Effect of constant electric field on electronic absorption spectra of dye-doped amorphous polymer films

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Abstract. The change of an electronic absorption coefficient of polymer films, doped by symmetric cationic polymethine dye is researched in an external constant electric field. This effect are characterised by an increase of intensity on the shortwave edge of a band and its decrease at the longwave edge. The charge distribution in dye cation in the model electric field 10^7–10^8 V/m of point charges and capacitor was calculated by the method AM1. Based on quantum chemical calculations, the spectral regularities in the electric field is interpreted by a change of the electronic charge value on the cation. The theoretical model based on changes of the value of eigenfrequencies inherent to charged anharmonic oscillators under the operation field is offered for the description of observed effects. The experimental spectra correlate well with those calculated theoretically.

Keywords: amorphous molecular semiconductors; absorption coefficient; anharmonic oscillator; constant electric field; electronic charge; polymethine dyes.

1. Introduction

The influence research of an external electric field on photophysical properties of molecules is an actual problem, as gives a key to creation of new electrooptics materials. In works [1,2] it is revealed, that in long-wavelength bands of electronic absorption of organic dyes occurs a redistribution of intensities in an external constant electric field. Such effects take place both in polymer matrices, and in fluid solutions [1,2]. It should be noted, that they are not connected to known phenomena of orientation change of dyes molecules (ions) in an external electric field, for example by the Freedericks' or Kerr effect [3]. In works [1,2], the electric fields with strength $E =$ $= 10^7$–10^8 V/m were used. Such fields are comparable to the value of intramolecular fields and do not caused an electrical breakdown of a polymer matrix. For targeted synthesis of dyes with given electrooptics properties, it is necessary to develop a physical model permitting to prognosticate and to quantitatively describe changes in optical spectra of dyes under operation of an electric field. The development of such model was the aim of this work.

2. Experimental

We performed experimental researches of E influence on electronic absorption spectra of symmetric cationic polymethine dyes 1,3,3,1',3',3' hexamethylindocarbocyanine tetrafluoroborate (HIC)[4], incorporated in polymer films based on photoconducting poly-N-epoxypropylcarbazole (PEPC) and non-photoconducting polyvinylethylal (PVE). Concentration of HIC in polymers was 1 mass %.

HIC

PEPC

PVE
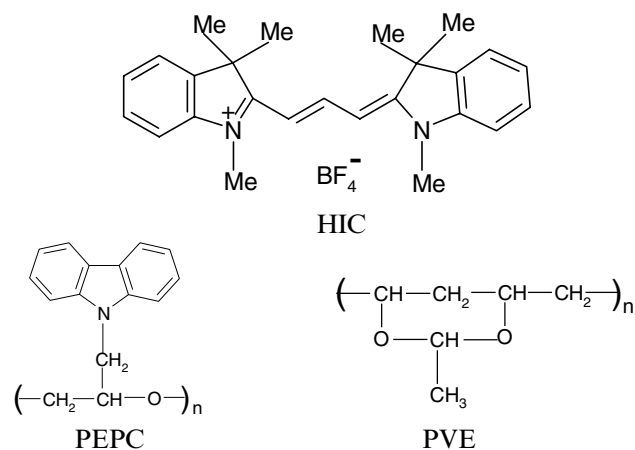
Samples prepared as structures with a free surface: a quartz substrate-SnO$_2$-dye-doped polymer film. An absorption coefficient of such films and its change in an external electric field were measured. For this purpose, in the beginning, at elected wavelengths of light (λ) determined an absorption coefficient (κ_0) of dye-doped polymer film without any application of an external electric field. Then we created an electric field in this film, registered change in time of an absorption coefficient before its new quasistationary value and determined an absorption coefficient (κ_E) in external electric field. Further calculated the value of the absorption coefficient change $\Delta\kappa$

$$\Delta\kappa = \kappa_E - \kappa_0 \qquad (1)$$

under the action of this field. The electric field was created in the film due to its charging in a corona discharge using the special electronic device [1,2]. The value E was $(6-10) \cdot 10^7$ V/m. This value was determined from the value of the free surface potential relatively to the potential of conducting layer SnO$_2$. Values κ_0 and $\Delta\kappa$ defined for light wavelengths in the range 400–1000 nm where the longwave absorption band of dye HIC is found. In this region, any absorption of PEPC and PVE is absent.

The quantum chemical calculations of a charge distribution in HIC cation in the absence and presence of a constant electric field were carried out by the semi-empirical method AM1 [5] (Table 1). The constant electric field was modeled by two external point charges $+Q_j$ and $-Q_j$ of the opposite sign placed at the distance $l = 10$ nm from each other. The values $+Q_j$ and $-Q_j$ are equal to 0 and 0 ($j = a$), +0.1 and –0.1 ($j = b$), +1 and –1 ($j = c$) of electronic charge, correspondingly. At such choice of external point charge values and the distance between them, the field in the region of a researched molecule with accuracy 5 % can be considered as uniform. The strength of the external electric field applied to this molecule, was defined by the relation (2).

$$E = \frac{|Q_j|}{\pi \cdot \varepsilon_0 \cdot l^2} \qquad (2)$$

where $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m – permittivity of vacuum. In the cases ($j = a$), ($j = b$) and ($j = c$) its values equal 0, 10^7 and 10^8 V/m correspondingly. The dye molecule is positioned in the field of charges in such manner, that its central atom (atom number 38, Fig. 1) of the polymethine chain occupies precisely the central point of a straight line connecting charges $+Q_j$ and $-Q_j$ (Fig. 2). It has al-
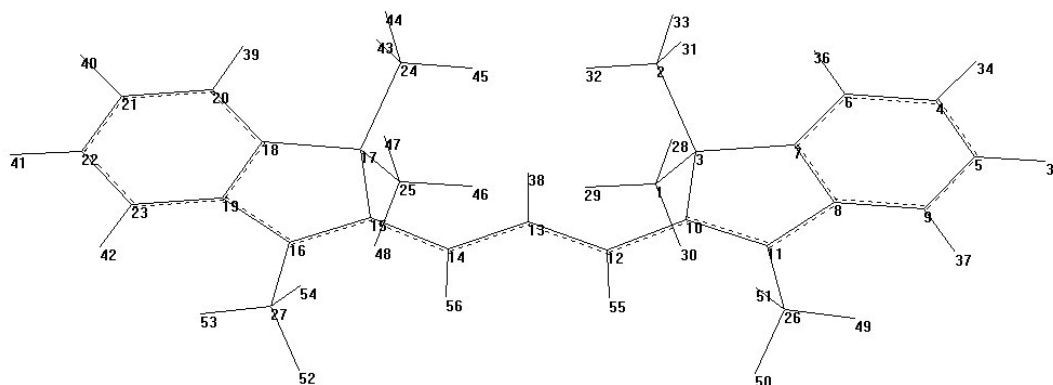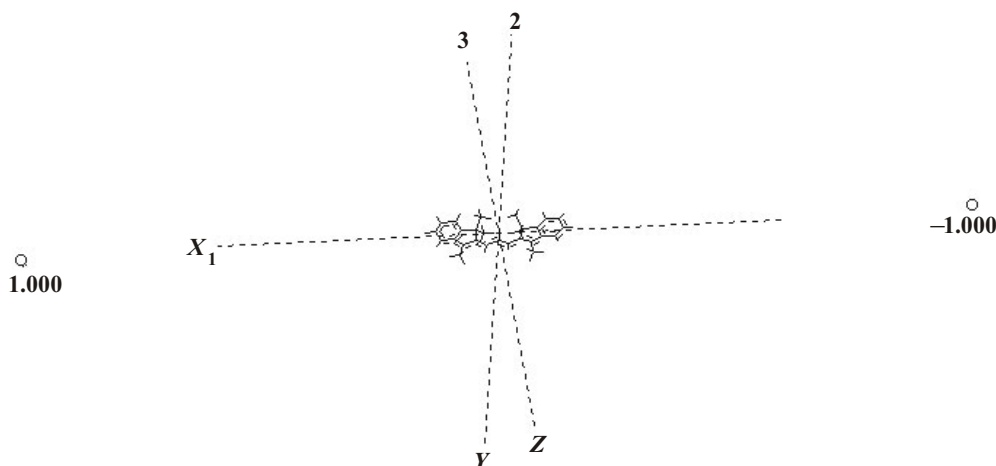
Fig. 1. Numbers of atoms in HIC cation.

Fig. 2. The view of HIC cation in constant electric field of external point charges $+Q_J$ and $-Q_J$ in the case of its disposition along the line, connecting these charges (along the X axis).

Table 1. The data of the quantum chemical calculations of electronic charge distribution in HIC cation by a semi–empirical method AM1 in absence ($j = a$) and presence of a constant electric field created by the point charges ($j = b,c$) and capacitor ($j = d$).

Atom number	Electronic charge ($j = a$)	Electronic charge ($j = b$)	Electronic charge ($j = c$)	Electronic charge ($j = d$)
1	–0.203226	–0.203215	–0.203173	–0.203213
2	–0.203226	–0.203221	–0.203185	–0.203203
3	0.000962	0.000930	0.000730	0.000896
4	–0.119442	–0.119320	–0.118175	–0.119061
5	–0.093161	–0.093106	–0.092586	–0.092993
6	–0.077162	–0.077195	–0.077476	–0.077266
7	–0.118677	–0.118675	–0.118726	–0.118702
8	0.016536	0.016344	0.014746	0.016004
9	–0.115417	–0.115288	–0.114187	–0.115008
10	0.194870	0.194906	0.195357	0.195034
11	–0.161586	–0.161301	–0.158918	–0.160752
12	–0.326877	–0.326857	–0.326588	–0.326770
13	0.099630	0.099640	0.099598	0.099619
14	–0.326888	–0.326920	–0.327154	–0.326965
15	0.194873	0.194827	0.194321	0.194693
16	–0.161589	–0.161847	–0.164223	–0.162416
17	0.000937	0.000942	0.001160	0.001006
18	–0.118609	–0.118604	–0.118528	–0.118590
19	0.016550	0.016711	0.018234	0.017097
20	–0.077210	–0.077165	–0.076843	–0.077122
21	–0.119389	–0.119515	–0.120569	–0.119789
22	–0.093202	–0.093245	–0.093776	–0.093372
23	–0.115379	–0.115509	–0.116672	–0.115769
24	–0.203235	–0.203241	–0.203301	–0.203244
25	–0.203234	–0.203219	–0.203273	–0.203254
26	–0.078340	–0.078424	–0.079168	–0.078609
27	–0.078342	–0.078263	–0.077487	–0.078081
29	0.077179	0.103657	0.103984	0.103711
28	0.103616	0.077111	0.076587	0.077004
30	0.100945	0.100962	0.101162	0.101055
31	0.100945	0.100975	0.101217	0.100996
32	0.077179	0.077110	0.076588	0.076999
33	0.103616	0.103660	0.103997	0.103699
34	0.154820	0.154917	0.155773	0.155086
35	0.156380	0.156504	0.157646	0.156778
36	0.150746	0.150755	0.150806	0.150739
37	0.153766	0.153824	0.154382	0.153975
38	0.139140	0.139144	0.139180	0.139131
39	0.150745	0.150752	0.150794	0.150729
40	0.154817	0.154729	0.153959	0.154530
41	0.156364	0.156241	0.155104	0.155967
42	0.153769	0.153697	0.153068	0.153581
43	0.100947	0.100919	0.100704	0.100842
44	0.103615	0.103590	0.103342	0.103496
45	0.077183	0.077252	0.077772	0.077358
46	0.077184	0.077239	0.077757	0.077363
47	0.103615	0.103582	0.103324	0.103510
48	0.100947	0.100914	0.100657	0.100901
49	0.117431	0.117531	0.118463	0.117774
50	0.104797	0.104825	0.105064	0.104933
51	0.104797	0.104833	0.105112	0.104883
52	0.104803	0.104767	0.104428	0.104735
53	0.117436	0.117334	0.116369	0.117101
54	0.104802	0.104767	0.104467	0.104685
55	0.159126	0.159135	0.159212	0.159179
56	0.159123	0.159106	0.158943	0.159092

lowed to shun the distortion in a symmetry of the charge distribution in this dye cation due to a dimensional effect. Really, in a zero field ($j = a$) the symmetry in a charge distribution is saved, and its numerical values coincide with the data of the calculation of charges values of an isolated molecule HIC.

The external electric field was also modeled using a parallel-plate capacitor. Each plate was set by a set of charges, equal in absolute values and laying in one plane. Each charge positively of charged plate mattered 0.03 and each charge negatively of a charged plate – (–0.03). Distance between the adjacent charges both in horizontal, and vertical rows was identical and constituted 2.5 nm. The amount of charges in each row equalled 5 (Fig. 3). The charges of one plate are disposed strictly symmetrically toward charges of other plate. Distance between unlike charges in all such symmetric pairs constitutes 10 nm. The field strength in the capacitor with the parameters described above was 10^8 V/m and calculated by the formula (3):

$$E = (n)^2 \frac{Q_j}{S \cdot \varepsilon_0} \qquad (3)$$

where n – charge number, S is the square of the capacitor plate.

The dye molecule positioned along the straight line, bonding central charges of plates. Herewith as well as in the case of point charges, the central atom of a dye coincided with center of the mentioned above line (Fig. 3).

3. Results and discussion

The E influence on electronic absorption spectra of dye-doped films based on PEPC and PVE is revealed. This influence appears after the application E in appearance of positive and negative maxima of dependence $\Delta\kappa(\lambda)$. Under E action in films with HIC, the intensity of absorption in the shortwave part of a band increases ($\Delta\kappa > 0$) and in the longwave part decreases ($\Delta\kappa < 0$) (Fig. 4). After the application of E, the value of an absorption coefficient varies with speed of charging of the film sur-
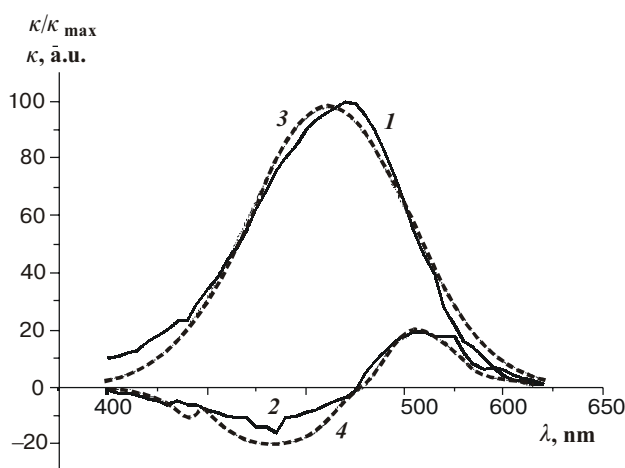
Fig. 4. A experimental spectrum of an absorption coefficient (1) and change of an absorption coefficient (2) in an external constant electric field of films PEPC+1mas.%HIC as well as corresponding to them calculated an spectra (3 and 4) by the formulas (11,18,19). Strength of an field is $E = 1 \cdot 10^8$ V/m.

face in time no more than 0.2 s. After turning E off, the absorption spectrum is reduced. In a researched range of E, the position of positive and negative maxima of dependence $\Delta\kappa(\lambda)$ does not depend on E and thickness of a polymer film, but $|\Delta\kappa|$ are increased with propagation E and this increase is proportional to E^2. Absolute values $\Delta\kappa$ do not depend on polarization of incident and transmitted light through a sample. Consequently, the observed effects in spectra under action of the electric field are not connected to orientation phenomena. They are not connected also to processes of an electron transfer in the system polymer – dye, as they take place both in photoconducting PEPC and non-photoconducting PVE. The exception of these factors gives the basis to assume that the spectral effects are caused by the change of an electronic structure of dyes under action of a electric field. It is reconfirmed by the data of the quantum chemical calculation of HIC cation (Table 1). There is a change of electronic charge on atoms of cation as is seen from Table 1, in a field of point charges $+Q_j$ and $-Q_j$, which corresponds to the strength value used in our experiments. It results in the induced electronic asymmetry of symmetric dyes HIC. The maximal change of a distributed charge in cation occur at orientation of dye cation along the straight line connecting point charges. At the perpendicular orientation of charges, the value practically do not vary. The similar tendencies are observed in a field of the capacitor.

To estimate the quantitative characteristic of integral change in the electronic charge distribution inside a molecule under action of the field, we have calculated coordinates of the center of this distribution from the formula (4)

$$\mathbf{r}_c^j = \sum_n q_j^n \cdot \mathbf{r}^n \qquad (4)$$

where q_j^n is the probability of presence of an optical electron of a molecule in absence of a field ($j = a$) and in an external electric field ($j = b, c, d$), created by external

Fig. 3. A view of HIC cation in constant electric field of capacitor.

charges $+Q_j$ and $-Q_j$ in a point of presence of atom n with the coordinate $\mathbf{r}^n$. The summation in (4) was performed on all atoms of a molecule. From the relation (4), if the elementary charge is equal 1 and under action of the field, only the electronic coordinates vary, and nuclei keep stationary values, we obtain the formula (5) for the change of the position of an optical electron center $\mathbf{r}_0$:

$$\mathbf{r}_0 = \mathbf{r}_c^a - \mathbf{r}_c^b \qquad (5)$$

The calculations by the formula (5) show that in going from a case ($j = a$) to ($j = b$) the value of center shift of an optical electron ($\mathbf{r}_0$) is 0.11 nm, and the shift happens along X axis (Fig. 2) in the direction from a charge $-Q_j$ to a charge $+Q_j$. It is accompanied by change, as follows from results of the quantum-chemical calculations, of the electronic transition energy value in the first singlet excited state of HIC molecule. With an increase of the value of external charges from 0 up to 0.1 and 1, this energy varies from 21253.5 cm^{-1} up to 21254 cm^{-1} and 21263 cm^{-1}. In capacitor, its value achieves 21255.6 cm^{-1}. The hypsochromic shift of the absorption band with increasing the field strength is caused by amplification of electronic asymmetry of a dye molecule.

It is expedient to find connection between values $\mathbf{r}_0$ and $\kappa(\lambda)$, λ. Then, on the quantum-chemical calculations of a charge distribution in the molecule, it will be possible to prognosticate theoretically the tendencies in change not only of the position but also of contour of absorption bands.

The contour of longwave absorption bands of polymethine dyes in the absence of strong intermolecular interactions is determined by vibronic interactions [6-10]. The main contribution to these interactions is given by the valence full-symmetric vibration of chromophore atoms in the excited state [6-10]. Therefore, as a first approximation, it is possible to consider that the spectral effects in an electric field are connected mainly to the change of a charge distribution in the dye ion. It allows to use a simple model of anharmonic oscillators for the description of the process of light absorption by dye molecules, the oscillators being in the electric field and interacting with a light wave [11]. Each of oscillators, interacting with the wave, is described by the equation (6) [11].

$$\frac{\partial^2 r}{\partial t^2} + 2\beta \frac{\partial r}{\partial t} + \omega_0^2 r + \alpha r^2 = \frac{eE}{m} + \frac{eE_0}{m} \exp(i\omega t) \qquad (6)$$

Here r is the deviation of an optical electron from the equilibrium position, β – damping coefficient, ω_0 – frequency of free vibrations of an oscillator, E_0 – amplitude value of an electric field strength of a light wave, m – electronic mass, α – coefficient defining an anharmonicity of an oscillator, ω – light frequency. The origin of coordinates is disposed in the location of an electron in the absence of an external field. The amplitude r, as follows from (6), is the complex value. It defines electrical dipole moment of a modeled molecule and modulus of the polarization vector P, as it is seen from the equation (7):

$$P = Ner, \qquad (7)$$

where N is the volume concentration of dye molecules. The parameter P is connected to the complex permittivity ε by the relation (8) [12]:

$$\varepsilon = 1 + \frac{P}{\varepsilon_0 E_0}, \qquad (8)$$

Its imaginary part looks like (9):

$$\mathrm{Im}\,\varepsilon = \frac{2Ne^2\omega\beta}{m\varepsilon_0[(\omega_0^2 - \omega^2)^2 + 4\beta^2\omega^2]} \qquad (9)$$

and is connected to the absorption coefficient of the medium $\kappa(\lambda)$ by a relation (10) [12]:

$$\kappa(\lambda) = \frac{2 \cdot \pi \cdot \mathrm{Im}\,\varepsilon}{n_r \cdot \lambda}. \qquad (10)$$

where n_r in the refraction coefficient of the medium. After substitution of the equation (9) into the equation (10) and using the expression $\omega = \dfrac{2 \cdot \pi \cdot c}{\lambda}$, we shall obtain the equation (11):

$$\kappa(\lambda) = \frac{2 \cdot \beta \cdot N \cdot e^2}{(2 \cdot \pi \cdot c)^2 \cdot c \cdot \varepsilon_0 \cdot m \cdot n_r} \cdot \frac{\dfrac{1}{\lambda^2}}{(\dfrac{1}{\lambda_0^2} - \dfrac{1}{\lambda^2})^2 + (\dfrac{\beta}{\pi \cdot c \cdot \lambda})^2} \qquad (11)$$

where c is the speed of light. When writing representation (11), it is necessary to take into account a possibility of existence of various sorts of oscillators, interacting with a light wave, which should give in appearance of appropriate summation in (11) on sorts of oscillators. However, the contribution of each sort of oscillators to the absorption coefficient is additive. Therefore, with the purpose to simplify the look, the sign and indexes of summation in the expression (11) are not given.

Within the framework of the model of anharmonic oscillators, the shift of the equilibrium position of the electronic density (oscillator) on the value r_0 under action of the external electric field takes place in accord with the equation (12) [12]:

$$r_0 = \frac{-\omega_0^2 \pm \sqrt{\omega_0^4 + \dfrac{4\alpha \cdot e \cdot E}{m}}}{2\alpha} \approx$$

$$\approx \frac{e \cdot E}{m \cdot \omega_0^2} - \frac{e^2 \cdot E^2 \cdot \alpha}{m^2 \cdot \omega_0^6} + \frac{2e^3 \cdot E^3 \cdot \alpha^2}{m^3 \cdot \omega_0^{10}} \ldots \qquad (12)$$

Its shift at presence of an anharmonicity causes change of eigenfrequency (eigenwavelength) of an oscillator modeling an optical electron on the value $\Delta\omega_0(\Delta\lambda_0)$:

$$\Delta\omega_0 = \frac{\alpha \cdot r_0}{\omega_o}. \qquad (13)$$

$$\Delta\lambda_0 = -\frac{\omega_0 \cdot \alpha \cdot r_0}{2 \cdot \pi \cdot c} \qquad (14)$$

The change of eigenfrequency (eigenwavelength) of the oscillator causes change of an absorption coefficient as follows (11). The change of the peak wavelength in the electric field based on expressions (12) - (14) can be presented as (15):

$$\Delta\lambda_0 = -\frac{2\cdot\pi\cdot c\cdot\alpha}{\omega_0{}^3}\times$$

$$\times[\frac{e\cdot E}{m\cdot\omega_0{}^2} - \frac{e^2\cdot\alpha\cdot E^2}{m^2\cdot\omega_0{}^6} + \frac{2\cdot e^3\cdot\alpha^2\cdot E^3}{m^3\cdot\omega_0{}^{10}}\cdots] \qquad (15)$$

To estimate the change of the absorption coefficient $\kappa_E(\lambda)$ under action of the external electric field, we shall replace in the equation (11) the value λ_0 by $\lambda_0 + \Delta\lambda_0$, and we shall substitute the expression (15) in it. So, we obtain the equation (16):

$$\kappa_E(\lambda) = \frac{2\cdot\beta\cdot N\cdot e^2}{(2\cdot\pi\cdot c)^2\cdot c\cdot\varepsilon_0\cdot m\cdot n_r}\times$$

$$\times\frac{\lambda^{-2}}{[((\lambda_0+\Delta\lambda_0)^{-2}-\lambda^{-2})^2 + \frac{4\beta^2}{(2\cdot\pi\cdot c\cdot\lambda)^2}]}, \qquad (16)$$

The change of this coefficient in practically realised cases $\Delta\lambda_0 << \lambda_0$ can be presented as (17):

$$\Delta\kappa(\lambda) = \frac{\beta\cdot N\cdot e^2}{(\pi\cdot c)^2\cdot c\cdot\varepsilon_0\cdot m\cdot n_r}\times$$

$$\times\frac{\lambda^{-2}\cdot\lambda_0{}^{-3}\cdot(\lambda_0{}^2-\lambda^2)}{[(\lambda_0{}^{-2}-\lambda^{-2})^2 + \frac{\beta^2}{(\pi\cdot c\cdot\lambda)^2}]^2}\cdot\Delta\lambda_0 \qquad (17)$$

Taking into consideration the relation (14), these equations can be transformed into the equation (18):

$$\Delta\kappa(\lambda) = -\frac{\beta\cdot\alpha\cdot N\cdot e^2}{(\pi\cdot c)^2\cdot c\cdot\varepsilon_0\cdot m\cdot n_r}\times$$

$$\times\frac{\lambda^{-2}\cdot\lambda_0{}^{-4}\cdot(\lambda_0{}^2-\lambda^2)}{[(\lambda_0{}^{-2}-\lambda^{-2})^2 + \frac{\beta^2}{(\pi\cdot c\cdot\lambda)^2}]^2}\cdot r_0 \qquad (18)$$

Within the framework of the offered model, the representation (18) allows to install interrelation between changes of the absorption coefficient of a sample in the external electric field and the value of center shift of an optical electron in the molecule (change of the electrical dipole moment of the molecule) which calculated by quantum-chemical methods.

It is necessary to take into account various orientations of molecular axes relatively to the external electric field, as the distribution of dopant molecules in amorphous polymer matrices and liquids is isotropic. In this connection, we obtain the equation (19):

$$\Delta k^{eff}{}_E = \frac{1}{2}\cdot(k_E(\lambda) - k(\lambda)) +$$

$$+ \frac{1}{2}\cdot(k_{-E}(\lambda) - k(\lambda)) \sim E^2 \qquad (19)$$

The graphs of the experimental and theoretical dependencies $\kappa(\lambda)$ (curve1,3) and $\Delta\kappa(\lambda)$ (curve2, 4) in films PEPC+1mas. of %. HIC are presented in Fig. 4. The curves (3,4) in the electric field were calculated using the value r_0 of a molecule HIC, determined through quantum-chemical calculations. Then, on the basis of expressions (11), (18) and (19), calculated was the dependence $\Delta k^{eff}{}_E$. The parameters (α, β, ω_0, N) as well as amount of oscillator sorts varied in such manner that the difference between the experimental and theoretically calculated values of the absorption coefficients was minimum.

The experimental dependencies $\Delta k^{eff}{}_E$ from E well correlate with calculated theoretically, as is seen from a Fig. 4. It should be noted that it is possible to decide also inverse problem, namely: to find the value r_0 from experimental spectra by the formula (18). The computation by this formula has given value 0.105 nm, that practically coincides with the analogous value, calculated by method AM 1, as mentioned above.

4. Conclusion

Thus, the offered model can be used for theoretical prediction of changes in absorption spectra of organic dyes in an external electric field connected with redistribution of electronic density(charge) in molecules. The results of such calculations are in accordance to the experimental ones. The offered model can be further applied not only for the purposes of spectroscopy, but also for another problems connected with conversion of light energy in dye-doped polymer materials.

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