерите генерират противоположно изградени спирални структури и този ефект може да се използва за тяхното различаване. Разработени са някои прости експериментални установки за регистриране на тези ефекти.