Annals of the Academy of Romanian Scientists
Series on Physics and Chemistry
Online ISSN **2559 – 1061** Volume **10**, Number 1/**2025**

INFRARED SPECTROSCOPY SUPPORTS THE MOLECULAR DYNAMICS OBTAINED BY DIELECTRIC SPECTROSCOPY FOR LIQUID CRYSTALS IN OXIDE NANOPOWDERS

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Rezumat. *Materiale oxidice sub formă de nanopulberi obținute în colectivul nostru au fost trecute în revistă: site moleculare, oxid de titan, oxizi micști în comparație cu aerosili model, de proveniență comercială. În aceste materiale au fost confinate într-o dimensiune, în două sau chiar trei dimensiuni, diferite molecule de cristale lichide nematice. Investigații prin spectroscopie dielectrică (de bandă largă) au arătat un proces de relaxare mult mai lent decât cele aparținând moleculelor din volum, şi a cărui dependentă de temperatură a timpului de relaxare nu se modifică la tranzițiile de fază. Am aplicat atunci măsurători complementare noi şi calcule teoretice pentru a explora dinamica de frecventă joasă datorată interacțiunilor intermoleculare în structura constransă. Aici am discutat date de spectroscopie IR pentru studiul structurii şi a interacţiilor din stratul de suprafață.*

Abstract. *Oxide nanopowdered materials obtained in our lab were reviewed: aerosils, molecular sieves, tin oxide, mixed oxides, some of them having semiconductor properties. Liquid crystals were confined in one, two or three dimensions of these materials, when special interactions were involved. Investigations by (broadband) dielectric spectroscopy of confined molecules have shown a relaxation process which is slower than those belonging to the bulk molecules. In addition, the temperature dependence of the corresponding relaxation time does not change at the phase transition temperatures in the bulk liquid crystals. We applied IR spectroscopy for studying structure and surface interactions and we employed novel complementary measurements and theoretical techniques to explore the low frequency intramolecular dynamics of model molecules in constrained structures. Here we discussed IR spectroscopy data for studying the structure and interactions in the surface layer.*

Keywords: Nematic liquid crystals, confinement, nanopowdered oxide materials, dielectric spectroscopy, infrared spectra

DOI **10.56082/annalsarsciphyschem.2025.1.59**

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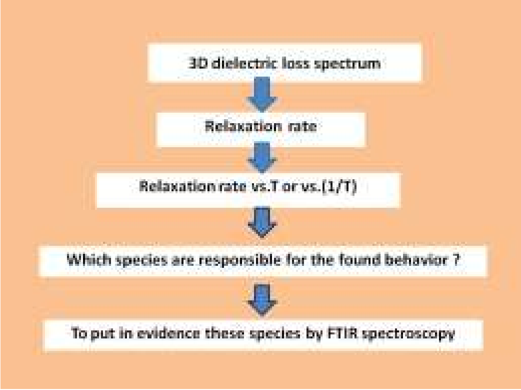
1. Introduction

This contribution makes an overview of our works concerning the characterization of oxide nano powders which are used in different applications and in fundamental research as well. So, we studied metallic oxides like Al_2O_3, SiO_2, semiconductor oxides like TiO_2, ZnO, molecular sieves as MCM-41, SBA-15 or even organic materials like polymers, carbon nanotubes etc. [1-10]. Model oxides like aerosils coming from known factories were also studied. The confinement of special molecules, which in fact have properties of monocomponent nematic liquid crystals (LCs) like cyano biphenyls or alkyl benzoates was performed, starting from solutions or pure LCs. As LC, a commercial E7 mixture (the symbols of its components being 5CB: 7CB: 8OCB: 5CT) was also used.

The characterization of all these pristine or confined molecules was complex, involving many modern techniques. The data concern the bulk and surface composition, the structure, the adsorption/absorption properties of materials. The techniques took into consideration the interaction of the oxide nanoparticles with molecular confined compounds.

From this complex characterization of the mentioned confined materials we retained here only a few of the data, namely tho infrared data which sustain the dielectric spectroscopy data. In the infrared spectra, the position of vibration peaks coming from the confining material may coincide with those of confined compounds. That is why the mixtures of the LCs with dispersed organic materials were not discussed here. See the schema of the study below.



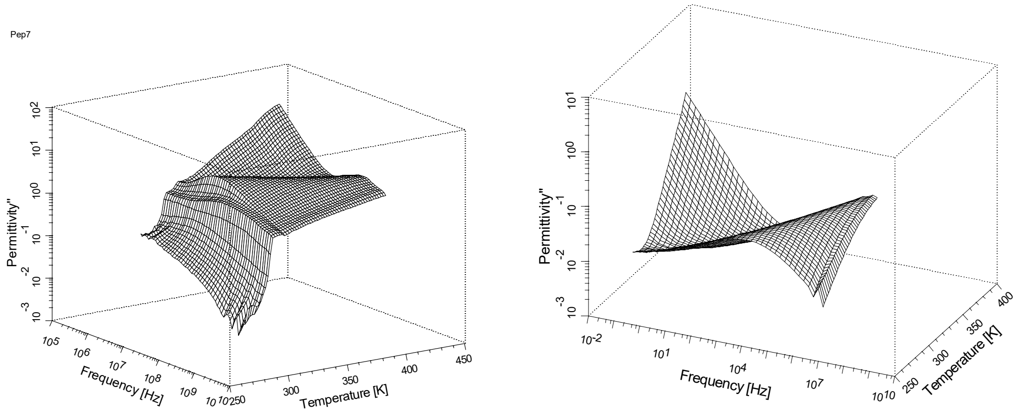
Schema of the study

In addition, the properties of the surface species confined in nanopowders were compared with those of the corresponding bulk compounds.

2. Processing the data of dielectric spectroscopy

The complex dielectric function is measured by broadband dielectric spectroscopy (BDS) in the frequency range 10^{-2}-10^{9} Hz. The temperature range is chosen to cover all phase transition temperatures of LCs. BDS measurements were performed isothermally by decreasing the temperature in steps from 473 K to 220 K. To analyze these data quantitatively and to separate the different relaxation processes the model function of Havriliak–Negami was employed [11].

Molecules of cyanophenyl alkyl benzoates (CPnBs) in the bulk state have an important dipole moment leading to different the relaxation processes [11]. To exemplify we have chosen bulk cyanophenyl heptylbenzoate (CP7B) and its composite with aerosil A380 (CP7B/A380) [12]. The temperature and frequency dependency of the dielectric loss in the case of CP7B are shown in Figure 1a. The shape of the dependency changes when the CP7B molecules are confined into the voids of aerosil A380 (from Degussa-Hüls) (Figure 1b); moreover, the frequency of the relaxation process seems to be lower than in the case of the bulk.



a) b)

Fig. 1. Dielectric loss *vs*. frequency and temperature in a 3D representation for a) bulk sample CP7B; b) confined sample CP7B/A380. Adapted from ref. [12]

Figure 2 represents the variation of the relaxation rates as function of 1/T. One observes the jump at the transition temperature for the bulk and the lower values of the relaxation rates in the case of the confined samples as compared to the bulk data [12]. In similar cases, such a lowering of the frequency was put on the species anchored to the surface of confining materials. To pursue these surface species, we have used infrared spectroscopy.

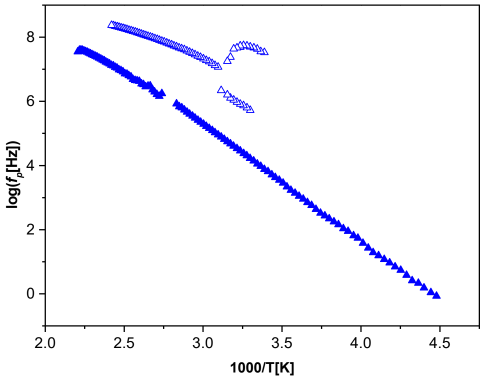


Fig. 2. Temperature dependence of the relaxation rates in the case of the confined sample CP7B (filled symbols) and the bulk CP7B (empty symbols). Adapted from ref. [12].

3. Processing the infrared data

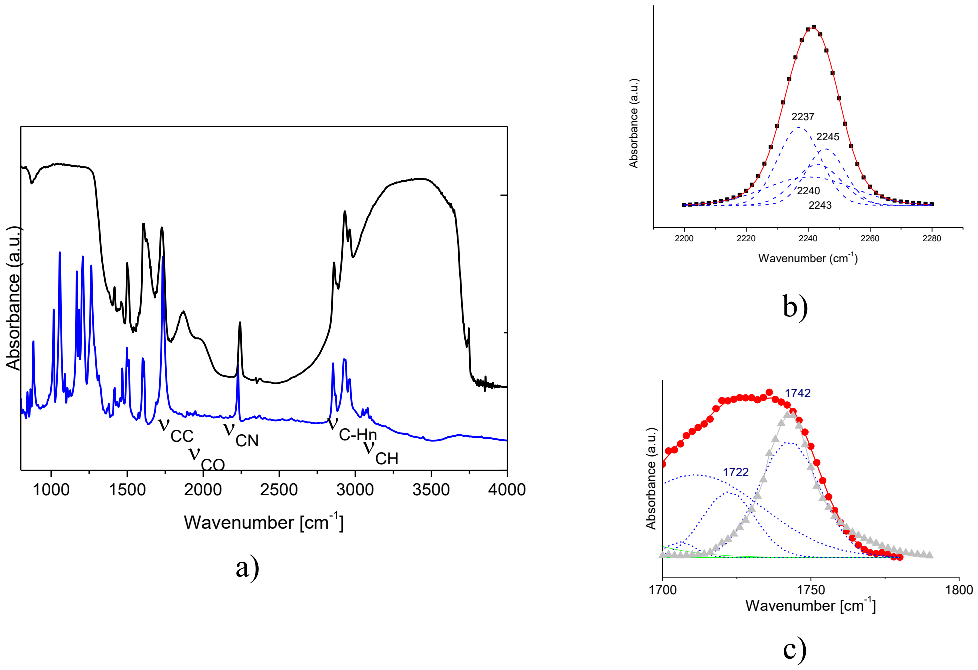
FTIR spectroscopy was employed to identify species resulting from the interaction of the functional (polar) groups with the surface of the aerosil particles. IR absorption spectra were collected with a Perkin Elmer Spectrum BX apparatus in the range 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and accumulating 128 scans at room temperature. To obtain these spectra, self-supported sample pellets were used or the samples were embedded in KBr matrices. The spectra were analyzed by the decomposition of the characteristic peaks using Gaussian profiles.

The following discussion regards the peaks of the bulk materials and their change by adsorption upon aerosil surface. The most suitable vibrations for this discussion are the stretching modes of the carbonyl/ester and cyan groups, and the OH stretching of the aerosil.

CP7B (in general, CPnBs) show strong IR absorptions (see Fig. 3a). The most isolated peaks are due to both the rigid (aromatic, cyan, ester) and the flexible (alkyl chain) parts of the molecules.

It is known that aerosil consists in silica nanoparticles of ~7 nm diameter, covered by hydroxyl (OH) groups. These groups and the Si-O groups lead to vibrations in the mid infrared region: the confined sample behaves as well.

Representative IR spectra of CP7B bulk and its composite are shown in Fig. 3a, the main assignments of the peaks are also given in accordance with the literature data for related compounds.



a)

b)

c)

Fig. 3. a) FTIR spectra at room temperature on unaligned samples (KBr matrix) of CP7B (blue line) and of confined sample CP7B/A380 (black line). Adapted from ref. [12]. b) and c) Details of two important peaks (experimental points) and their decomposition into Gaussian curves (dashed lines). Gaussian sum is also shown.

Figures 3b and 3c give the chosen peaks for CP7B confined in A380 which are due to the stretching vibrations of the cyan group and to the stretching vibrations of C=O bond in the ester group respectively. These peaks are composed from several components coming from several absorbing species which might differ a bit by conformations or structure. The lower wavenumber (and the broadening when comparing with the monomers) components of the cyan band are due to the existence of dimers with antiparallel orientation of these two molecules [3]. The carbonyl band decomposes in a peak situated as in the bulk (grey symbols in Fig. 3c) and other peaks at lower wavenumbers, ca. 1720 and 1700 cm^{-1}. The main peak at 1740 cm^{-1} may arise free noninteracting groups while the others might be due stretching vibrations of interacting groups which are responsible for the absorption at lower wavenumbers having a longer bond length.

Species bonded to the surface means that their groups are bonded mostly by hydrogen bonds. The corresponding molecules are responsible for the branch of lower frequency in Fig. 2.

The ester part of the molecules might also be bonded to the surface, as results from Figure 3c: the CP7B molecules are well anchored to the surface of aerosil by two types of hydrogen bonds.

A similar behavior as that of aerosil composites can be observed for the composites formed with LCs having C=O or CN groups and other nanopowdered oxides.

4. Conclusions

For the composites made of liquid crystals and nanopowder oxides, the relaxation rates of the low frequency process found by dielectric spectroscopy have a curved dependence on the temperature in the whole temperature range. This relaxation is due to the surface layer.

Fourier-transform infrared (mid region, 4000–400 cm^{-1}) was employed to measure spectra in the confined samples: This region is particularly sensitive to the detailed structural and environmental properties of complex hydrogen-bonded species in this surface layer.

The specific molecular vibrations of the sample constituents can be observed, providing qualitative and quantitative information to explore the low frequency intramolecular dynamics of model molecules with constrained structures.

Surface layer behaviour was investigated separately from the bulk.

Acknowledgment

The work is funded by the Core Program of the National Institute of Materials Physics, granted by the Romanian Ministry of Research, Innovation and Digitization through the PC3-PN23080303 (IZ).

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