Electronic-vibrational spectra of nitrobenzene in solutions, liquid phase and orientationally arranged wall-adjacent layers

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The electronic-vibrational spectra of nitrobenzene in the frequency region $\nu \cong 50000$—30000 cm^{-1} were investigated. The shape and main parameters of five fundamental absorption bands were determined. The absorption spectrum of ultrathin wall-adjacent orientationally ordered layers (with thickness $d \leq 100$ nm) formed near a lyophilic quartz surface (so called epitropic liquid crystals — ELC) differs essentially from that of a bulk specimen and alters with decreasing thickness. In particular the half width of the intramolecular charge transition band decreased, and a bathochromic shift was observed. Parameters of other bands also change. It is probably connected with existence of ELC phase internal inhomogeneity.

Key words: wall-adjacent orientational arrangement, structural homogeneity, electronic-vibrational spectra, iteration procedure of spectral deconvolution.

It was determined earlier[1] that liquids with anisometric molecules in certain cases form orientationally ordered wall-adjacent layers similar to nematic liquid crystals on a lyophilic solid matrix. These layers measure ~100 molecular lengths in thickness, and they are separated from isotropic volume liquids by a rather sharp interface (of the phase type). The arrangement as well as the main thermodynamic and structural parameters are thereby constant, which is characteristic of the layer area beginning at ~20—30 nm from the matrix surface up to the interface.[2] This fact as well as the presence of phase interface were the reasons to classify the layers involved as a new liquid-crystal phase called epitropic liquid crystals (ELC). ELC phase organization and its properties are due to the joint action of the field of long-range surface forces directed from the solid matrix,[3,4] anisotropic intermolecular interaction, and short-range surface forces determined by the concentration and the type of active centers on the matrix surface. Later, we succeeded in studying a thinner liquid area near the surface. A considerable inhomogeneity of the structurally changed wall-adjacent layer was found; a structure with a higher degree of order, the quasi-smectic phase layer, emerges within the range of 5—20 nm from the matrix.[5]

It is obvious, that the field of surface forces, which is, together with other factors, responsible for ELC organization, must also, due to its inhomogeneity expressed by the decrease in potential value while distancing from the matrix, lead to a certain inhomogeneity of physical properties within the limits of each phase. Therefore, monotonic change of certain structurally sensitive properties should be expected for such wall-adjacent layers as the distance from the foundation increases. The aim of this work consisted in the determination of structural inhomogeneity within the ELC layer and its correlation with the field potential of surface forces. For this purpose, we carried out the investigations of changes in electronic-vibrational spectra of ELC phase of nitrobenzene, formed on a quartz surface, as liquid interlayer thickness reduces.

Procedure of spectral measurements

A Specord M40 spectrophotometer was used to study absorption spectra in the wavelength range of 30—$50 \cdot 10^3$ cm^{-1}, which allowed recording of analog and digital spectra with its further computer processing. The reproduction accuracy of the wavelength value in the indicated range is not worse than $\Delta\nu \simeq 5$ cm^{-1}, the resolving power is ~10 cm^{-1}, the intensity measurement accuracy is $\Delta I/I \simeq (0.005$—$0.001)$.

Due to the fact that another range of electronic absorption spectra of nitrobenzene (with longer wavelengths of $\nu = (25$—$40) \cdot 10^3$ cm^{-1}) was studied earlier,[6—8] we carried out preliminary spectral measurements of nitrobenzene solutions in polar and nonpolar solvents. A set of quartz cells with gaps of 5—50 μm was used for these measurements.

In order to study ELC phase spectra, as the liquid interlayer thickness changes, we used the procedure[2,3]

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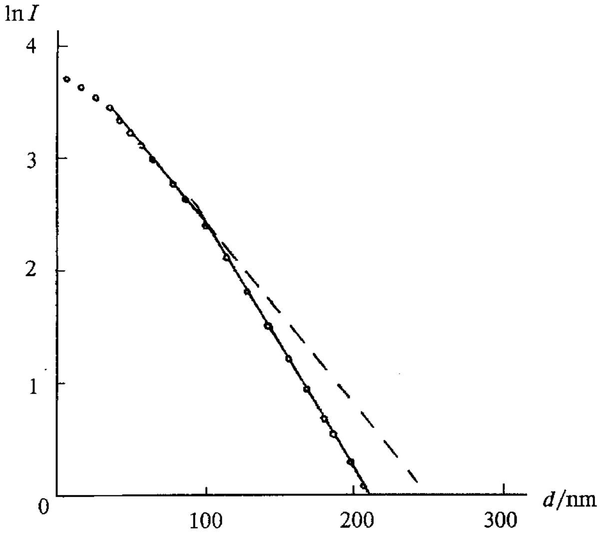

Fig. 1. Experimental absorption light dependence of nitrobenzene in wedge cell for the maximum of the ICT band.[3,4]

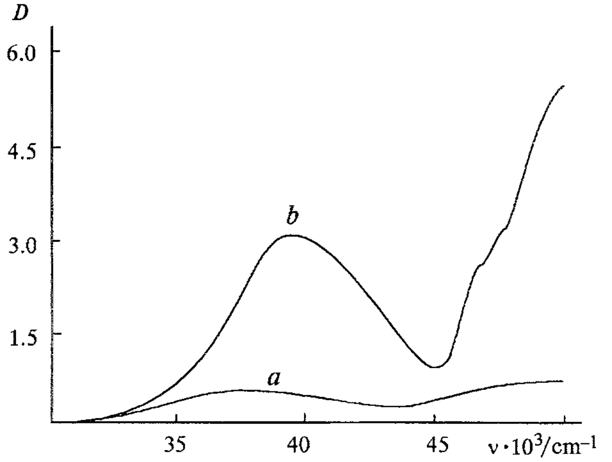

Fig. 2. Experimental electronic-vibrational absorption spectra of nitrobenzene: *a*, in bulk liquid phase; *b*, in octane solution.

of thickness scanning of wedge liquid layer formed between optically polished quartz supports. The topography of the gap was determined previously (before being filled with the compound) by the interferometry in transmitted light on several wavelengths in the near UV range. The extremum positions of interference picture allowed us to reestablish reliably enough the gap profile up to 20—30 nm thickness. After filling the cell with liquid, we investigated the absorption on the frequency of the most marked spectral band maximum, which is of intramolecular charge transfer (ICT—$\nu_0 \simeq 38000$ cm^{-1}). The transmitted light intensity was measured as a function of layer thickness d, and $\ln I = f(d)$ relationship was plotted, which looked like a convex broken line (see Fig. 1). The analysis of the latter allowed us (by the slopes of its segments) to establish linear coefficient values of ELC absorption (μ_s) and volume phase (μ_{iso}), phase homogeneity (by the nearness degree of the graph segments to linearity), to calculate a scalar arrangement parameter S and to determine phase thickness (by the position of breaking point).

Then, the measurements of spectra for the same wedge liquid interlayer was carried out. These spectra represent the relationship between optical density D ($D = \ln (I/I_0)$, where I and I_0 are the intensity of the light passed through the layer of the investigated compound and through the layer of nonabsorbing liquid filling the gap between the same supports, respectively) and incident light frequency ν. Each measurement corresponded to different thicknesses of liquid interlayer in the 20—180 nm range. In the case of two-phase interlayer (d = 110 nm) we determined additionally difference spectra, which are isotropic volume phase absorption spectra, and then we carried out the main series of spectral measurements within the limits of ELC phase thickness.

Spectra processing procedure

Experimental absorption spectra of nitrobenzene in bulk liquid phase (*a*) and its solution in octane (*b*) are given in Fig. 2 as an example. As can be seen from the figure, the spectrum represents a number of electronic-vibrational structureless bands that overlap each other. For further analysis we performed deconvolution of the experimental spectrum into fundamental bands by the scheme given below.

The possibility to approximate spectral band shape with Lorentz or Gauss functions by means of its linearization and verification of its linearity was sounded initially. As it was established, the shape of ICT band long-wave decline is determined by Gaussian. Then, to find the following band parameters: absorption coefficient (μ_0) corresponding to absorption band maximum frequency ν_0 and band half width (σ), we calculated the parameters of the linear dependence:

$$\left(\ln \frac{\mu_0}{\mu}\right)^{1/2} = f(\nu). \qquad (1)$$

Then, the reproduced band was subtracted from the experimental spectrum, and parameters of following spectral bands were determined with the similar method. The above described method allowed us to deconvolute spectra without complete spectral information and to discover a number of weak masked bands.

However, this approach has some restrictions connected with the fact that only one band must dominate within linear segments (that is the contribution of neighboring bands to the total spectral intensity must be negligible), what is not always possible. Moreover, since linear range of spectral interval is narrow (1), criteria which determine its limits do not have sufficient statistical grounds. For this reason we then carried out more exact refinement of its shape and parameters with a more rigorous method.[9]

Let a spectrum $f(\nu)$ consist of n symmetrical bands $\phi(\nu)$:

$$f(\nu) = \sum_{i=1}^{n} \phi_i(\nu). \tag{2}$$

Using the condition of symmetry

$$\phi_i(n) = \phi_i(2\nu_{oi} - \nu),$$

where ν_{oi} is the i^{th}-band maximum position, the following iterative procedure was realized:

$$\begin{aligned}\varphi_k^{(j)} = {} & \frac{1}{2}\left[f(2\nu_{oi} - \nu) + f(\nu)\right] - \\ & - \frac{1}{2}\sum_{k=1}^{n}\left[\varphi_k^{(j)}(2\nu_{oi} - \nu) + \varphi_k^{(j)}(\nu)\right] - \\ & - \frac{1}{2}\sum_{k=i+1}^{n}\left[\varphi_k^{(j-1)}(2\nu_{oi} - \nu) + \varphi_k^{(j-1)}(\nu)\right]\end{aligned} \tag{3}$$

Iterative procedure (3) is similar to the Seidel method often applied to solve a linear equation system. Numeral experiments carried out with model spectra show that the procedure converges regardless of the starting approximation choice. However, the condition of symmetry is not sufficient to make a well-defined deconvolution, and additional information about band shape is necessary. If the particular shape of the fundamental bands is known (for example, near to Gaussian), a well-defined deconvolution can be obtained according to the following algorithm: 15—20 iterations are carried out, then, fundamental band shape is approximated by means of Gaussian curves, and its shape is refined again according to scheme (3). The procedure is repeated as long as the band parameters (width and intensity) do not stop changing within a fixed accuracy.

Results and Discussion

We studied absorption spectra of nitrobenzene in polar solvents (water, aliphatic alcohol), nonpolar solvents (octane, hexane), and, for comparison, vapor and bulk liquid phases. The general appearance of the spectrum and the results of its deconvolution into fundamental bands (1—5) are given in Fig. 3 (saturated water solution). ICT bands (2) and the second primary band (β-band of benzene (5), $\nu_0 \simeq 52000$ cm^{-1}) are distinctly separated; the band with $\nu_0 \simeq 47000$ cm^{-1} (4) is also visible though almost completely masked by a more intense β-band (5). Bands with maxima $\nu_0 \simeq 33000$ cm^{-1} (1), $\nu_0 \simeq 42500$ cm^{-1} (3) are masked completely and can be discovered only in the process of deconvolution of the experimental spectrum. According to literature data the band with $\nu_0 \simeq 33000$ cm^{-1} (1) is related to intermolecular charge transfer, and, therefore, it has a low intensity even in concentrated solution. Bands with maxima $\nu_0 \simeq 42500$ cm^{-1} (3) and $\nu_0 \simeq 47000$ cm^{-1} (4) are not described in the literature, and their nature is not clear to this moment.

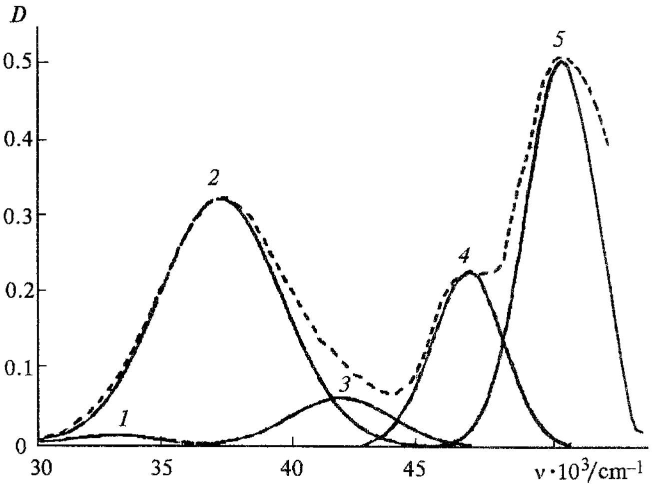

Fig. 3. Experimental absorption spectrum of water solution of nitrobenzene (dashed line) and its deconvolution (solid lines) into fundamental bands 1—5.

It is established that when passing from vapor to solution and, accordingly, to the increase in intermolecular interaction, ICT band has a batochromic shift, whereas the shifts of the other bands are not significant and are within experiment error. Band maximum shift value $\Delta\nu$ is satisfactorily governed by "universal interaction function $f(\varepsilon,n)$"[10] (see Fig. 4), which is a linear combination of addends related to different intermolecular interactions: of orientation, induction, dispersion and polarization types. It was shown that the contribution of the orientation interaction to a frequency shift value is comparable with the total contribution of the other interactions for anisometric molecules of nitro-

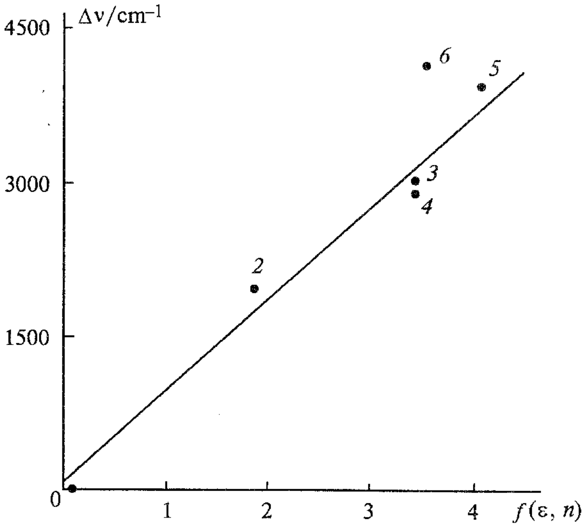

Fig. 4. Dependence of frequency shift $\Delta\nu$ of ICT band maximum in nitrobenzene spectrum on universal interaction function $f(\varepsilon, n)$. The numbers correspond to different solvents or phase states: *1*, vapor; *2*, octane; *3*, isobutyl alcohol; *4*, ethanol; *5*, volume phase; *6*, water.

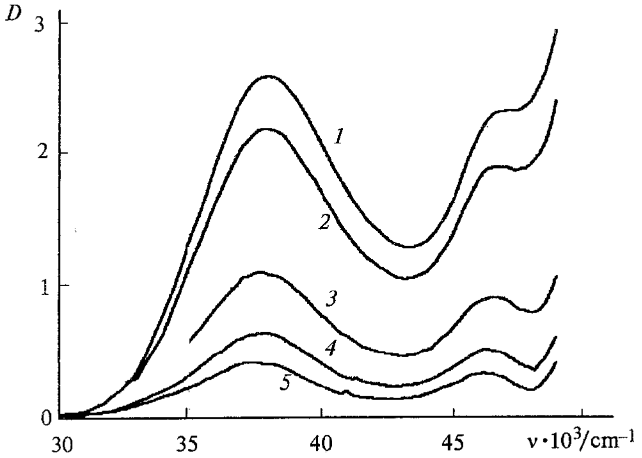

Fig. 5. Experimental absorption spectra of wall-adjacent layers of nitrobenzene for different thicknesses d (nm) of liquid interlayer, d: 180 (*1*), 158 (*2*), 83 (*3*), 59 (*4*), 33 (*5*).

benzene, which have a considerable dipole moment (P_e = 4.3 D).

Figure 5 displays absorption spectra series of symmetrical nitrobenzene interlayers which correspond to different ELC phase thicknesses. As seen from the picture, as interlayer thickness is reduced, a band with ν_0 = 47000 cm^{-1} gets more and more isolated because the parameters of neighboring bands change. The maximum and half width position of the most intense band, ICT band, changes as well. Parameters of single spectral bands for a number of interlayer thickness, which correspond to its state (d < 100 nm) are given in Table 1. Results, shown in the Table, suggest a bathochromic shift of ICT band and decrease in its half width, as the interlayer is reduced. The observed changes have the same tendency for the other bands, but they are expressed less clearly in connection with the less intensity and decrease in reliability of the obtained results for upper limit of the investigated spectral range.

The changes of ICT band parameters such as $\Delta\nu$ (maximum frequency shift) and its half width are presented graphically in Fig. 6, *a*, *b* as a function of ELC layer thickness d.

The observed spectral changes are due to the change of ELC phase structural parameters when the distance from the foundation increases, which is determined, in the end, by the change of surface force potential value. The half width diminution apparantly suggests the increase in system regulation degree and may be connected with the rise of arrangement parameter P_4 responsible for regulation dispersion of molecular axes. The observed frequency shift is due to the influence of foundation surface forces on ELC phase structure.

Table 1. Parameters (ν_0/cm^{-1}, σ/cm^{-1}, μ_0/mcm^{-1}) of fundamental Gaussian bands of nitrobenzene absorption spectrum as a function of interlayer thickness d

Band	d = 88 nm			d = 68 nm			d = 37 nm		
	μ_0	ν_0	σ	μ_0	ν_0	σ	μ_0	ν_0	σ
ICT (2)	12.4	37980	2570	11.3	37890	2520	11.9	37500	2400
Band 3	3.30	42910	1080	2.35	42510	890	2.65	42700	770
Band 4	10.3	46350	1560	8.80	45880	1430	9.45	45870	1440
β-Band of benzene (5)	15.9	50330	1330	11.8	50610	1200	13.5	49540	890

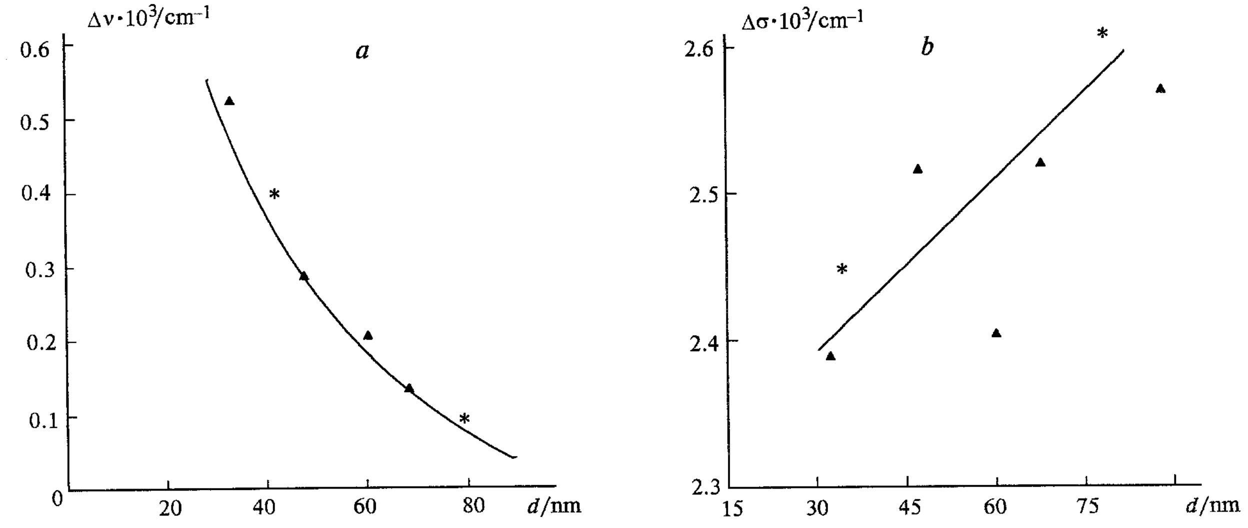

Fig. 6. Dependence of maximum shift $\Delta\nu$ of ICT absorption band for ELC phase of nitrobenzene (related to maximum position ν_0 of bulk liquid) (*a*) and its half width σ (*b*) on compound interlayer thickness (d).

In conformity with the ELC phenomenological model proposed earlier,[3] its organization is due not only to surface (long- and short-range) forces of the foundation, but also to anisotropic intermolecular interaction. On the strength of such complexity of the investigated object, it is difficult to suppose for the moment even a qualitative mechanism connecting the observed spectral regularities with structural changes in the ELC phase.

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