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UDC 539

**EXCITED STATE MOLECULAR  
PARAMETERS DETERMINED BY SPECTRAL MEANS**

*The possibility to characterize the electronic excited state of a spectrally active molecule based only on the solvatochromic study of electronic absorption spectra is demonstrated. The values of the regression coefficients given the contribution of universal interactions to the spectral shift and their theoretically established dependences on the solute molecule microscopic parameters are used. The values of the dipole moment, polarizability, and ionization potential in the ground electronic state of a spectrally active molecule are established by quantum mechanical methods. Two azo dye molecules are chosen in order to exemplify this method.*

*Keywords:* electronic absorption spectra, excited state dipole moment, azobenzene derivatives.

**1. Introduction**

For the molecules showing absorption and fluorescence spectra, there are studies, in which the dipole moment of an excited state and the angle between the dipole moments in the ground and excited states were estimated [1–10], when the dipole moment of the ground electronic state was experimentally determined or it was computed using quantum chemistry methods.

Some information about the excited state parameters of non-fluorescent molecules can be obtained from the absorption spectra [8–10]. The solvatochromic analysis offers a possibility to characterize a molecule in its excited state, when the contribution of the universal interactions to spectral shifts is higher than the contribution of the specific interactions. The theory of simple liquids applied to the diluted solutions expresses the contribution of the universal interactions to spectral shifts as a function of the solvent macroscopic parameters and of the solute microscopic parameters in its electronic states participating in the absorption process.

The results regarding the characterization of two azo-benzene dyes are discussed here, by combining the quantum mechanical analysis and the solvatochromic study.

Azo-benzene compounds have a widespread field of applications [11, 12] such as in the dye stuff in-

dustry, photo-aligning substrates for liquid crystals, acid-basic indicators, optical storage media, food colorants, sensitizers in photo-dynamical therapy, or as inhibitors of the tumor growth [13, 14].

The nature of the interactions between the azobenzenes and the solvents (and so the spectral behavior in solutions) is determined by their donor or acceptor substituents in para positions of the aromatic groups [15–17]. The results obtained by quantum mechanical calculations and by solvatochromic studies were previously [17] correlated, and the dipole moments of three azo-benzene derivatives were estimated using the hypothesis of colinearity between molecular dipole moments of the electronic states participating to the  $\pi \rightarrow \pi^*$  transition responsible for the azo-benzenes' visible band appearance. This study offers an additional information regarding the excited state dipole moment and its orientation relative to the ground state dipole moment.

**2. Theoretical Background**

In liquids, the universal (long-range) and specific (short-range or quasichemical) interactions can act [18–20].

The universal interactions exert a global influence on the spectrally active molecules. They are non-oriented and non-saturated and can cause spectral shifts of the electronic absorption/fluorescence bands.

The specific interactions reveal themselves in the processes with charge transfer (such as the formation

of hydrogen bonds or electron migration) between the atomic systems. Specific interactions act locally, being evidenced especially in vibration spectra, but they can cause supplementary spectral shifts in electronic spectra directly affected by universal forces.

Due to the complexity of the liquids, the theories regarding intermolecular interactions cannot be applied on a large category of solutions. Some models (McRae [18], Bakhshiev [20], and Abe [21]) developed for various liquids have limited applicability due to simplifying hypotheses corresponding to the type of a liquid, for which they are made. For example, in the most of the theoretical descriptions, the specific interactions are neglected. In order to accord the theory with the experiment, the researchers added empirical terms to the theoretical relations to describe the influence of the specific interactions on the electronic spectra. Some empirical scales (Kosower [22], Kamlet and Taft [23], Catalan [discussed in 24], etc.) were proposed in this aim.

The existent theories regarding the solvent influence on the electronic spectra [18–21] are usually developed under restrictive conditions imposed on the interacting molecules, which are considered neutral (from the electrical point of view), but polarizable spheres arranged in concentric solvation shells. A spectrally active molecule is placed at the center of the solvation shells surrounding it. The interaction energy (considered as being additive) depends on the distance between the interaction molecules. The total interaction energy of a spectrally active molecule and the solvent molecules is obtained by summarizing the interaction energies in molecular pairs.

Statistical methods (considering all terms established in various theories expressing the solvent influence on the electronic absorption spectra) are preferred, when the contribution of each type of interactions to the total spectral shift [9, 10, 15–17] must be estimated. A part of the considered terms corresponding to diverse types of interactions can be eliminated for statistical reasons. Only terms with real importance for the spectral shifts are kept in the statistical analysis.

Usually, multiple linear relations of the type:

$$X_{\text{calc.}} = X_0 + \sum_i C_i \chi_i \quad (1)$$

are considered in statistical methods. In relation (1), the spectral parameter influenced by the solvent na-

ture is  $X$  (it can be the wavenumber in the electronic band maximum), and  $\chi_i$  are the solvent parameters (refractive index, electric permittivity, ability to donate or to accept electrons, ...) theoretically or empirically introduced to account for each type of molecular interaction in a liquid solution. The indices attached to the spectral parameter reflect the computed ( $X_{\text{calc.}}$ ) and the experimental value for the gaseous phase ( $X_0$ ).

The contribution of the universal interactions to the position of the electronic absorption bands is usually expressed by functions of the electric permittivity ( $\varepsilon$ ) and the refractive index ( $n$ ) of the types:

$$f(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon + 2} \quad \text{and} \quad f(n) = \frac{n^2 - 1}{n^2 + 2} \quad (2)$$

or by the Kamlet–Taft empirical parameter  $\pi^*$  (see [16]), which linearly depends on  $f(\varepsilon)$  and  $f(n)$  [19].

The specific interactions neglected in the existent theories are considered by the empirical parameters  $\alpha$  and  $\beta$  describing the ability of a solvent to form hydrogen bonds by donating or accepting protons, respectively.

Usually, relation (1) can be written as a sum of the contributions of the universal and specific interactions [9, 10, 16, and 17]:

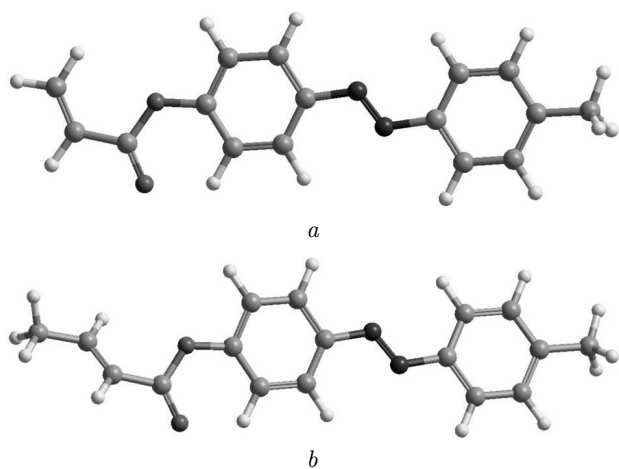
$$\begin{aligned} \nu_{\text{calc.}} (\text{cm}^{-1}) &= \nu_0 (\text{cm}^{-1}) + C_1 f(\varepsilon) + \\ &+ C_2 f(n) + C_3 \beta + C_4 \alpha. \end{aligned} \quad (3)$$

The coefficients  $C_i$ ,  $i = 1, 2, \dots, n$ , reflect, by their values and sign, the strength of the corresponding interaction and, respectively, the sense of a spectral shift relative to the initial position of the electronic band (in the gaseous phase of a spectrally active molecule).

The coefficients multiplying the functions  $f(\varepsilon)$  and  $f(n)$  describe the contribution of universal interactions to the total spectral shift, and they are dependent on the microscopic parameters of the spectrally active molecule as it follows [9, 10]:

$$C_1 = \frac{2\mu_g (\mu_g - \mu_e \cos \phi)}{hcr^3} + 3kT \frac{\alpha_g - \alpha_e}{r^3}, \quad (4)$$

$$\begin{aligned} C_2 &= \frac{\mu_g^2 - \mu_e^2}{hcr^3} - \frac{2\mu_g (\mu_g - \mu_e \cos \phi)}{hcr^3} - \\ &- 3kT \frac{\alpha_g - \alpha_e}{r^3} + \frac{3}{2} \frac{\alpha_g - \alpha_e}{r^3} \frac{I_u I_v}{I_u + I_v}. \end{aligned} \quad (5)$$



**Fig. 1.** Optimized chemical structures of the studied azobenzene derivatives: MOAAB (a) and MOMAB (b)

The statistically determined dependence of the type (1) allows estimating the contribution of each type of interaction to the spectral shift recorded in a given solvent.

The values of the coefficients  $C_i$ ,  $i = 1, 2, \dots, n$ , from relation (1) can be evaluated by statistical methods based on the results obtained in the solvatochromic analysis and on the solvent parameters  $\chi_i$ ,  $i = 1, 2, \dots, n$ , previously determined.

The dipole moment and the polarizability of a studied molecule in its ground electronic state can be estimated by quantum-mechanical calculations. So, some information about the dipole moment and the polarizability in the excited state can be obtained by using relations (4) and (5) based on the values of these coefficients and the electro-optical parameters calculated by quantum-chemical procedures for the ground state of a spectrally active molecule. We note that, in quantum-chemical estimations, the dipole moment and polarizability are obtained for an isolated molecule, and their values are used in the solvatochromic study, in which the molecule is included in a solution, where its electro-optical parameters in the ground state are modified by the reactive field of solvent molecules.

### 3. Experimental Details

Two azo-derivatives are considered in this paper in order to verify the possibility to estimate some electro-optical parameters in their excited state:

- 4-Methyl-4' – oxyacryloyl azo-benzene (MOAAB)
- 4-Methyl-4' – oxymethacryloyl azo-benzene (MOMAB).

The chemical structures of two azobenzene derivatives are illustrated in Fig. 1.

Two azo-derivatives were prepared, as is indicated in [15–17], and previously solvatochromically analyzed from the point of view of the excited state parameters [17] in the frame of the hypothesis that their dipole moments in the ground and excited states are collinear.

The spectral grade solvents were achieved from Merck and Fluke (Sigma-Aldrich) and used without purification. The electronic absorption spectra were recorded at a Specord UV Vis Carl Zeiss Jena spectrophotometer with data acquisition system. The spectral data published in [16, 17] were verified and used in this paper.

The solvents parameters and the results of solvatochromic analysis are given in [16, 17]. The Kamlet–Taft solvent parameters were taken from <http://www.stenutz.eu/chem/solv26.php>.

### 4. Results and Discussions

In view of [16, 17], the wavenumbers at the maximum of the visible  $\pi \rightarrow \pi^*$  electronic absorption band of the two studied azo-derivatives can be written as follows:

$$\nu_{\text{comp.}} = 31830 - 771.8f(\varepsilon) - 5121.9f(n) - 54.6\beta + 238.7\alpha \quad (\text{MOAAB}), \quad (6)$$

$$\nu_{\text{comp.}} = 31860 - 319.9f(\varepsilon) - 7087.1f(n) - 243.5\beta + 268.3\alpha \quad (\text{MOMAB}). \quad (7)$$

Coefficients  $C_1$  and  $C_2$  from relations (6) and (7) are the regression coefficients in Eq. (1) that multiply the functions  $f(\varepsilon)$  and  $f(n)$ , respectively. Their dependence on the molecular parameters is expressed in relations (4) and (5).

The quantum-mechanical characteristics [17] of two studied molecules were established by the HyperChem 8.0.6 software [25]. The optimized structures of the studied molecules were obtained by AM1 semiempirical methods with the Polak Ribiere algorithm, and RMS 0.001 kcal/mol.

Semiempirical calculations are used extensively, when a molecule is of moderate size.

The semiempirical method [Austin Model 1 (AM1)] used in our article for the quantum calculation of a molecular electronic structure was developed by M. Dewar and co-workers and published in 1985 (J. of Amer. Chem. Soc. 107 (13): 3902). Semiempirical methods are based on the Hartree–Fock formalism. The parameters obtained from the Hartree–Fock formalism are fitted with some parameters from data included in the database program used in the modeling process. The complexity of the parametrization problem in AM1 is characterized by the number of parameters per atom between 13 and 16, unlike other semiempirical methods with 7 parameters per atom.

The ground-state dipole moment, polarizability, ionization potential, and molecular radius were obtained by HyperChem 8.0.6 in the limits of AM1 methods for the isolated molecule.

Based on relation (4) for regression coefficient  $C_1$  and with the values from Table 1 for MOAAB, one obtains:

$$\alpha = 34.6464\mu_e \cos \varphi - 217.1315. \quad (8)$$

After replacing the numerical values, the sum of (4) and (5) gives:

$$\mu_e^2 - 393.4976\mu_e \cos \varphi + 2327.9754 = 0. \quad (9)$$

The last equation has real solutions for its positive or null discriminator:

$$\Delta = 154840.3612 \cos^2 \varphi - 9311.9018 \geq 0. \quad (10)$$

This condition is accomplished for  $\varphi \leq 75.80$  degree.

Let us vary with 10 degrees, step-by-step, the angle between the dipole moments in the electronic states participating to the visible absorption. For MOAAB, one obtains the data from Table 2.

Let us define the ratio  $R_1$  between the components  $C_{1\mu}$  and  $C_{1\alpha}$  of the regression coefficient  $C_1$  depending on  $\mu$  and  $\alpha$  as follows:

$$C_{1\mu} = \frac{2\mu_g(\mu_g - \mu_e \cos \varphi)}{hca^3}, \quad (11)$$

$$C_{1\alpha} = 3kT \frac{\alpha_g - \alpha_e}{a^3}, \quad (12)$$

and their ratio

$$R_1 = \frac{C_{1\mu}}{C_{1\alpha}}. \quad (13)$$

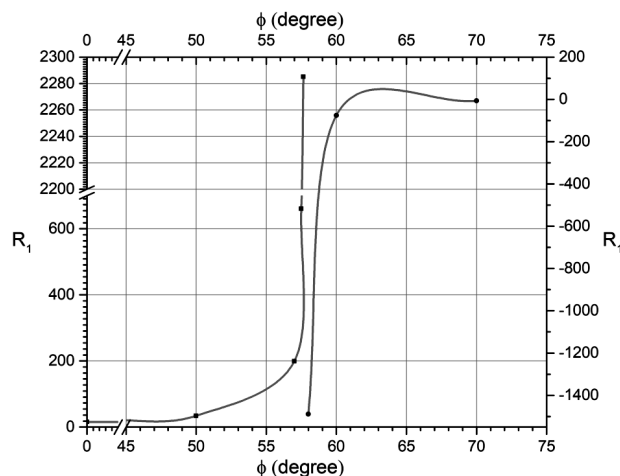


Fig. 2.  $R_1$  vs.  $\varphi$  for MOAAB

The ratio  $R_1$  defined by (13) changes its sign near 57.65 degrees (see Table 2), by suggesting that, in a vicinity of this value, the solutions for the angle  $\varphi$  in the case of the  $\pi \rightarrow \pi^*$  transition responsible for the visible MOAAB band appearance must be situated. In the graph representing  $R_1$  vs. the angle between the molecular dipole moments in the electronic states of the  $\pi \rightarrow \pi^*$  transition, a discontinuity appears (see Fig. 2) in the interval  $57.65^\circ \leq \varphi \leq 57.7^\circ$ .

Having in view that the electronic transition is a rapid modification of the molecular valence electronic cloud, the discontinuity of  $R_1$  can indicate the angle, at which the  $\pi \rightarrow \pi^*$  transition takes place. The dipole moment of this transition is oriented in the triangle of dipole moments (Fig. 3), which determines an angle in the interval  $57.65^\circ \leq \varphi \leq 57.7^\circ$  between the dipole moments in the ground and excited states. This could be the true solution of the problem solved only with the use of the electronic ab-

Table 1. Molecular parameters obtained by HyperChem and regression coefficients in relations (4) and (5) for (MOAAB) and (MOMAB) [17, 25]

Nr.	Parameter	MOAAB	MOMAB
1	Radius (Å)	4.852	4.802
2	Ionization potential (eV)	8.96	8.94
3	Dipole moment (D)	2.102	2.452
4	Polarizability (Å <sup>3</sup> )	30.02	31.86
5	$C_1$ (cm <sup>-1</sup> )	-771.8	-319.9
6	$C_2$ (cm <sup>-1</sup> )	-5121.9	-7087.1

Table 2. Angle between dipole moments, dipole moment  $\mu_e$  (D), polarizability  $\alpha_e$  ( $\text{\AA}^3$ ) in the excited state, components of the regression coefficient  $C_1$ ,  $C_{1\mu}$  ( $\text{cm}^{-1}$ ), and  $C_{1\alpha}$  ( $\text{cm}^{-1}$ ), and their ratio  $R_1$  in the case of MOAAB

Nr.	Angle	$\mu_e$ (D)	$\Delta\alpha$ ( $\text{\AA}^3$ )	$\alpha_e$ ( $\text{\AA}^3$ )	$C_{1\mu}$ ( $\text{cm}^{-1}$ )	$C_{1\alpha}$ ( $\text{cm}^{-1}$ )	$R_1$
1	0	6.008	-8.98	39.00	-723.79	-48.03	15.07
2	10	6.107	-8.77	38.78	-724.94	-46.91	15.46
3	20	6.411	-8.42	38.44	-726.83	-45.03	16.4
4	30	6.965	-8.14	38.16	-728.18	-43.54	16.72
5	40	7.923	-6.86	36.88	-735.10	-36.71	20.02
6	50	9.564	-4.13	34.15	-749.69	-22.11	33.90
7	57	11.47	-0.72	30.74	-767.90	-38.61	198.86
8	57.5	11.65	-0.20	30.22	-770.70	-1.08	660.29
9	57.65	11.709	-0.05	30.07	-771.51	-0.27	2285.01
10	57.7	11.735	0.143	29.98	-772.56	0.74	-1039.19
11	58	11.832	0.097	29.92	-772.30	0.52	-1488.64
12	60	12.645	1.92	28.10	-782.27	10.26	-76.22
13	70	20.37	24.26	5.74	-901.54	129.75	-6.95

sorption spectra. In the interval  $57.65^\circ \leq \varphi \leq 57.7^\circ$ , the polarizability in the excited state is equal to the ground-state polarizability, and the dipole moment in the excited state is near 11.7 D.

If one considers the values of the ground-state dipole moment  $\mu_g = 2.102D$  (resulted from quantum-mechanical estimations), the excited-state dipole moment  $\mu_e = 11.74 D$ , and the angle  $\varphi = 57.7^\circ$  between the dipole moments resulted from these calculations, one can solve the triangle of the dipole moments (Fig. 3) in the following way. Using the notations from Fig. 3, one can write

$$\varphi + \alpha + \beta = 180^\circ \quad \text{or} \quad \alpha + \beta = 122.3^\circ, \quad (14)$$

$$\frac{\mu_g}{\sin \beta} = \frac{\mu_e}{\sin \alpha} = \frac{\Delta\mu}{\sin \varphi}. \quad (15)$$

From (14) and the first equality in (15), we get  $\beta = 9^\circ$  and  $\alpha = 113.9^\circ$ . With these values, the transition dipole moment is  $\Delta\mu = 10.81 D$ .

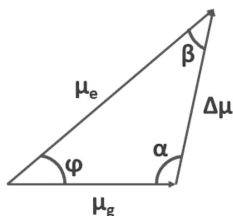


Fig. 3. Triangle of the dipole moments in the  $\pi \rightarrow \pi^*$  transition of the studied dyes

In the case of  $\varphi = 0$  [17], one obtains the excited-state dipole moment  $\mu_e = 10.17 D$ , a value that equalizes the transition dipole moment computed in this paper.

The same reasons can be applied for the MOMAB molecule. From relation (4), one obtains

$$\alpha = 40.4154\mu_e \cos \varphi - 157.0809. \quad (16)$$

After replacing the numerical values, the sum of (3) and (4) gives:

$$\mu_e^2 - 458.429\mu_e \cos \varphi + 1612.8429 = 0. \quad (17)$$

The last equation has real solutions for its discriminator

$$\Delta = 210157.148 \cos^2 \varphi - 7127.0296 \geq 0. \quad (18)$$

Condition (18) is accomplished for  $\varphi \leq 79.90$  degree.

Let us vary the angle between the dipole moments in the electronic states participating to the visible absorption with 10 degrees. Using relations (16) and (17), one obtains the data from Table 3.

The ratio  $R_1$  changes its sign near 73.0 degrees, by suggesting that, in a vicinity of this value, the solution for the angle  $\varphi$  must be situated. The solution of the problem solved only with the use of the electronic absorption spectra is  $72.5^\circ \leq \varphi \leq 73.0^\circ$ . In this interval for the angle  $\varphi$ , the polarizability in the excited state is equal to the ground-state polarizability

Table 3. Angle between dipole moments, dipole moment  $\mu_e$  (D), polarizability  $\alpha_e$  ( $\text{\AA}^3$ ) in the excited state, components of the regression coefficient  $C_1$ ,  $C_{1\mu}$  ( $\text{cm}^{-1}$ ), and  $C_{1\alpha}$  ( $\text{cm}^{-1}$ ), and their ratio for compound MOMAB

Nr.	Angle	$\mu_e$ (D)	$\Delta\alpha$ ( $\text{\AA}^3$ )	$\alpha_e$ ( $\text{\AA}^3$ )	$C_{1\mu}$ ( $\text{cm}^{-1}$ )	$C_{1\alpha}$ ( $\text{cm}^{-1}$ )	$R_1$
1	0	3.546	-13.77	45.63	-243.94	-75.96	3.21
2	10	3.605	-13.60	45.46	-244.88	-75.03	3.26
3	20	3.781	-13.47	45.33	-245.50	-74.87	3.28
4	30	4.099	-13.61	45.47	-244.77	-75.08	3.26
5	40	4.648	-13.19	45.05	-247.14	-72.76	3.40
6	50	5.578	-12.17	44.03	-252.76	-67.14	3.76
7	60	7.267	-10.24	42.10	-263.45	-56.48	4.66
8	70	11.054	-4.29	36.15	-296.22	-23.65	12.52
9	72	12.480	-1.21	33.10	-313.13	-6.65	47.10
10	72.5	12.907	-0.22	32.08	-318.57	-1.21	-263.80
11	73	13.373	0.95	30.91	-325.16	5.25	-61.91
12	75	15.660	6.72	25.14	-356.95	37.06	-9.63

and the dipole moment in the excited state is near 13.0 D. The function representing the ratio of the universal interactions due to the orientation and induction becomes discontinuous, by suggesting a rapid modification of the molecular parameters.

Tables 2 and 3 imply that, by substituting the atomic group  $\text{CH}_2\text{CHCOO}^-$  by  $\text{CH}_3\text{CH}=\text{CHCOO}^-$ , when passing from MOAAB to MOMAB, the transition  $\pi \rightarrow \pi^*$  is made in a changed direction, which modifies the angle between the electronic transition dipole moments and, consequently, the values of the excited-state dipole moment.

If one considers the values of the ground-state dipole moment  $\mu_g = 2.45$  D (resulted from quantum-mechanical estimations), the excited-state dipole moment  $\mu_e = 13.37$  D and the angle  $\varphi = 73.0^\circ$  between the dipole moments resulted from these calculations, one can solve the triangle of the dipole moments (Fig. 3) in the following way:

$$\alpha + \beta = 107^\circ, \quad (19)$$

$$\frac{\mu_g}{\sin \beta} = \frac{\mu_e}{\sin \alpha} = \frac{\Delta\mu}{\sin \varphi}. \quad (20)$$

From (19) and the first equality in (20), we get  $\beta = 10.9^\circ$  and  $\alpha = 96.1^\circ$ . With these values, the transition dipole moment is  $\Delta\mu = 12.86$  D.

In the case of  $\varphi = 0$  [17], one obtains for the excited-state dipole moment  $\mu_e = 4.68$  D, which differs from the value computed in this paper.

The values of the excited-state dipole moment and of the transition dipole moment computed in

this paper for two azo-benzene dyes having appropriate chemical structures are comparable, and one can consider that this method offers a good estimation of the changes induced by the  $\pi \rightarrow \pi^*$  transition in molecules of the studied azo-benzene dyes.

## 5. Conclusions

The existent theories, in which the spectral shifts due to the universal interactions are expressed as functions of the microscopic parameters of the spectrally active molecules and of the solvent macroscopic parameters, can be applied to the electronic absorption spectra in order to estimate the variation of the dipole moment and polarizability in the absorption process.

In view of the limits, in which the existent theories regarding the solvent influence on the absorption spectra are developed, and that the ground-state molecular parameters used in numerical evaluations correspond to isolated molecules, the obtained results for the excited dipole moments of the studied azobenzenes are good approximations. The values obtained for the excited-state dipole moments of the studied azo-dyes are in accordance with the literature data obtained with the use of correlations between the electro-optical parameters computed by quantum-mechanical calculations and the solvatochromic parameters of spectrally active molecules in the absorption process [17, 26, and 27].

The method used here for the estimation of the excited-state dipole moment is based on the fact that the ratio between the values of the solvatochromic coefficients shows a discontinuity, by giving us a possibility to estimate the angle between the dipole moments of the studied molecule in its electronic states participating in the absorption process.

The method could be applied especially to the molecules inactive in fluorescence spectra.

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МОЛЕКУЛЯРНІ ПАРАМЕТРИ  
ЗБУДЖЕНОГО СТАНУ, ВИЗНАЧЕНІ  
ЗА СПЕКТРАЛЬНИМ СЕРЕДНІМ

Резюме

Показана можливість охарактеризувати електронний збуджений стан спектрально активної молекули на основі ли-

ше сольватохромного дослідження електронних спектрів поглинання. Використані величини коефіцієнтів регресії з урахуванням внеску універсальних взаємодій у спектральний зсув і їх теоретично встановлені залежності від мікроскопічних параметрів розчинених молекул. Квантово-механічні методи застосовані для розрахунку дипольного моменту, поляризованості і потенціалу іонізації основного стану. Метод ілюстрований на прикладі двох молекул азобарвника.