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NEW METHOD FOR EXPERIMENTAL DETERMINATION OF THE LOCAL FIELD PARAMETERS IN UNIAXIAL MOLECULAR MEDIA

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Abstract A new method of experimental determination of the local-field parameters of the light wave in uniaxial molecular media from spectral data has been suggested and realized for several tens of doped liquid crystalline and anisotropic polymeric systems. Anisotropy of the effective local-field tensor for the solute molecules has been found to be determined mainly by the matrix's anisotropic optical properties and also to depend on the specific features of the solute molecules' electronic structure but not to depend on the shape and character of the orientational order of the solute molecules.

Keywords: local fields, doped liquid crystals, polymer films, polarized spectroscopy

INTRODUCTION

Recent development of molecular engineering and the perspectives of using uniaxial statistically ordered molecular media (liquid crystals, Langmuir-Blodgett films, biopolymers and membranes, anisotropic polymeric films, etc.) as the elementary base of molecular electronics stimulated a great interest to investigate the structure of these systems by the methods of polarized IR and UV spectroscopy.^{1–2} Modern experimental techniques allow the measurement of the linear dichroism of the absorption bands with precision up to 10^{-6} .^{3,4} Therefore, for the quantitative interpretation of the experimental data it is of importance to take into account the difference between the local field $\underline{E}_1 = \underline{f} \underline{E}$ of the light wave acting on a molecule and the mean macroscopic field \underline{E} in a medium. The amplitudes \underline{E}_1 and \underline{E} of these fields are connected one to the other by the effective local-field tensor \underline{f} , which is uniaxial for the uniaxial molecular media considered.⁵

Unlike the liquid crystals⁵ and the Langmuir-Blodgett films^{6,7} for which the methods of determination of the local-field parameters had been previously proposed, the situation for another molecular media indicated above remains unclear and the interpretation of the spectral polarizational measurements have been done in the approximation of the oriented molecular gas.¹⁻⁴ In investigations of the specific features of the orientational ordering of impurity molecules as well as their vibrational and electronic structure such assumption is insufficient even for the anisotropic polymeric films⁸⁻¹⁴ and liquid crystals¹⁵ with low birefringence, as it is shown by some nonphysical consequences from the experimental data. On the other hand, a question about specific features of the local field in the doped statistically-ordered anisotropic molecular media has been discussed⁵ and requires experimental solution.

In the present paper, a new approach has been proposed, and for a large number of doped systems allowed the determination of the local-field parameters in uniaxial molecular media from the polarized spectroscopy data. This method completes the known spectral methods⁵ and is free from their usual restrictions. In the second part of the paper the formal side of the method is presented. In the third part the results of the experimental determination of the local-field parameters for a series of the impurity molecules in various anisotropic polymeric and liquid-crystalline matrices are presented and their discussion is given. In conclusion the main results of the paper are outlined briefly.

DETERMINATION OF THE LOCAL-FIELD PARAMETERS FROM SPECTRAL DATA

To start with we consider uniaxial statistically-ordered molecular medium with the optical axis \underline{n} . For the intrinsic or dissolved molecules the orthogonal frame (x,y,z) is chosen, which is connected with a rigid molecular fragment having the local symmetry

not lower than C_{2v} or D_{2h} . Then the directions of the x, y, z axes are determined by the elements of the fragment's symmetry group. The 4,4'-substituted phenyl ring can be considered as an example of such fragment^{12,16} for which the z axis is parallel to the 4,4'-direction and the ring plane coincides with the yz plane. With such a fragment present, well separated absorption bands polarized along the axes $j=x, y, z$ with maxima positions λ_j are observed in the vibrational or electronic molecular spectrum.

The parameters measured experimentally are the following dichroic ratios

$$N_{1j} = \frac{D_{\parallel}(\lambda_j)}{D_{\perp}(\lambda_j)}, \quad N_{2j} = \frac{D_{\perp}(\lambda_j)}{D_i(\lambda_j)}, \quad N_{3j} = \frac{D_{\parallel}(\lambda_j)}{D_i(\lambda_j)} \quad (1)$$

of the optical densities $D_{\parallel, \perp, i}$ of the sample for three absorption bands studied. Subscripts \parallel, \perp and i belong to the polarizations of the light wave $\underline{E} \parallel \underline{n}$, $\underline{E} \perp \underline{n}$ in the orientational-ordered state of absorbing molecules and to the disordered state (i), which for the liquid crystals corresponds to the isotropic-liquid phase.

Orientational ordering of the axes of the molecular frame chosen with respect to \underline{n} is characterized by the Saupe order parameters¹

$$S_j = \langle 3 \cos^2 \Theta_{j\underline{n}} - 1 \rangle / 2 \quad (2)$$

where $\Theta_{j\underline{n}}$ is the angle between the j -th molecular axis and \underline{n} , the brackets $\langle \dots \rangle$ mean the statistical average over all the molecules considered. Each value S_j can be obtained using Eq. (1) by the next three ways⁵

$$S_{1j} = \frac{N_{1j}g_{1j} - 1}{N_{1j}g_{1j} + 2}, \quad S_{2j} = 1 - N_{2j}g_{2j}, \quad S_{3j} = (N_{3j}g_{3j} - 1)/2, \quad (3)$$

where the correction factors $g_{kj}=g_k(\lambda_j)$ for each band are given by the expressions

$$g_1 = \frac{n_{\parallel}}{n_{\perp}} \left(\frac{f_{\perp}}{f_{\parallel}} \right)^2, \quad g_2 = \frac{\rho_i n_{\perp}}{\rho n_i} \left(\frac{f_i}{f_{\perp}} \right)^2, \quad g_3 = \frac{\rho_i n_{\parallel}}{\rho n_i} \left(\frac{f_i}{f_{\parallel}} \right)^2 \quad (4)$$

Here $n_{\parallel, \perp, i}$ and $f_{\parallel, \perp, i}$ are the background refractive indices and the local-field tensor components within the chosen absorption band in anisotropic and isotropic phases, ρ and ρ_i are the densities of these phases, respectively. In Eq. (4) for $g_{2,3}$ the thicknesses of the anisotropic and isotropic samples are assumed to be identical.

Equation (3) for S_{2j} and S_{3j} are correct if the oscillator strengths of the corresponding molecular transitions do not depend on the anisotropy of the molecular orientational distribution. In this case application of the identity $\sum_j S_j = 0$ for the parameters S_{2j} and S_{3j} gives

$$\sum_j N_{2j} g_{2j} = 3, \quad \sum_j N_{3j} g_{3j} = 3 \quad (5)$$

Using expressions⁵

$$f_{\parallel, \perp} = 1 + L_{\parallel, \perp} \left(n_{\parallel, \perp}^2 - 1 \right), \quad f_i = \left(n_i^2 + 2 \right) / 3 \quad (6)$$

in Eqs. (4) and (5) with the known values $n_{\parallel, \perp, i}(\lambda_j)$ one can see that the first relation in Eq. (5) is the equation with respect to unknown parameter L_{\perp} and the second one is the equation with respect to parameter L_{\parallel} . Solution of these equations gives the possibility to find parameters $L_{\parallel, \perp}$ directly from experimental data without additional assumption $\text{Tr} \underline{L} = 1$, used earlier for determination of \underline{L} and \underline{f} in liquid crystals from refractometric and spectral data.⁵

If all three absorption bands, λ_j are isolated from influence of the neighboring spectral bands and placed in the same spectral region with low dispersion $n_{\parallel, \perp, i}(\lambda_j)$, then the dispersion $g_k(\lambda)$ can be neglected and one can put $g_k(\lambda_j) = g_k$ for the bands

discussed. This approximation is quite reasonable for the isolated absorption bands in the IR region where the dispersion of the background values $n_{\parallel,\perp}(\lambda)$ is low.¹⁷ Then from Eq. (5) we obtain

$$g_2 = 3/\left(\sum N_{2j}\right), \quad g_3 = 3/\left(\sum N_{3j}\right) \quad (7)$$

and relations (3) can be rewritten in the following form

$$S_{2j} = 1 - \frac{3N_{2j}}{\sum N_{2j}}, \quad S_{3j} = \frac{1}{2} \left(\frac{3N_{3j}}{\sum N_{3j}} - 1 \right) \quad (8)$$

Thus, the values $S_{2,3j}$ corresponding to the correct accounting of the optical anisotropy of a medium and the local-field anisotropy can be obtained only from the spectral measurements of $N_{2,3}(\lambda_j)$.

Really the assumption that the oscillator strengths of the molecular transitions do not depend on the molecular orientational distribution may be violated because of disturbance of the vibrational or electronic molecular structure by intermolecular interactions. Therefore it is preferable to use in Eq. (3) the relation for S_{1j} since the dichroism N_{1j} does not depend on the change of the oscillator strengths of the bands λ_j . The identity $\sum_j S_{1j} = 0$ gives the equation

$$g_{1x}g_{1y}g_{1z} + \frac{g_{1y}g_{1z}}{N_{1x}} + \frac{g_{1x}g_{1z}}{N_{1y}} + \frac{g_{1x}g_{1y}}{N_{1z}} - \frac{4}{N_{1x}N_{1y}N_{1z}} = 0 \quad (9)$$

For the conditions pointed out above, when the dispersion $g_1(\lambda_j)$ can be neglected we obtain from here the following equation

$$g_1^3 + g_1^2 \left(\frac{1}{N_{1x}} + \frac{1}{N_{1y}} + \frac{1}{N_{1z}} \right) - \frac{4}{N_{1x}N_{1y}N_{1z}} = 0 \quad (10)$$

This equation has one physical positive real root

$$g_1 = a \left\{ 2 \cos \left[\frac{1}{3} \arccos \left(\frac{b}{a^3} - 1 \right) \right] - 1 \right\} \quad (11)$$

where the following notation is used

$$a = \frac{1}{3} \left(\frac{1}{N_{1x}} + \frac{1}{N_{1y}} + \frac{1}{N_{1z}} \right), \quad b = \frac{2}{N_{1x}N_{1y}N_{1z}} \quad (12)$$

Measurement of three dichroic ratios N_{kj} for each of three absorption bands allows one to make conclusions about the possible change of the oscillator strengths of these bands by the comparison of the value g_1 (11) with the value

$$g_1 = g_3/g_2 = \left(\sum N_{2j} \right) / \left(\sum N_{3j} \right) \quad (13)$$

which follows from Eqs. (4) and (7). For the isotropic absorption oscillator as well as for the anisotropic one in the spherically symmetric molecule we have $N_{kx}=N_{ky}=N_{kz}=N_k$ and from Eqs. (7) and (11) obtain the known result $g_k=1/N_k$.^{5,18,19}

The approximation of the oriented gas means $g_{kj}=1$ and in the general case for $g_{kj} \neq 1$ we have

$$\left\langle \cos^2 \Theta_{j\parallel} \right\rangle = \frac{N_{1j}g_{1j}}{N_{1j}g_{1j} + 2} \neq \frac{N_{1j}}{N_{1j} + 2} \equiv K_j \quad (14)$$

Therefore, the systematic deviations $\sum k_j \neq 1$ observed experimentally⁸⁻¹⁵ are the natural results of the approximation used. It should be mentioned that the same result may be caused also by the possible breaking of the molecular symmetry as well as the change of the moment's orientation for some molecular transitions in the condensed matter.¹³ However the latter reasons may be considered only after properly accounting for the birefringence and local-field anisotropy.

From the right-hand side of Eq. (14) the next relation

$$3 + 12a + 2b \sum N_{1j} = \left[1 + 6a + 2b \left(2 + \sum N_{1j} \right) \right] \sum K_j \quad (15)$$

follows. By putting $\Sigma K_j = 1$ we obtain $1 + 3a = 2b$ that corresponds to $g_1 = 1$ in Eq. (10). In the case $\Sigma K_j \neq 1$ we have $g_1 = 1 + \alpha$ and for $\alpha \ll 1$ our consideration can be restricted to terms linear in α in Eq. (10). Then the substitution of the parameter b from Eq. (15) into Eq. (10) gives the relation

$$g_1 = 1 + B \left(1 - \Sigma K_j \right) \quad (16)$$

where

$$B = \frac{3 + 12a + (1 + 3a)\Sigma N_{1j}}{(3 + 6a) \left[2 - \left(1 - \Sigma K_j \right) \left(2 + \Sigma N_{1j} \right) \right]} \quad (17)$$

Thus, for $\left(\Sigma K_j \right) \geq 1$ the inequalities of $g_1 \leq 1$ are fulfilled. The linear dependence $g_1(\Sigma K_j)$ can be expected for the fixed system in the case of changing the orientational molecular ordering because of the temperature change (for liquid crystals) or the preparation method (the degree of stretching — for the anisotropic polymeric films). Both possibilities $\left(\Sigma K_j \right) \geq 1$ are observed experimentally.⁸⁻¹⁵

TEST MATERIALS, RESULTS AND DISCUSSION

In order to test the method described, the precision published data have been used for the parameters K_j (14) measured in the IR region for the solute molecules in the anisotropic matrices of various types: polyethylene (PE), perdeuterated high-density polyethylene (PED) and the liquid crystal trans-trans-n-butyl-4'-cyanobicyclohexyl (4CCH). The stretched polymeric sheets are widely used as orienting matrices for studying the electronic and vibrational structure of the solute molecules¹ although the information about the features of the local-field for them is very limited¹⁹ and has been obtained using the optical probing method¹⁸ from the dichroism N_1 of the electronic absorption of the octahedral solute molecules $\text{Mo}(\text{CO})_6$. For the liquid crystals with low birefringence to which 4CCH belongs, the features of the local field have been

explored experimentally in the framework of other methods⁵ and therefore it is of interest to compare the results of various approaches.

The solute molecules chosen have a variety of chemical natures and differ from one another by the electronic structure and shape changing from rod-like to disk-like. These factors are of interest from the standpoint of their influence on the local-field parameters as well as dependence of the latter parameters on the features of the intermolecular correlations.⁵

The results of determination of the parameters g_1 , Eq. (11), $S=S_{1z}$ and $G=S_{1y}-S_{1x}$ from the known values K_j , Eq. (14), are presented in the Table. The parameters K_j have been obtained by averaging corresponding values over a large number of the spectral bands of the same polarization in order to make weaker the possible depolarizing influence of the nearest or overlapping bands with various polarization on the values N_{1j} measured. After such averaging, the values of K_j are practically insensitive to the possible deviation of some transition-moment's orientation from the molecular frame axes. The dependence $g_1(\Sigma K_j)$ for the investigated systems is presented at the Figure. The values g_1 calculated by Eqs. (16) and (17) differ from that obtained by Eq. (11) not more than 0.002.

In spite of the various types of the impurity molecules in the matrix PE for the systems 21–26 with $g_1 \leq 1$ the dependence $g_1(\Sigma K_j)$ has the form (16) with parameter $B=1.6$ independent of the electronic structure and peculiarities of the orientational ordering of impurity molecules. For the system with $g_1 \geq 1$ all values $g_1(\Sigma K_j)$ are within the narrow region between the lines (16) with parameters $B=1.6$ and 1.805. Such coincidence of the dependences (16) for various molecules in the same matrix (systems 1,2,4,8 and 3,5,7,9,12–15) shows the main role of matrix in the features of the local field acting on the impurity molecule. From here the possibility follows of

TABLE I The composition of the doped systems and parameters K_j (I4), g_I (II), $S=S_{Iz}$ and $G=S_{Iy}-S_{Ix}$ corresponding to them.


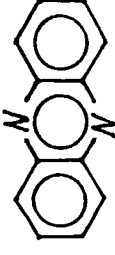
N syst.	Impurity	Matrix	K_x	K_y	K_z	$\sum K_j$	Ref.s	g_I	S	G
1	$H_3C-C\equiv C-CH_3$	PED	0.287	0.287	0.390	0.964	I3	1.057	0.105	0
2	$H_2C=C(CH_3)_2$	PED	0.267	0.346	0.361	0.974	I3	1.040	0.055	0.120
3	PE	PE	0.248	0.358	0.371	0.977	I3	1.039	0.070	0.164
4	$H_3C-O-CH_3$	PED	0.284	0.313	0.366	0.963	I3	1.058	0.069	0.045
5	PE	PE	0.260	0.310	0.423	0.993	I3	1.011	0.138	0.075
6		PED	0.123	0.265	0.597	0.985	I0	1.027	0.405	0.216
7	PE	PE	0.112	0.261	0.626	0.999	I0	1.002	0.441	0.225
8		PED	0.220	0.280	0.485	0.985	I0	1.024	0.236	0.090
9	PE	PE	0.212	0.258	0.521	0.991	I0	1.015	0.286	0.069
10	4CCH	4CCH	0.200	0.280	0.520	1.000	I5	1.000	0.280	0.120

TABLE I (continuation)

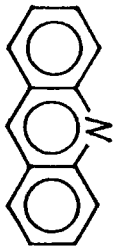
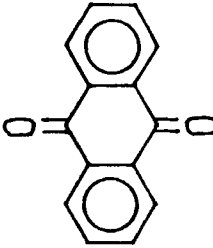
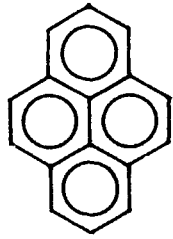
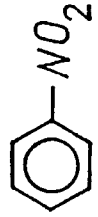
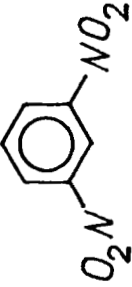

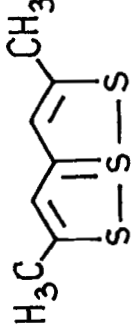


N syst.	Impurity	Matrix	K _x	K _y	K _z	ΣK _j	Ref.s	g _I	S	G
I1		PE	0.141	0.281	0.542	0.964	10	1.065	0.336	0.218
I2		PE	0.138	0.259	0.580	0.977	10	1.042	0.385	0.187
I3		PE	0.150	0.250	0.590	0.990	12	1.018	0.391	0.152
I4		PE	0.120	0.340	0.520	0.980	8	1.036	0.294	0.338
I5		PE	0.120	0.330	0.530	0.980	12	1.037	0.309	0.323
I6		4CCH	0.110	0.340	0.530	0.980	15	1.036	0.308	0.352
I7		PE	0.170	0.310	0.490	0.970	9	1.050	0.253	0.215
I8		4CCH	0.290	0.340	0.370	1.000	15	1.000	0.055	0.075

TABLE I (continuation)

N syst.	Impurity	Matrix	K_x	K_y	K_z	$\sum K_j$	Ref.s	g_I	S	G
19		4CCH	0.220	0.350	0.400	0.970	I5	1.048	0.117	0.198
20		4CCH	0.170	0.320	0.480	0.970	I5	1.051	0.238	0.230
21	PE		0.210	0.280	0.520	1.010	I4	0.984	0.274	0.104
22		PE	0.220	0.290	0.510	1.020	I4	0.968	0.253	0.103
23	PE		0.200	0.290	0.510	1.000	I4	1.000	0.265	0.135
24	PE		0.230	0.290	0.490	1.010	I4	0.984	0.229	0.089
25		PE	0.065	0.413	0.525	1.003	I1, I2	0.995	0.286	0.522
26	PE		0.226	0.285	0.502	1.013	II	0.979	0.245	0.087
27		PE	0.217	0.290	0.488	0.995	II	1.009	0.235	0.110

using the fixed molecule-probe with the known absorption band polarization for the investigation of the local field in various anisotropic matrices.

The general feature of the matrices presented is low optical anisotropy. This explains the closeness of the dependences (16) for the same molecules in various

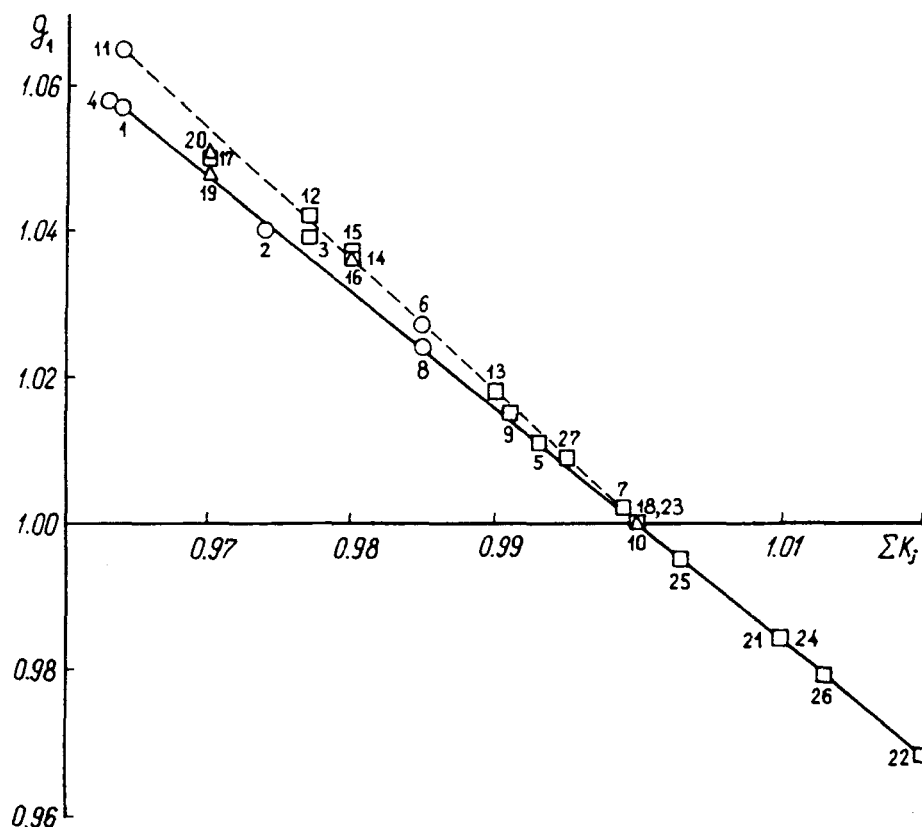


Figure 1. The dependence of parameter g_1 (11) on summ ΣK_j of parameters K_j (14) for the molecules presented in Table 1 in matrices PE (\square), PED (\circ) and 4CCH (\triangle). The numbers 1-27 are the system numbers from the Table. Solid and dashed lines are the dependences (16) for $B=1.6$ and 1.805 respectively.

matrices (systems 4-5, 6-7, 8-10, 14-16, 17-18) as well as the low value of the local-field anisotropy. For PE films with $n_1=1.51$ for a six-fold degree of stretching^{8,10,13} the

birefringence $n_{\parallel} - n_{\perp} \approx 0.04^{20}$ and $n_{\parallel} / n_{\perp} \approx 1.26$. Therefore, for all the systems one has $f_{\parallel} \approx f_{\perp}$ which is in accordance with the expected isotropic nature of the tensor \underline{f} in the anisotropic molecular media with low Δn^5 and with the independent experimental data.¹⁹

In spite of the low anisotropy of \underline{f} caused by the matrix's anisotropic properties small peculiarities of \underline{f} appear which reflect the specific features of solute molecules. So in the PE matrix for the systems 3,12,14,15 and 17 the inequality $f_{\perp} > f_{\parallel}$ appears but for the systems 5,7,9,13,21–27 one has $f_{\perp} < f_{\parallel}$. Analogous correlations $f_{\perp} \geq f_{\parallel}$ have a place for various molecules in the same matrices PED or CCH4. It should be pointed out that for different impurity molecules in the same matrix the correlation between the anisotropy of \underline{f} and the molecular orientational order parameters S and G is absent. For the systems 1,4,14, values g_1 are close to one another although the shape of the impurity molecules, values S and the correlation of the parameters S and G are significantly different. The same can be noticed for systems 19 and 12. These show a negligible dependence of the local field on the shape and character of the orientational ordering of the impurity molecules, that is in full accordance with the known data of the independent method for the liquid crystals.⁵ Differences between parameters g_1 for systems 6 and 11 as well as for systems 12 and 13 with the close values S and G shows the dependence of the anisotropy of \underline{f} on the specific features of the electronic structure of the solute molecules.

CONCLUSION

The results of the investigation carried out show that the method proposed for the experimental determination of local-field parameters from spectral data can be used for a self-consistent study of the molecular orientational ordering and local-field features in a uniaxial statistically-ordered molecular media of various types. Unlike

the known spectral methods⁵ this approach is not limited by (i) the supposition $\text{Tr}\underline{L}=1$ for the effective Lorentz tensor \underline{L} in Eq. (6), (ii) the assumption of the independence oscillator strengths of the anisotropy of molecular orientational distribution and (iii) the necessity to use data on D_i for the orientational-disordered (isotropic) state of the molecular ansamble studied. Experimental determination of parameter g_1 with the same accuracy as dichroism N_1 allows one to verify various theoretical approaches to the calculation of tensor \underline{f} in anisotropic doped systems.^{5,19}

The data obtained give new information about the influence of the matrix's and impurity molecules' properties on tensor \underline{f} for these molecules. Side by side with the general contribution to the anisotropy of \underline{f} determined by the matrix's anisotropic properties the dependence of \underline{f} on the specific features of the electronic structure of impurity molecules is significant. It is of interest to use the method discussed for the experimental determination of the local-field parameters in uniaxial molecular media with high optical anisotropy.

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