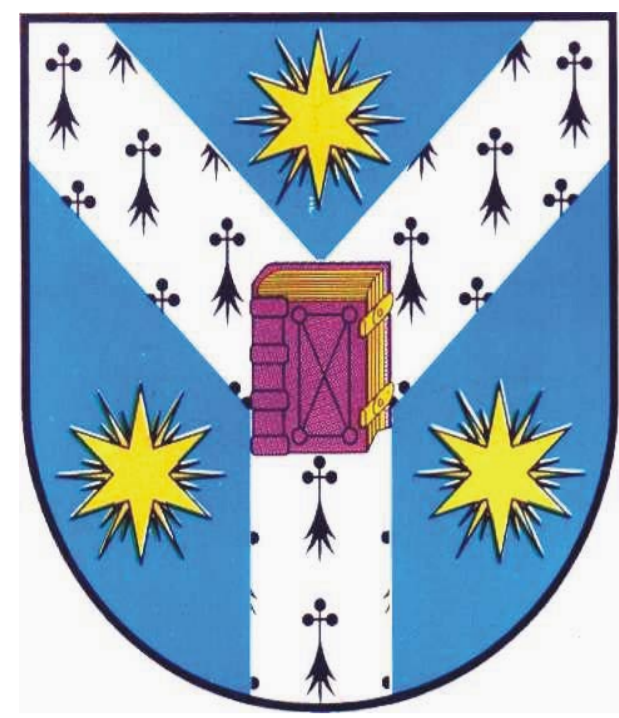# SPECTRAL METHODS FOR ESTIMATING THE EXCITED STATE DIPOLE MOMENTS OF THE SPECTRALLY ACTIVE MOLECULES

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The spectral methods used in estimating the excited dipole moments are discussed in this research. In the case of the spectrally active molecules, both in absorption and fluorescence spectra, the spectral shifts recorded in the two kind of spectra are used to determine the excited state dipole moment and its orientation relative to the ground state dipole moment, when the electro-optical parameters of the molecule are computed by quantum-mechanical software.

When only electronic absorption spectra are available for a given molecule, the solvatochromic study and a variational method can be used to estimate the excited dipole moment. Some cases are discussed for the spectrally active molecules only in absorption, based on the variational method.

Theoretical background

Some multilinear correlations between the electronic band wavenumber and the functions of the macroscopic and microscopic parameters of the solvent are used, as for example the next one

$$\bar{\nu}\left(cm^{-1}\right) = \bar{\nu}_0 + C_1 f(\varepsilon) + C_2 f(n) + C_3 \beta + C_4 \alpha \qquad (1)$$

where the terms depending on ε and n result from theoretical meanings, while the last two terms were introduced to give the strength of the specific interactions by hydrogen bond with donating (β) or accepting (α) by the solute molecule. The experimental data regarding the wavenumber in the maximum of the electronic band and the solvent parameters are supposed to a statistical analysis and the values of the correlation coefficients, $\bar{\nu}_0$ and $C_1 - C_4$, are determined.

When the solute molecule shows both absorption and fluorescence band, the solvatochromic study allows the estimation of the dipole moments of the molecule in the two states participating to the electronic transition. One obtains the following relations:

$$\bar{\nu}_a - \bar{\nu}_f = m_1 \frac{2n^2+1}{n^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + const. \qquad (2)$$

$$\bar{\nu}_a + \bar{\nu}_f = -m_2 \frac{2n^2+1}{n^2+2}\left\{\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + 3\left[\frac{n^4-1}{\left(n^2+2\right)^2}\right]\right\} + const. \qquad (3)$$

In the above relations, the wavenumbers are indexed with a for absorption and f for fluorescence, respectively. If linear dependences are obtained in the plots $\bar{\nu}_a - \bar{\nu}_f$ and $\bar{\nu}_a + \bar{\nu}_f$ vs. the solvent functions, their slopes are dependent on the electric dipole moments of the solute molecule in its electronic states responsible for the band's appearance. The dependences are given by:

$$m_1 = \frac{2\left(\mu_e - \mu_g\right)^2}{hcr^3} \qquad m_2 = \frac{\mu_e^2 - \mu_g^2}{hcr^3} \qquad (4,5)$$

where μ_e and μ_g are the solute dipole moment in the excited (e) and ground (g) states of the electronic transitions in absorption and fluorescence, respectively, while r is the cavity radius of the solute molecule. The value of r can be computed function on the molecular weight (M) and the solute density (ρ).

In the case of the substances without fluorescence, a variational method can be applied for the estimation of the excited state dipole moment, if the ground state dipole moment is known. Thus, the expressions of the coefficients C_1 and C_2 from Eq. 1 are:

$$C_1 = \frac{2\mu_g\left(\mu_g - \mu_e\cos\varphi\right)}{hcr^3} = 3kT\frac{\alpha_g - \alpha_e}{r^3} \qquad C_2 = \frac{\mu_g^2 - \mu_e^2}{hcr^3} - C_1 + \frac{3}{2}\frac{\alpha_g - \alpha_e}{r^3}\frac{I_u I_v}{I_u + I_v} \qquad (6,7)$$

with α polarizabilities, I the ionization potential, φ the angle between the ground state and excited state dipole moments, respectively, u and v indexes for the solute and the solvent molecules, respectively. It results:

$$\alpha_e = \alpha_g - \frac{2\left(I_u + I_v\right)}{3hcI_u I_v}\mu_e^2 \qquad \frac{2\left(I_u + I_v\right)kT}{I_u I_v}\mu_e^2 - 2\mu_g\mu_e\cos\varphi + \left(2\mu_g^2 - C_1 hcr^3\right) = 0 \qquad (8,9)$$

From Eq. 9 we obtain:

$$\Delta = 4\mu_g^2\cos^2\varphi - \frac{8kT\left(I_u + I_v\right)}{I_u I_v}\left(2\mu_g^2 - C_1 hcr^3\right) \geq 0 \qquad \mu_e^{1,2} = \frac{2\mu_g\cos\varphi \pm \sqrt{\Delta}}{\frac{4\left(I_u + I_v\right)kT}{I_u I_v}} \qquad (10,11)$$

Condition 10 imposes the range for the values of φ. The value of φ is varied in this range until the value of μ_e is obtained for which the condition $\alpha_e \cong \alpha_g$ is fulfilled.

The Abe's model can be also approached for the determination of the excited state dipole moments. The model neglects the specific interactions between the solute and solvent molecules and it considers the solvation energies as being of the van der Waals type (orientation, induction and dispersion). A linear dependence is obtained:

$$B = A\alpha_e(u) + \mu_e^2(u) - \mu_g^2(u) \qquad (12)$$

where

$$A = \frac{\frac{3}{2}I_g(v)\alpha_g(u)\frac{I_g(v)\left(I_g(u) - hc\nu_1\right)}{I_g(v) + I_g(u) - hc\nu_1}}{\frac{3}{4\pi N_A}\frac{M_v}{\rho_v}\left[\frac{\left(\varepsilon_v - n_v^2\right)\left(2\varepsilon_v + n_v^2\right)}{\varepsilon_v\left(n_v^2+2\right)^2}\right] + \frac{n_v^2-1}{n_v^2+2}} \qquad (13)$$

$$B = \frac{-\frac{\nu_s - \nu_0}{C}\frac{3}{2}\alpha_g(u)\alpha_g(v)\frac{I_g(v)I_g(u)}{I_g(v) + I_g(u)}}{\frac{3}{4\pi N_A}\frac{M_v}{\rho_v}\left[\frac{\left(\varepsilon_v - n_v^2\right)\left(2\varepsilon_v + n_v^2\right)}{\varepsilon_v\left(n_v^2+2\right)^2}\right] + \frac{n_v^2-1}{n_v^2+2}} \qquad (14)$$

$$C = \frac{1}{hc}\sum_p R_{uv}^{-6}(p) = \frac{16\pi^3 N_A^2}{9hc}\left(\frac{\rho_v}{M_v}\right)^{\frac{2}{3}}\left\{\left[\left(\frac{M_u}{\rho_u}\right)^{\frac{1}{3}} + \left(\frac{M_v}{\rho_v}\right)^{\frac{1}{3}}\right]^{-4} + \left[\left(\frac{M_u}{\rho_u}\right)^{\frac{1}{3}} + 3\left(\frac{M_v}{\rho_v}\right)^{\frac{1}{3}}\right]^{-4} + ...\right\} \qquad (15)$$
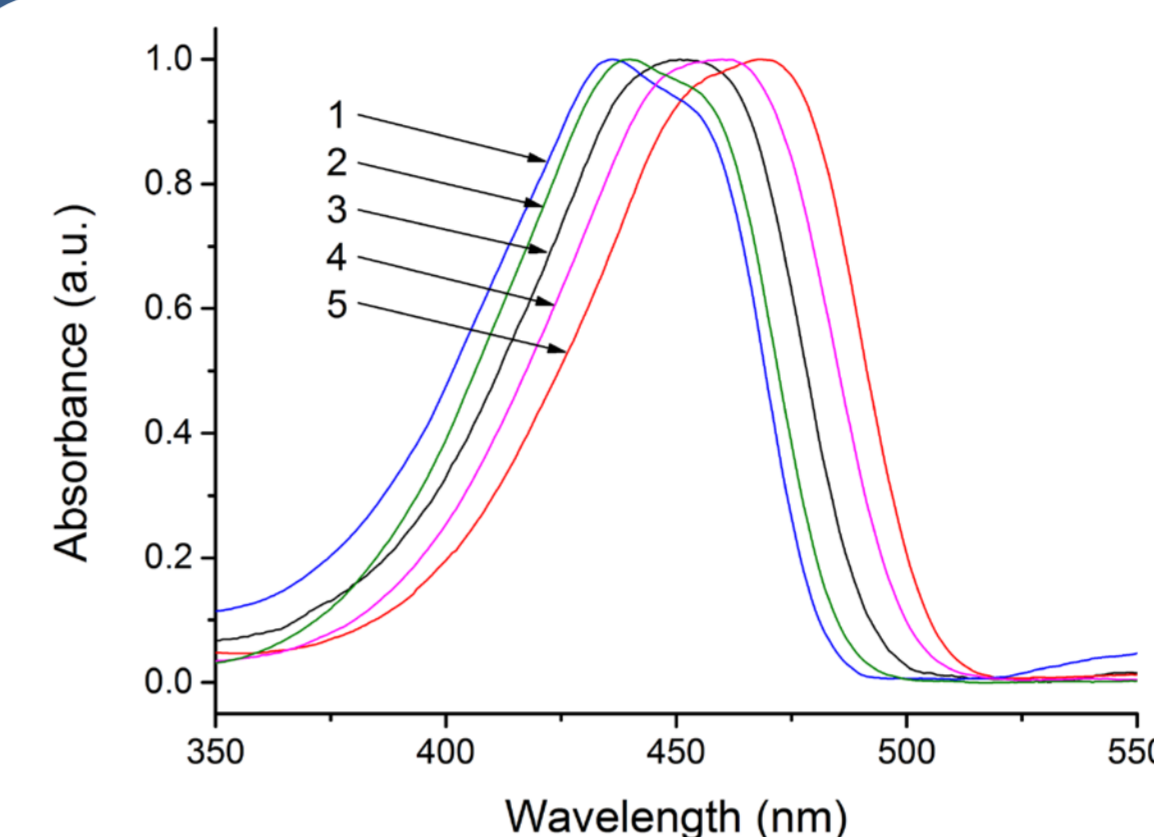

Fig. 1: Electronic absorption band of coumarin 6 recorded in solution with 2-propanol (1), benzyl alcohol (2), dioxane (3), dimethylformamide (4) and ethyl acetate (5)
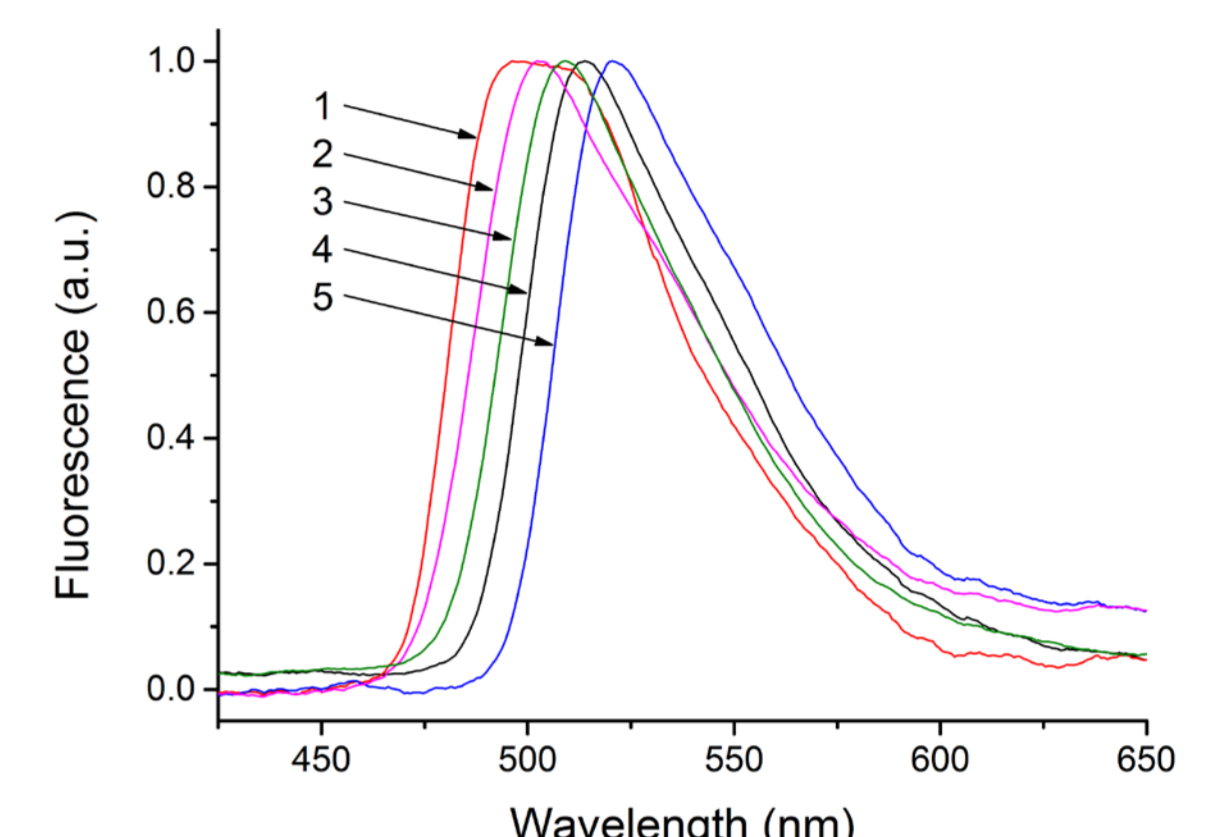

Fig. 2: Electronic fluorescence band of coumarin 6 recorded in solution with dimethylformamide (1), dioxane (2), dimethyl sulfoxide (3) hexanol (4) and methanol (5)

Table 1: Values of the excited state dipole moment and polarizability for coumarin 6

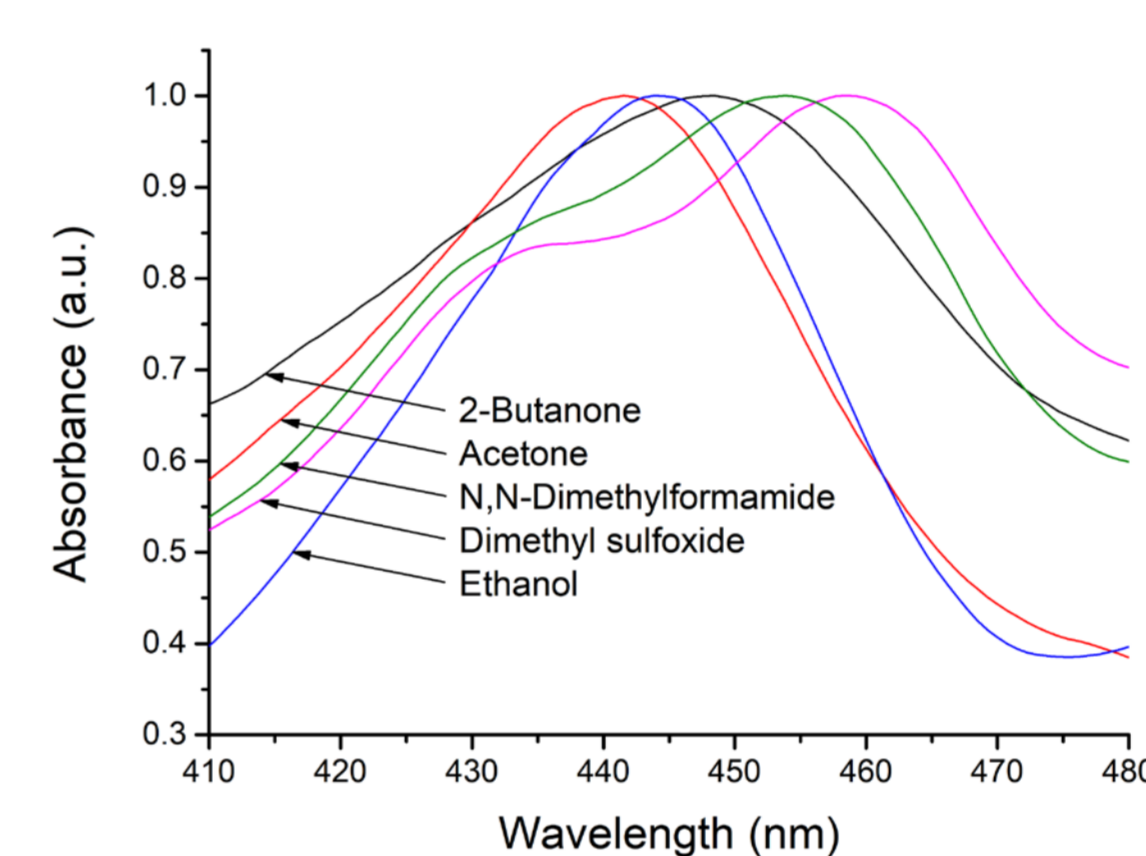| Angle (degree)	Excited state dipole moment (Debye)	Polarizability (Å)
0	8.33	67.00
25	9.16	64.42
50	13.66	46.25

Fig. 3: Visible electronic absorption band of fluorescein in five solvents
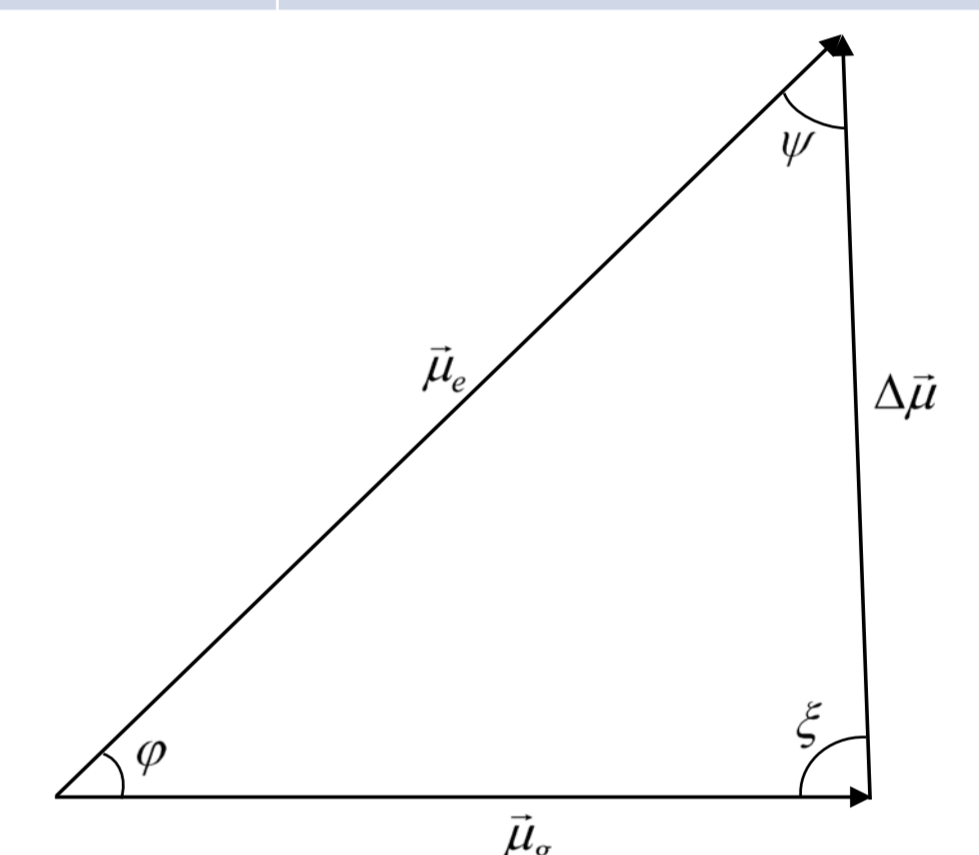

Fig. 4: The triangle of the dipole moments for electronic absorption process (fluorescein)

Table 2: Excited state dipole moment and polarizability for different angles, for the visible absorption band of fluorescein

| Nr.	Angle φ (degrees)	Equation	μ_e (D)	α_e (Å³)
1	0	$0.0183\mu_e^2 - 15.88\mu_e + 122.8060 = 0$	7.80	75.75
2	10	$0.0183\mu_e^2 - 15.6386\mu_e + 122.8060 = 0$	7.93	75.46
3	20	$0.0183\mu_e^2 - 14.9223\mu_e + 122.8060 = 0$	8.31	64.51
4	30	$0.0183\mu_e^2 - 13.7525\mu_e + 122.8060 = 0$	9.04	72.62
5	40	$0.0183\mu_e^2 - 12.1648\mu_e + 122.8060 = 0$	10.25	69.09
6	44.8	$0.0183\mu_e^2 - 11.2680\mu_e + 122.8060 = 0$	11.10	66.36
7	44.9	$0.0183\mu_e^2 - 11.2483\mu_e + 122.8060 = 0$	11.25	66.29
8	50	$0.0183\mu_e^2 - 10.2075\mu_e + 122.8060 = 0$	12.30	62.12
9	60	$0.0183\mu_e^2 - 7.9400\mu_e + 122.8060 = 0$	16.06	46.05
10	70	$0.0183\mu_e^2 - 5.4313\mu_e + 122.8060 = 0$	24.66	-6.72
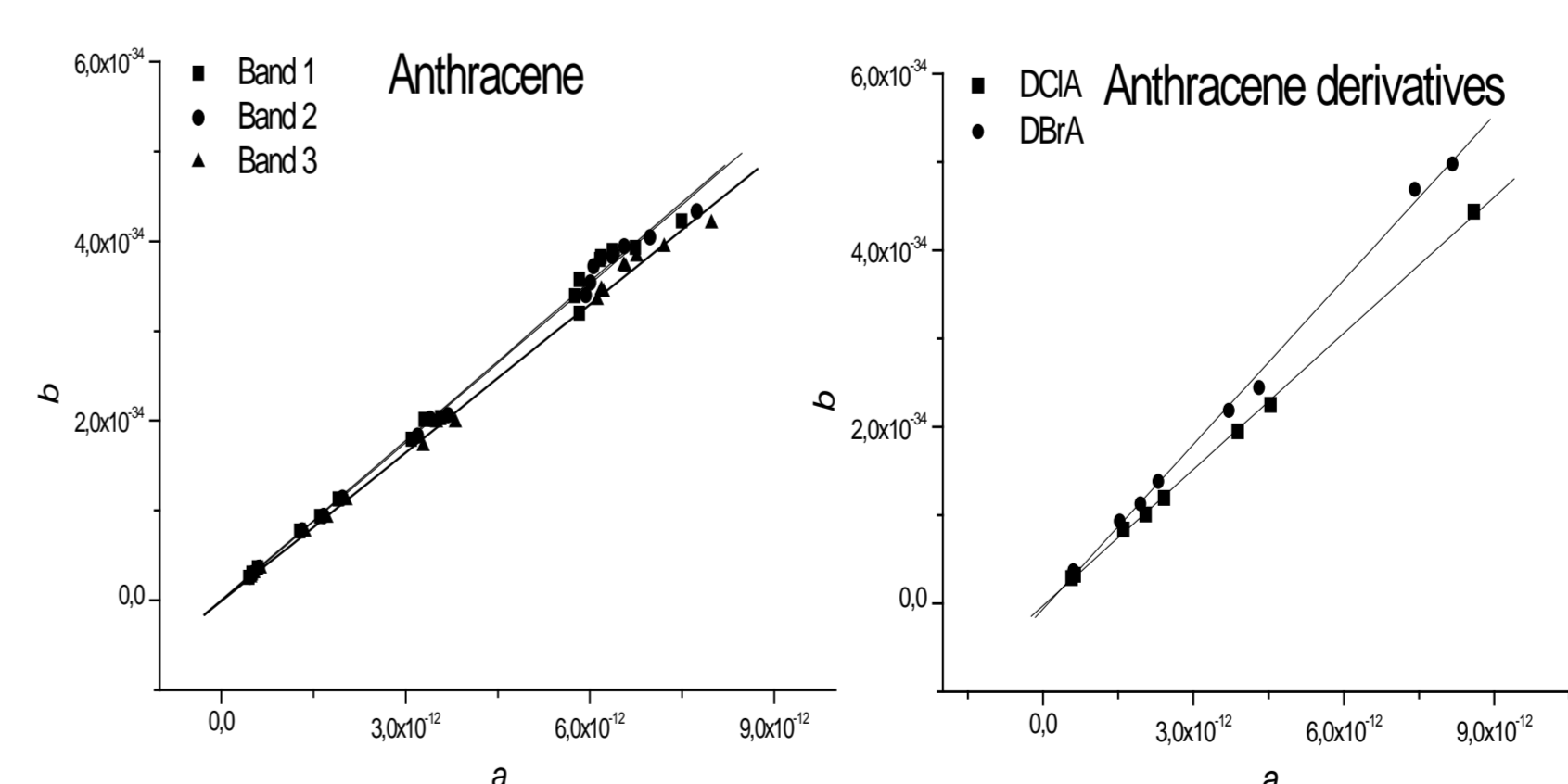
Fig. 5: Abe's model applied to the study of anthracene and two of its derivative

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