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Solvatofluorochromy of Cationic Cyanine Dyes

A. A. Ishchenko, V. A. Svidro & N. A. Derevyanko

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR,
252660 Kiev-94, Murmanskaya 5, USSR

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ABSTRACT

As a result of mathematical analysis, using the method of moments, of the electronic spectra of symmetrical cyanine dyes based on indolenine, the following observations were noted.

(1) Loss of mirror symmetry of the absorption and fluorescence bands caused by narrowing of the latter. These effects increase with increase of the solvent nucleophilicity and with lengthening of the polymethine chain of the dyes.
(2) Decrease of solvatofluorochromic effects in comparison with solvatochromic effects; this is especially apparent in the change of the bandwidth;
(3) An excellent correlation between the mean frequency of the fluorescence band and the solvent refractive index function (Bayliss) (this correlation is absent in absorption).

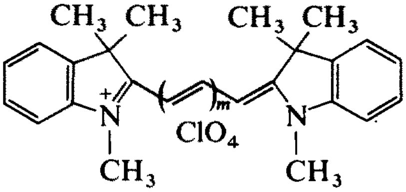
On the basis of the quantum-mechanical calculations of the cationic dyes, the relationships discovered were attributed to the weakening of specific electrostatic interactions (nucleophilic solvation) in the excited state of the dyes due to a decrease of charge values on their cations upon excitation.

INTRODUCTION

The cyanine dyes are suitable compounds for studies of the colour of organic substances[1] and several fundamental principles exist relating colour to chemical structure and nature of the solvent.[1-4]. Studies of the effects of the solvent have been limited to absorption spectra[2-4] and no data have been published on the solvatofluorochromy of this class of organic dyes. The object of this work is to study the effects of the nature of solvents on the position and form of the fluorescence bands of the indolenine dyes **I–III**.

2 MATERIALS

The dyes studied were of formulae **I–III**.



I ($m = 1$); **II** ($m = 2$); **III** ($m = 3$)

Dye **III** has a longer polymethine chain (PC) and as a result, it possesses a stronger solvatochromy than **I** and **II**[4] and was therefore studied in more detail. Solvents of different chemical type were used, and it was possible to vary the range of various parameters of solvent polarity over extremely broad limits, this being necessary in order to study the relationship between the nature of the solvent and the spectral-luminescence characteristics of the dyes. Essentially non-polar solvents were not utilised, because cyanine dyes exist in these solvents in the form of ion-pairs, which have specific spectral properties.[3,5,6]

3 EXPERIMENTAL METHODS

In order to characterise quantitatively the influence of the solvent on the changes in the position, intensity and shape of the fluorescence bands of the dyes, a mathematical analysis of the bands was carried out using the method of moments.[7]

$$S_1 = \int_{\text{Band}} \nu^l \rho(\nu)\, d\nu$$

$$M_1 = (1/S_0) \int_{\text{Band}} (\nu - \bar{\nu})^l \rho(\nu)\, d\nu$$

where S_1 is the initial moment; M_1 is the central moment; $\rho = \varepsilon(\nu)/\nu$, or $\rho = W(\nu)/\nu^4$; ε is the extinction; W is the fluorescence intensity; ν is the wavenumber; and l is the moment order.

TABLE 1
Spectral Characteristics of Dyes I–III in Different Solvents

Dye	*Solvent*	λ^f_{max} (*nm*)	$\bar{\nu}^f$ (cm^{-1})	σ^f (cm^{-1})	γ^f_1	γ^f_2	F^f	λ^a_{max} (*nm*)	$\bar{\nu}^a$ (cm^{-1})	σ^a (cm^{-1})	γ^a_1	γ^a_2	F^a	ν_{00} (cm^{-1})	S_v (cm^{-1})	ϕ (%)
III	*o*-Dichlorobenzene (DCB)	797	12 228	735	−1·71	5·4	0·092	767	13 408	791	1·84	5·5	0·103	12 780	1 180	30
III	Methylene chloride (MC)	783	12 418	747	−1·73	5·1	0·091	758	13 628	831	1·92	6·3	0·106	12 970	1 210	34
II	MC	671	14 359	871	−1·49	3·5	0·082	652	15 801	875	1·64	4·5	0·090	15 100	1 442	31
I	MC	570	16 915	1 090	−1·31	3·0	0·065	550	19 011	1 092	1·31	3·0	0·064	17 550	2 096	4
III	Nitrobenzene	795	12 217	756	−1·74	5·3	0·087	760	13 629	951	1·91	6·0	0·109	12 850	1 412	22
III	Benzonitrile	793	12 261	760	−1·69	5·2	0·088	760	13 708	969	1·81	5·2	0·105	12 870	1 447	25
III	Pyridine	792	12 287	759	−1·68	5·0	0·085	757	13 751	976	1·86	5·6	0·105	12 920	1 464	26
III	Ethanol	775	12 536	778	−1·68	4·9	0·085	742	14 099	1 103	1·83	5·4	0·106	13 180	1 563	28
II	Ethanol	667	14 506	875	−1·47	3·6	0·077	640	16 074	953	1·61	4·3	0·087	15 280	1 566	25
I	Ethanol	568	17 033	1 046	−1·09	1·5	0·057	545	19 084	1 051	1·11	1·6	0·059	17 640	2 051	3
III	Nitromethane	777	12 506	780	−1·68	4·8	0·086	742	14 106	1 120	1·85	5·5	0·111	13 160	1 600	26
III	Acetonitrile	772	12 578	781	−1·68	4·8	0·086	740	14 226	1 139	1·76	4·8	0·097	13 240	1 648	27
III	Acetone	773	12 551	783	−1·67	4·8	0·085	742	14 204	1 151	1·65	4·2	0·094	13 200	1 653	29
III	Dimethylsulphoxide (DMSO)	783	12 380	790	−1·67	4·6	0·083	750	14 108	1 198	1·62	4·1	0·092	13 000	1 728	32
III	Dimethylformamide (DMFA)	778	12 447	793	−1·67	5·1	0·085	746	14 140	1 205	1·69	4·5	0·100	13 180	1 693	26
II	DMFA	670	14 465	876	−1·40	3·1	0·072	642	16 076	990	1·60	4·2	0·089	15 240	1 611	28
I	DMFA	570	16 912	1 035	−1·08	1·3	0·054	550	19 026	1 043	1·11	1·7	0·057	17 540	2 114	3

The first moment of normal distribution of photons, $\bar{\nu} = S_1/S_0$, determines their mean frequency. The centre of gravity of the band (ν) determines the position of the band on the frequency scale, independent of the photon distributions form and is a more accurate measurement than the maximum.[7] The second central moment is related to the spectral band width by the relationship $\sigma = \sqrt{M_2}$. These widths, σ, in contrast to the halfwidth used traditionally, make it easier to compare different forms of bandwidth. The third and fourth central moments are non-dimensional coefficients, viz. asymmetry, $\gamma_1 = M_3/\sigma^3$, and excess, $\gamma_2 = M_4/\sigma^4 - 3$, which respectively characterise the asymmetry and sharpness of the peak of the spectral bands.

The entropy of the spectral band gives information about the degree of its fine structure. For a quantitative value of the latter, we introduced the coefficient of fine structure F, which represents the difference in entropy of the normal and experimental distribution of absorbing or emitting photons, depending on the frequency of the same width.

$$F = H_{\text{gaus}} - H_{\text{exp}} = 0{\cdot}6162 + \log \sigma - \log S_0 + (1/S_0) \int_{\text{Band}} \rho(\nu) \log \rho(\nu)\, d\nu$$

The experimental characteristics of fluorescence (f) and absorption (a) bands are listed in Table 1, together with the frequencies of purely electronic transitions ν_{00}, the values of the Stoke's shifts S_ν calculated from the mean frequency, and the quantum yield of fluorescence ϕ. The value of ϕ in different solvents was determined relative to the quantum ratio in ethanol of dyes **I–III**.[8,9]

The fluorescence spectra of solutions of the investigated dyes were measured on an SDL-1 spectrometer. The data of the absorption spectra of the same compounds are taken from Refs 3 and 4. The ^{1}H-NMR spectra were measured on a Bruker-200 spectrometer, and the quantum-chemical calculations of the cation of dye III were fulfilled by the simple HMO method with the parameters.[10]

4 RESULTS AND DISCUSSION

It can be seen from the data in Table 1 that the position of the fluorescence bands, as does that of the absorption bands, depends upon the nature of the solvent. However, both these values change with the solvent, the position of the fluorescence band shifting less than that of the absorption band. Thus, the range of change of the maximum and mean frequencies of the fluorescence bands of the indotricarbocyanine **III** are 400 cm^{-1} and 361 cm^{-1}, respectively, and for the absorption bands 470 cm^{-1} and 818 cm^{-1} respectively. The value of σ^f is considerably less sensitive to changes in the nature of the solvent. Thus, the range of change in the values for this parameter is only 58 cm^{-1} for the dye **III**, whereas for σ^a it is 414 cm^{-1}. By comparing σ^f, γ_1^f, γ_2^f and F^f with analogous data for the absorption bands it is apparent that the values are quite different. These differences increase with elongation of PC (Table 1). Hence, the law of mirror symmetry is not strictly observed, otherwise the following equalities would hold:

$$\sigma^f = \sigma^a; \quad \gamma_1^f = \gamma_1^a; \quad \gamma_2^f = \gamma_2^a; \quad F^f = F^a$$

This conclusion is important because in the fluorescence spectra of the dyes, as in the absorption spectra, the vibrational maximum is displayed distinctly (Fig. 1). Usually in this case it is presumed that spectral bands have mirror symmetry. Only application of the method of moments has made apparent the non-obvious effects, viz. the sharp narrowing, decrease of asymmetry, sharpness of the peak and fine structure of the fluorescence bands in comparison with the absorption bands. For example, it is difficult to detect the effects in the spectral curves of the dye III in DCB (Fig. 1), but using the values of σ^f, γ_1^f, γ_2^f, F^f and σ^a, γ_1^a, γ_2^a, F^a they are quite easy to detect. The breach of the law of mirror symmetry, and the lower solvatofluorochromy effects compared with solvatochromy effects of the dyes I–III, are indicated by a reduction of solvation in their excited state in comparison with the ground state.

Solvation of the cationic cyanine dyes is brought about by general and specific interactions.[2–4] The initial effect is due to dispersive interactions,[2,3] because the cyanine dyes have long chromophore chains with easily

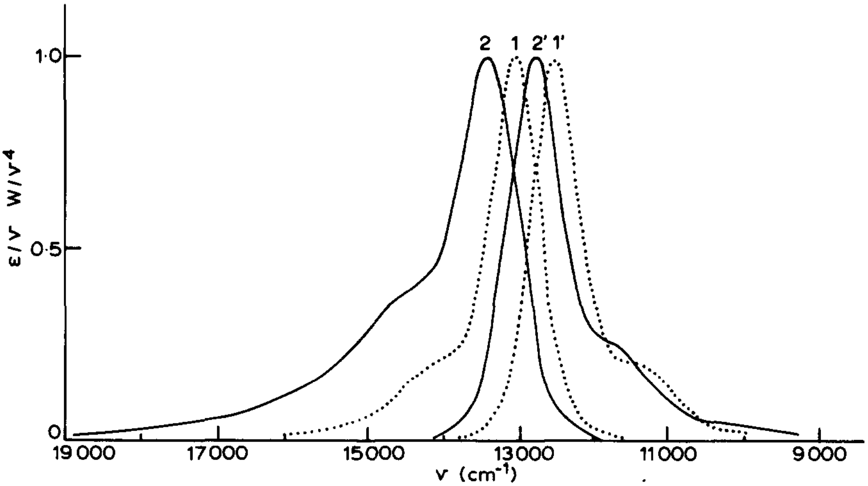


Fig. 1. Absorption spectra of solutions of dye III in DCB (1), DMFA (2) and fluorescence spectra in the same solutions (curves 1′ and 2′ respectively).

polarised bonds. These interactions should not result in any essential reformation of the solvation shell in the excited state. Consequently the π-systems differ little from each other in these states. Only the bonds of the excited state became polarised more easily and this leads to an increase of dispersive interactions in this state. This increase brings about degradation of its energy and a bathochromic shift of the bands, the extent of which should increase with increase in the refractive index n_D of the solvent.[2,3] The influence of this interaction on the form of the bands is weak.[3]

Specific solvation of the cyanines occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules. The main contribution to the specific solvation of cationic dyes is by nucleophilic solvation,[3,4] which leads to the formation of specific solvated forms of dyes (SSFD). The greater the charge on the cation and the nucleophilicity B in a given solvent,[3,4] the more the dye is subject to specific solvation.

According to quantum-mechanical calculations of the indotricarbocyanine **III** (Fig. 2) the charges in the excited state are, as a rule, smaller in value than those in the ground state. The overall positive charge, which determines the nucleophilic solvation,[4] decreases on excitation (in the ground state it has a value of 1·885 and in the excited state a value of 1·695). Therefore, electrostatic interactions in the excited state (nucleophilic solvation), in contrast with dispersion interactions, should weaken considerably, and thus cause a decrease of solvatofluorochromy effects in comparison with solvatochromy effects. If this conclusion is correct, the difference in the above-mentioned effects should be more influenced by change in nucleophilicity, than by change in polarisibility. In fact, on changing the solvent from MC to DMFA (solvents of different B values, but identical n_D values[3]), $\bar{\nu}^f$ of the dye **III** shifts hypsochromically only by 29 cm^{-1}, while $\bar{\nu}^a$ changes by 512 cm^{-1}. Replacement of benzonitrile by

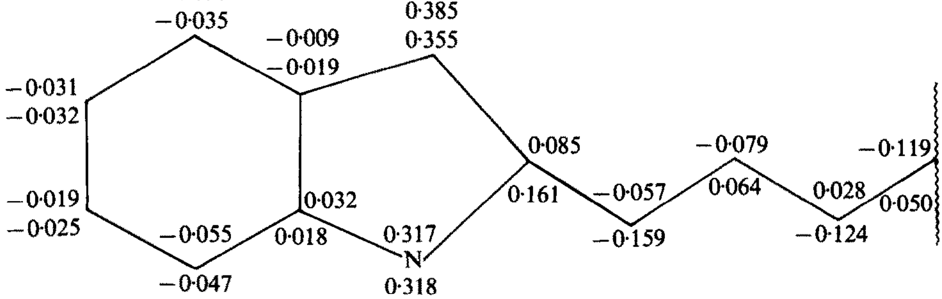


Fig. 2. Distribution of the charge in the cation of dye **III** in the ground state (numbers below) and in excited state (numbers above).

acetonitrile (solvents of different n_D, values but identical B values[3]) results in essentially little difference in the shifts ($\bar{\nu}^f = 317\,\text{cm}^{-1}$, $\bar{\nu}^a = 518\,\text{cm}^{-1}$). Similar tendencies in investigated pairs of solutions can be seen in the changes of σ^f and σ^a (Table 1). Additionally, the minimum values of S_v and of the difference $\sigma^a - \sigma^f$ are observed in DCB and MC, these having the smallest nucleophilicity of the solvents used,[3] and maximum values in DMSO and DMFA, which have the greatest B values.[3]

It can also be noted that in pyridine, a solvent which has the greatest value of the parameter B, Stokes shifts and the difference between the absorption band widths and fluorescence band widths do not have maximal values. This can be explained by the fact that, for aromatic solvents, even those having very polar groups such as C_6H_5CN and $C_6H_5NO_2$, the possibility of nucleophilic solvation is considerably lessened by the ability of the molecules to orientate themselves in the electric field of the dye, in the first solvation shell, almost parallel to its plane.

This is confirmed by ^{1}H-NMR spectra data measured for dye **I** in CD_3OD, C_5D_5N, CD_3NO_2 and $C_6D_5NO_2$ at a concentration of 10^{-3} M. Absorption spectra at these concentrations in a thin cuvette ($l = 0{\cdot}1$ mm) are identical to those at a concentration of 10^{-5} M ($l = 1$ cm) and hence association of the dyes did not occur during the measurement of ^{1}H-NMR spectra. It was observed that in aromatic solvents the signals of the protons in the ^{1}H-NMR spectra were closer (α-protons shifted to lower field, β-protons to higher field) in contrast to the signals in non-aromatic solvents. The chemical shifts of the α- and β-protons in the chain (on the δ scale) were, respectively: 6·89 ppm and 8·25 ppm in C_5D_5N; 6·52 ppm and 8·37 ppm in $C_6D_5NO_2$; 6·36 ppm and 8·43 ppm in CD_3OD; 6·38 ppm and 8·52 ppm in CD_3NO_2. The closing up of the signals is possible only if the molecules of the polar aromatic solvents are oriented in the same direction as the first solvate shell parallel to the plane of the chromophore, because in this case protons of one kind may be situated in the ring current shield (i.e. they may shift to higher field) whilst protons of the other kind may be deshielded (i.e. may shift to lower field). It is noticeable from the chemical shift data that aromatic solvents are usually disposed above the *meso*-carbon atom of the chain, being slightly shifted to the side of the β-hydrogen atom. This atom therefore falls under the plane of the ring (the field of shielding). α-Hydrogen atoms will then be situated outside the boundary of the ring (the field of deshielding), and the protons of the hetero residue, which are more remote, thus have no essential effect on the ^{1}H-NMR spectra, as is observed experimentally.[1]

During the nucleophilic solvation of the cationic charges by the polar groups of the aromatic solvents, its molecules should be orientated almost perpendicularly to the plane of the dye. In this case, the protons of the chain do not fall in the field of ring-current of the benzene ring and the closing up of the signals of the α- and β-protons does not occur. In fact, in polar non-aromatic solvents such as CD_3OD or CD_3NO_2 it is not observed at all, the signals of the α- and β-protons shifting in the same direction.

It is important to note that the spin–spin coupling constants of the protons of the polymethine chain do not change significantly in the solvents used for the ^{1}H-NMR spectra, and have the value of 13 Hz. This indicates that these dyes exist in all solvents completely in the form of the *trans* isomers.

In strong nucleophilic non-aromatic solvents the difference between σ^a and σ^f is more significant, and hence the breach of the mirror symmetry law can be observed by the forms of the curves (see the spectra in DMFA in Fig. 1).

Strong redistribution of the charges occurs due to electronic excitation of the cations in the cyanine dyes (Fig. 2). Thus, SSFD, formed in the ground state, become unstable in the excited state and will tend to change their structure (lifetime of the excited state of dyes **I**–**III** is quite sufficient for this change[11]) and some of the SSFD should disintegrate completely. These influences will most likely affect the same SSFDs, which are formed due to the charge of the polymethine chain, since the charge becomes opposite on excitation (Fig. 2) (i.e. from positive to negative or *vice versa*). For the majority of atoms, whose charges are not changed, the probability of formation of SSFD in the excited state must decrease due to the decrease in absolute values of the majority charges in this state compared with the ground state. As a result, the solvent will have less influence on σ^f compared with its influence on σ^a, and as a result of this, the fluorescence bands of dyes **I**–**III**, which show elongation in PC, in contrast to the absorption bands, should become narrow even in the strongly nucleophilic ethanol and DMFA (Table 1). This is connected with the decrease of vibrational interactions by elongation of PC.[4] The vibrational interactions in the excited state, due to weakening of specific solvation, have a deciding influence on the change of σ^f. The weakening of these solvation effects causes also the narrowing of the fluorescence band compared with the absorption band, and consequently, the breach of mirror symmetry (the latter is particularly noticed in strongly nucleophilic solvations) since in these cases the maximal difference is achieved between the absorption and emission SSFD). Additional narrowing of the fluorescence bands, in comparison with the absorption bands, and a decrease of the solvent influence on σ^f, can take place as a result of non-radiative direct transfer of light energy from the 'blue' to the 'red' solvates.[12] As a result of these transfers in emission, as compared with absorption, not all SSFD take place, but mainly those at long wavelength and with non-specific solvates absorbing in the more 'red' regions as compared with SSFD.[4]

The availability of this energy transfer, in conjunction with the fact that the quantum ratio of fluorescence in strongly nucleophilic solvents (ethanol, DMFA), is, as a rule, lower than in the more weakly nucleophilic DCB and MC (Table 1) (because of the probability of SSFD formation), means that dissipation of excitation energy for the first group of solvents is higher. However the values σ^a and ϕ do not always change symbiotically and this is related to the fact that the quantum ratio depends not only on the nucleophilicity of the medium, but also on its other properties, e.g. viscosity. Thus, in the more viscous DMSO in spite of its strong nucleophilicity, rather high ϕ values are observed.

The Stoke's shifts increase practically in the same order of solvents as the increase in bandwidths. This is caused by the increase in hypsochromy of the shifts $\bar{\nu}^a$, resulting in a greater decrease of ground-state energy of the dye in comparison with the excited state due to the increase of nucleophilic solvation of the first state.[3,4]

These solvations are so significant, that the characteristics of the position of the absorption bands have generally poor correlations with the Bayliss function of refractive index (p)

$$p = \frac{n_D^2 - 1}{2n_D^2 + 1}$$

(Fig. 3), a parameter widely used in investigation of analogous dependence in cyanines.[2,3] The above relationship is distinctly displayed for $\bar{\nu}^a$ (coefficient of correlation $r = 0{\cdot}807$), and the correlation equation may therefore be written as:

$$\bar{\nu}^a = -8934p + 15\,782$$

This may be explained on the basis that the mean frequency is very sensitive to change in the band form. Influence of the solvent on this change takes place mainly due to specific electrostatic interactions (nucleophilic solvation)[3] and not to universal ones. Consequently, the above correlation does not follow in this case. The solvatochromic shift of the band maxima depends more on the degree of polarity of the medium, than on its nucleophilicity.[3] Thus we already have an approximate correlation between $\nu^a_{\max}$ and the Bayliss function ($r = 0{\cdot}912$):

$$\nu^a_{\max} = -5840p + 14\,537$$

A clearer picture is observed for ν_{00}, since the vibrational transfer connected with the band maximum becomes somewhat indistinct under the influence of the solvent, due to SSFD formation. The degree of diffusion depends on the nature of solvent. Thus, in contrast to ν_{00}, the band maximum in various solvents should be dictated by the different vibrational transfers on the sublevel of the excited state of SSFD. But, in spite of the advantages of the

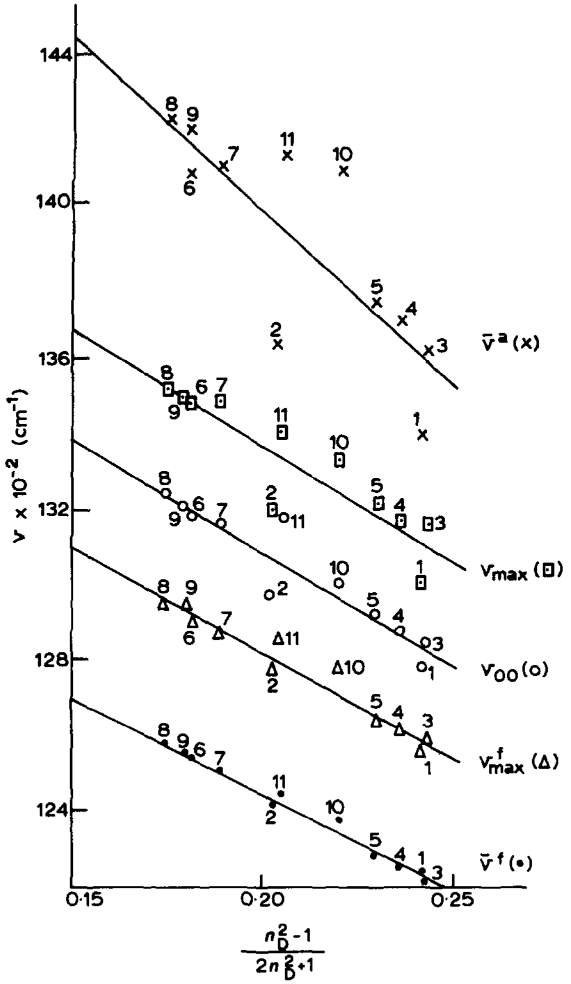


Fig. 3. Dependence of $\bar{\nu}^f$, ν^f_{max}, ν_{00}, ν^a_{max} and $\bar{\nu}^a$ of dye **III** on the Bayliss function (the means of n_D are taken from Ref. 3).

frequency ν_{00} transfer, a satisfactory correlation between ν_{00} and the function of refractive index is not attained ($r = 0{\cdot}942$):

$$\nu_{00} = -5978p + 14\,285$$

This further indicates the significant contribution of specific interactions in the solvation of cationic dyes. The satisfactory dependence of the band characteristics mentioned above with respect to the refractive index, takes place only in non-charged substances.[13,14] Thus it is striking to observe that in fluorescence of the dye **III**, whether charged in the ground state or in the excited state (Fig. 2) an excellent correlation for $\bar{\nu}^f$ is attained in contrast to that in absorption ($\bar{\nu}^a$) ($r = 0{\cdot}993$):

$$\bar{\nu}^f = -5159p + 13\,482$$

and ν^f_{max} also shows a generally satisfactory correlation ($r = 0{\cdot}974$):

$$\nu^f_{max} = -5608p + 13\,941$$

where p is the function of refractive index of Bayliss.

These facts confirm our conclusion that there is a significant weakening of nucleophilic solvation in the excited state compared with the ground state, due to the decrease of positive charges (Fig. 2). From the correlations described above, it follows that the use of the mean frequency of the absorption and fluorescence bands in identical relations is reliable, compared with the use of band maxima. the ν^a and ν^f being averages of all vibrational transfers characterise the energy of vertical transfer[7] more clearly and the value S_v characterises the change of Stoke's shifts more reliably than corresponding values calculated using ν_{max}. The mean frequency, being more influenced by universal and specific interactions, may be used as a quantitative characteristic of the relationship of these interactions in the ground and excited states of the dye molecules.

Thus, the main role in solvation in the excited state of cationic cyanine dyes is played not by specific electrostatic interactions, but by dispersive interactions. Therefore the solvatofluorochromy of the dyes is characterised mainly by the change of band positions. In the solvation of the ground state of the dyes here investigated, the essential contribution introduced is specific interactions due to solvatochromy, characterized by distinct change not only of the position of bands, but also of the form, particularly the bandwidth.

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