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The dependence of photoinduced adiabatic transformations and fluorescence in 2,4,6-triarylsubstituted pyridinium cations on environment

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Abstract

Investigation of the intermolecular interaction effect on the fluorescent properties of the 2,4,6-triarylsubstituted pyridinium cations has been carried out by steady-state absorption and fluorescent spectroscopy using the structural modelling in solvents with different polarities and viscosities at room temperature as well as when the viscosity changes with variations of the temperature from 180 to 340 K. The unspecific Coulomb and polarization cation–solvent interactions result in the small absorption and fluorescence band spectral shifts ($\Delta\nu_a^{\max} \approx 800 \text{ cm}^{-1}$ and $\Delta\nu_f^{\max} \approx 400 \text{ cm}^{-1}$) and therefore cannot be responsible for the fluorescence band anomalous Stokes shift (ASS) ($\Delta\nu_{a-f} \approx 10000 \text{ cm}^{-1}$). The ASS is conditioned by the barrierless process of the adiabatic structural relaxation (ASR) associated with rotation of aryls in the 2nd and 6th positions. The ASR is described satisfactorily by the continual relaxation model and proceeds through the several main stages differing in the ASS dependence on viscosity. One of the stages is the linear ASS dependence on the logarithm of the solvent viscosity. The ASS is considered as a function of the interaction between the cation and its microenvironment in the concrete solvent ('microviscosity') and therefore, its dependence on viscosity may be considered as the microviscosity–macroviscosity correlation. The qualitative interpretation of dependence of the specific fluorescence parameters (quantum yield, band half-width, lifetime) on temperature (viscosity) is also discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Adiabatic structural relaxation; Fluorescence; Anomalous Stokes shift; Viscosity effect; Microviscosity

1. Introduction

Our recent works [1–4] have shown that the triarylsubstituted pyridinium cations are very favourable models for the study of the photoinduced adiabatic structural relaxation (ASR) due to their specific electronic and molecular structure. The detailed experimental investigations of the cation structure influence on the nature of the lowest electron transitions (in the absorption), ASR mechanism and formation of the fluorescence with anomalous Stokes shift (ASS) (ASS-fluorescence) have been carried out [1–4]. However, the nature of the dependence of the photoinduced processes on the properties of the environment remains one of the essential problems which has not been solved up to now. It is especially important as the investigations of the intermolecular interactions give unique information on the ASR mechanism.

The present work, therefore, deals with detailed experimental study of the influence of the solvent polarity, viscosity and temperature on the ASR and ASS fluorescence in the triarylpyridium cations. The 2,4,6-triarylsubstituted

pyridinium cations **Ia–Ic** as well as the model compounds **II** and **III** (Scheme 1) were used in the investigations.

2. Experiment

2.1. Materials

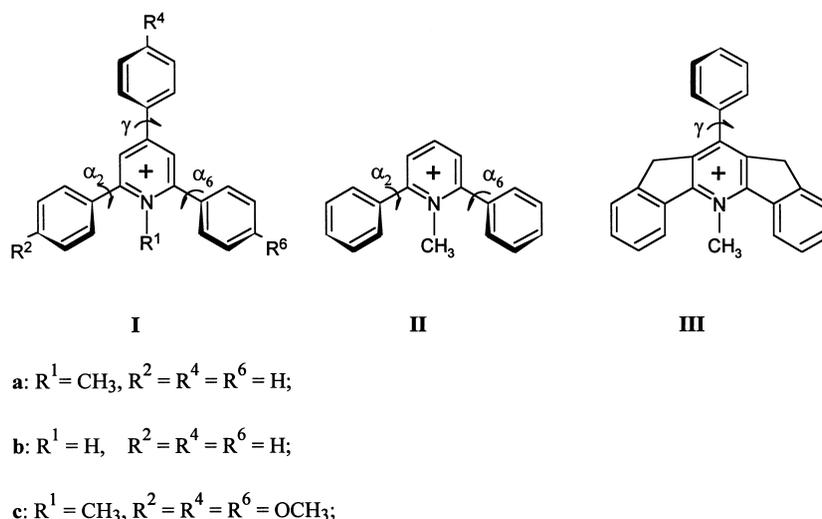
The cations **Ia–Ic**, **II** and **III** were prepared in the form of the perchlorates (anion ClO_4^-) by known methods [5], purified by recrystallization and products were checked by fluorescence after each recrystallization step as described previously [1–3]. Catalytic amounts of the chlorine acid (HClO_4) are added in the solvents for the stabilization of the cation **Ib**.

Commercially available organic solvents employed in experiments were found to give no detectable fluorescence under experimental conditions.

2.2. Spectral investigations

The absorption and fluorescence steady-state spectroscopy have been used for comparative investigations of cations **I–III**. Absorption spectra were recorded with a

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Scheme 1.

Specord M40 and a Specord UV–Vis spectrophotometers (Germany) in the quartz cells with the variable thickness.

The fluorescence emission and excitation spectra were measured on an ELUMIN 2M spectrofluorimeter (Russia) and were corrected to instrumental response.

A device having optical cryostats for absorption and fluorescence spectra measurements in the temperature region 77–303 K (to precision of 1%) was utilized.

The fluorescence quantum yields Φ_f at 295 K were obtained by the relative method [6] (to a precision of 10%) with phenanthrene ($\Phi_f = 0.13$, ethanol, 295 K [7]) and 9,10-diphenylanthracene ($\Phi_f = 0.84$, benzene, 295 K [8]) as references. The refractive index corrections were made [6] to adjust for the different solvents used. The quantum yield changes with temperature variation were corrected both with respect to the refractive index [9] and density [10] changes of the solvent.

The measurements of the fluorescence lifetime were performed on a nanosecond spectrometer SP-70A (GB) in Moscow State University.

3. Results and discussion

3.1. The influence of the nonspecific interactions on the absorption and fluorescence spectra

The absorption and fluorescence parameters of the studied compounds are presented in Table 1.

Since the ASR in **I** and **II** is characterized by the ASS value [1–4] the influence of solvents on this process may be estimated correctly only by taking into account and excluding the contribution of the nonspecific interactions (cation–solvent) which can lead to the considerable spectral shifts of the absorption and fluorescence bands in the liquid solvents especially.

The contribution of the ion–dipole interactions to the displacement of the absorption and fluorescent bands may be characterized by the dependence of the absorption and fluorescence bands maximum position on the functions $f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$ and $f(n) = (n^2 - 1)/(2n^2 + 1)$ [11] (Fig. 1).

The data indicate the rather moderate shortwave shift of the absorption band ($\Delta\nu_a^{\text{max}} \approx 800 \text{ cm}^{-1}$) correlating with the increase of $f(\varepsilon)$. This blue shift is possibly associated with the decrease in the relative energy of the dipole (solvent) and ion (solute) interaction, and also with the corresponding relative energy of stabilization, $\Delta E_{S1}/\Delta E_{S0}$, in the S_0 and S_1 states with the solvent polarity increase (Fig. 2a). This relative energy diminution may be explained by the growth of the charge distribution radius (Born radius) [12] in the S_1 state by the light-induced charge transfer from the 2 and 6 phenyl rings to the hetero ring in the cation **Ia**.

The failure of a general rule in the case of some solvents may be caused by the specific or polarizational and dispersive interactions. For analysis of this situation the absorp-

Table 1
The long wavelength absorption band and fluorescence characteristics of the cations **Ia–Ic** (ethanol, 295 K)

Cation	$\nu_a, (\text{cm}^{-1}) (\varepsilon, \text{cm}^{-1} \text{ M}^{-1})$	$\nu_f (\text{cm}^{-1}) (\lambda_f, \text{nm})$	$\Delta\nu_{a-f} (\text{cm}^{-1})$	Φ_f	$\tau_f (\text{ns})$
Ia	32600 (40000)	22340 (448)	10260	0.32	1.85
Ib	32560 (22100)	24700 (405)	7860	0.37	1.00
Ic	28640 (54000)	19510 (513)	9130	0.56	4.35

ν_a, ν_f : wavenumbers; ε extinction coefficient; $\Delta\nu_{a-f}$: Stokes shift; Φ_f : fluorescence quantum yield; τ_f : fluorescence lifetime.

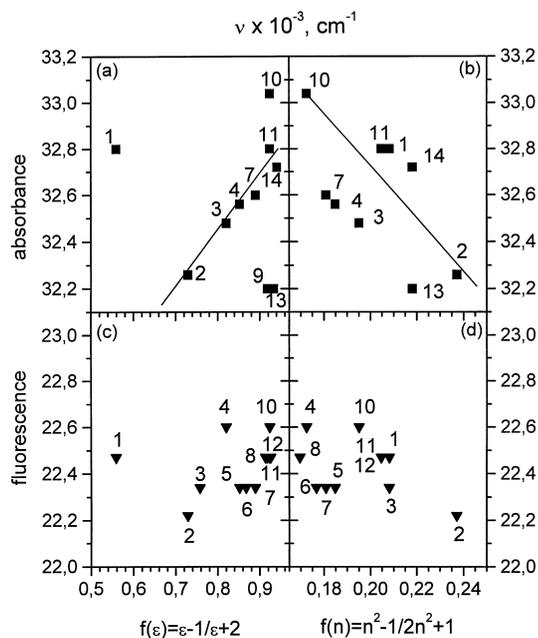


Fig. 1. The spectral shifts of the long wavelength absorption band (a, b) and the fluorescence band (c, d) of cation **Ia** vs. the polarity $f(\epsilon)$ (a, c) and polarizability $f(n)$ (b, d) of solvent. The numbers near the plotted points correspond to a solvent list from Table 2.

tion band shifts were studied in the solvents having similar $f(\epsilon)$ values and strongly differing values of the refractive index functions responsible for the polarizational ($f_1(n) = (n^2 - 1)/(2n^2 + 1)$) or dispersive ($f_2(n) = (n^2 - 1)/(n^2 + 1)$) components of the absorption band solvent shift [11]. The appreciable absorption band ‘red’ solvent shift ($\Delta\nu_a \approx 450 \text{ cm}^{-1}$) with $f(n)$ increase (Fig. 1b) may be associated with the growth of the polarization or dispersive cation–solvent interactions owing to the cation polarizability (molecular volume) increase in the excited S_1 state [13].

So the general shift of the absorption band is connected with the non-specific ion–solvent interactions and does not exceed 800 cm^{-1} . At the same time the maximum fluorescence band solvent shift is about 400 cm^{-1} (the shift in

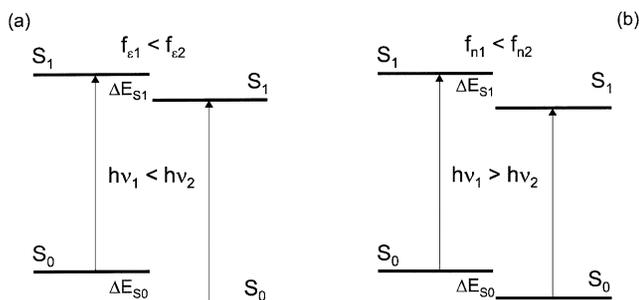


Fig. 2. The qualitative schemes of influence of the solvent polarity $f(\epsilon)$ (a) and the polarizability $f(n)$ (b) on the spectral shift of the long wavelength absorption band.

glycerol at 298 K is caused by the strong viscosity influence on ASR as it will be shown below) (Table 2, Fig. 1c, d) and does not correlate with variation of ϵ and n for different solvents. The ASS fluorescence quantum yield ($\Phi_f = 0.30\text{--}0.38$) does not change quite (Table 2).

Any dependence of the absorption ($c = 10^{-5}\text{--}10^{-3} \text{ M}$) and fluorescence ($c = 10^{-6}\text{--}10^{-1} \text{ M}$) spectra on the cation concentration in the alcohols, acetonitrile or 1,2-dichloroethane has not displayed and the appreciable concentration fluorescence quenching is observed at the concentration of more than 0.03 M. Thus, the findings presented above testify against the intermolecular nature of ASS as dimer or the excimer formation or display of the non-specific interactions with the solvent and confirm the intramolecular nature of ASS formation caused by ASR.

3.2. The anomalous Stokes shift dependence on the solvent viscosity at room temperature

Recent investigations [1–4] give good reasons to suppose the ASR mechanism associated with the formation of the fluorescent structure due to the flattening of the 2 and 6 aryl rings. In this case, one can suppose that the ASR rate and consequently, the ASS value have to be regulated by the steric interactions of the bulky phenyl rings with the ion solvate shell, i.e. depend on both its rigidity (the free volume value, microviscosity of the surroundings [14,15]) and the cation structure.

One can expect also that just such microinteractions have to stipulate the dependence of the ASR parameters and especially ASS values on solvent viscosity and this dependence may be used for the study of the influence of the microinteractions on ASR.

Therefore, the detailed investigation of the ASS dependence on the solvent viscosity has been carried out. At the first step, the influence of the solvents with the various viscosity at the room temperature (295–298 K) has been studied.

The obtained results (Tables 1 and 2) show that the Stokes shift for the studied cations is anomalously large ($\Delta\nu_{a-f} \approx 8000\text{--}10\,000 \text{ cm}^{-1}$), and diminishes with the solvent viscosity increase in accordance with the simple empirical expression (Fig. 3) for **Ia** and **Ic**:

$$\Delta\nu_{a-f} = \Delta\nu_{a-f}^{\max} - A \ln \eta \quad (1)$$

where $\Delta\nu_{a-f}^{\max}$ is the maximum Stokes shift value observed in the solvent of the minimum viscosity with the fluorescence band position coinciding with that of the flattened model structure **III**, η is viscosity in millipoises (mP) and $A > 0$ is the constant.

For the cations **Ia** and **Ic** the lowest limit of the Stokes shift $\Delta\nu_{a-f}^{\min} \approx 8000 \text{ cm}^{-1}$ does not depend on the cation structure and corresponds to the solvent with maximum viscosity at room temperature.

However the Stokes shift for the cation **Ib** does not exceed this limit value even at minimum solvent viscosity.

Table 2

Absorption and fluorescence wavenumbers, Stokes shift, quantum yield of cation **1a** in the different solvents at 298 K

	Solvent	ϵ^a	n^b	ν_a (cm ⁻¹)	ν_f (cm ⁻¹)	$\Delta\nu_{a-f}$ (cm ⁻¹)	Φ_f
1	Chloroform	4.806	1.4310	32800	22470	10330	0.32
2	Chloromethane	9.08	1.5341	32260	22220	10040	–
3	1,2-Dichloroethane	10.36	1.4472	31800	22340	9460	0.32
4	Isoaminol	14.7	1.4277	32480	22600	9880	0.30
5	Isopropanol	18.3	1.3747	32560	22340	10220	0.32
6	Acetone	20.74	1.4703	–	22340	–	–
7	Ethanol	25.2	1.3613	32600	22340	10260	0.32
8	Methanol	32.67	1.3286	–	22470	–	–
9	Glycerol, 328 K	34.7	–	32200	22470	9730	0.31 ^c
10	Acetonitrile	37.4	1.4817	33040	22600	10440	0.38
11	DMFA	37.6	1.4310	32800	22470	10330	–
12	Ethylene glycol	38.7	1.4319	–	22470	–	–
13	Glycerol, 298 K	42.4	1.4744	32200	24100	8100	0.52
14	DMSO	48.9	1.4783	32720	–	–	–

^a Data from [9,10].^b Data from [9,17].^c At 311 K.

Therefore, the Stokes shift value for **1b** does not depend on the room temperature solvent viscosity which is not sufficient for the ensuring of the influence on the Stokes shift.

The upper limit of the Stokes shift $\Delta\nu_{a-f}^{\max}$ (in the solvent of the minimum viscosity) and A , the parameter estimating the efficiency of the viscosity influence, decrease strongly in the above series of the compounds ($\Delta\nu_{a-f}^{\max} = 10600, 9430, 8450$ cm⁻¹ and $A = 330, 165, 0$ cm⁻¹ for **1a**, **1c** and **1b**, respectively). Such a structure dependence can be conditioned by the decrease of the 2,6 phenyl rings acoplanarity in the initial ground state structure in this series of the compounds (see also [4]) owing to the electron (**1c**) or steric (**1b**) factors.

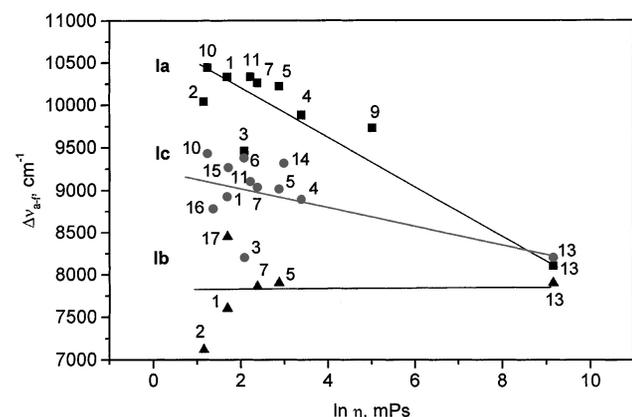


Fig. 3. The Stokes shift dependence on the solvent viscosity at room temperature for compounds **1a**, **1b**, and **1c**. The numbers near the points correspond to a solvent list from Table 2. The solvents with numbers 15, 16, 17 for cations **1b** and **1c** correspond to toluene, isobutanol, tetrahydrofuran, respectively. The data of the solvent viscosity are taken from [17].

The following is noteworthy. The chlorine containing solvents such as 1,2-dichloroethane and chloroform reveal peculiarities associated with the display of specific microinteractions resulting in the too large microviscosity characterized by the anomalously small Stokes shift for a given viscosity.

3.3. The temperature dependence of the fluorescence characteristics on viscosity

Fluorescence of the cations **1a–1c** is the sensitive indicator of the microenvironment and its influence on the ASR (see also [1,14] and above). One of the most effective methods of the investigation such as microenvironment formation and ASR mechanism is, therefore, the observation of the temperature dependence of the fluorescence parameters (ASS, band half-width, quantum yield, lifetime) reflecting the connection between ASR, microviscosity and viscosity with temperature variations.

With this purpose, the solvents sharply differing in viscosity and their temperature dependence (glycerol, isopropanol, and acetone) have been selected for the study.

The Stokes shift can be considered as the immediate reflection of the micro- and macroviscosity correlation which is a temperature function typical for the given cation (**1a**) and solvent (Fig. 4).

In the first ASR step the 2 and 6 phenyl rings rotation does not ‘feel’ any resistance of the microenvironment, i.e. even at very large viscosities, the microviscosity is small in the limit, characterising a ‘free volume’ typical for the given solvent and cation. In this case, the ASR leads to the formation of more flattened structures responsible for the fluorescence with sufficiently large Stokes shift. The lowest Stokes shift limit depending on the solvent nature remains, therefore, sufficiently large ($\Delta\nu_{a-f}^{\min} \approx 5800$ cm⁻¹ in glycerol, Figs. 4 and 5a) even in rigid frozen (77 K) solvents

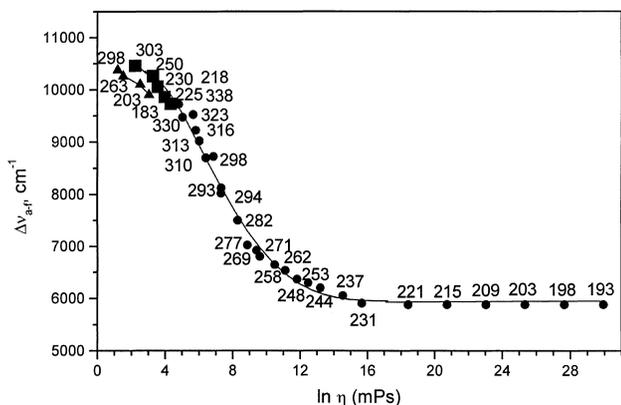


Fig. 4. The Stokes shift dependence of cation **Ia** on viscosity as a function of temperature in acetone (triangles), isopropanol (squares) and glycerol (circles). The numbers near the plotted points correspond to the solvent temperature (K). The data of the solvent viscosity are taken from [17].

and polymeric matrices. This limit depends also on the cation structure and falls considerably to 4400 cm^{-1} with introduction of the bulky donor (e.g. OCH_3) substituents especially into phenyl ring in the 4th position.

At the following stage, in all studied solvents, when the viscosity decreases with temperature growth, the monotonous longwave fluorescence band shift is observed with invariable position of the absorption (excitation) bands, i.e. the monotonous Stokes shift increase takes place (Figs. 4 and 5a) and the distinct linear correlation is observed

between Stokes shift (microviscosity) and the logarithm of the viscosity as well as for the various solvents at the room temperature (see above).

At last, in the small viscosity region at high temperature the deviation from the initial linear dependence is observed with a decrease of the Stokes shift susceptibility to the viscosity variations with temperature. This function changes continuously with the transition to the region of considerably lesser viscosity from glycerol to isopropanol. It can be associated with the similar natures of the microenvironment (and microviscosities) in the alcohol solvents.

On the other hand, in the functional dependence of the Stokes shift on viscosity with the transition in the same Stokes shift region from glycerol (or isopropanol) to acetone, a drastic disruption is observed (Fig. 4). It is evident that the fixed value of the microviscosity for the cation **Ia** is reachable in acetone at a lower viscosity value than in glycerol (or isopropanol).

The most longwave position of the fluorescence band coinciding with that of the model flattened structure **III** (i.e. the maximum Stokes shift) can be reached by lowering the solvent viscosity with appropriate rise of the temperature.

A comparison of the Stokes shift dependence (Figs. 3 and 4) shows that the observed linear dependence (Eq. (1)) holds only within the definite solvent viscosity limits ($\ln \eta$, from 4 to 8, Fig. 4). The qualitative interpretation of the linear semi-logarithmic dependence (Eq. (1)) is possible by modification of the known Riman's phenomenological formula for viscosity [16]:

$$\eta = B(T) \exp\left(\frac{W(T)}{kT}\right) \quad (2)$$

where $B(T)$ and $W(T)$ are weak functions of temperature, W has the meaning of the energy of formation of some cavity in which the molecule is located due to its volume (conformation) change. In this case the formula (Eq. (1)) is equivalent to the equation

$$\Delta\nu_{a-f} = \Delta\nu_{a-f}^{\max} - \frac{AW(T)}{kT} + C(T) \quad (3)$$

where $C(T)$ is also a weak function of the temperature.

Thus, when the value $1/T$ is constant or changes a little ($1/T \approx 0.003\text{--}0.006/\text{K}$) the Stokes shift value $\Delta\nu_{a-f}$ typical for the given medium is determined by the energy W of the formation of the corresponding microvolume where the cation acoplanar structure develops adiabatically into fluorescent more coplanar one.

It should be noted that the above-presented findings concerning monotonous fluorescence band shift with the solvent viscosity change testify to the lack of the intrinsic (intramolecular) potential barrier in the S_1 state for 2 and 6 aryl ring rotation resulting in the flattened fluorescent structure.

The path of this process must be described by the model analogous to that of the rotatory relaxation of the solvents [11,18].

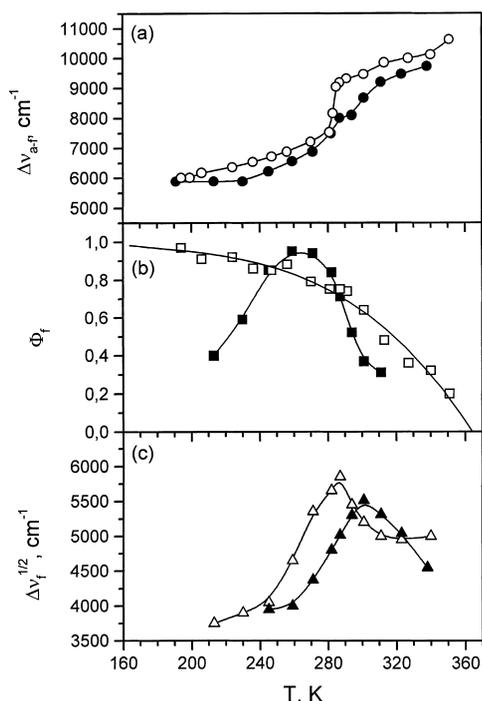


Fig. 5. The Stokes shift (a), the fluorescence quantum yield (b) and half-width of the fluorescence band (c) dependence on temperature for cations **Ia** (solid shape) and **II** (open shape) in glycerol.

This ASR model gives the basis for the qualitative interpretation of the dependence of the various fluorescence parameters on the solvent viscosity to utilize this dependence for the more detailed consideration of the ASR mechanism.

In this connection, it is possible to suppose that the ASS fluorescence band may be considered as being inhomogeneously broadened owing to simultaneous emission of the continual distribution of the conformations with the various acoplanarities. This distribution depends on the properties of the medium (mainly on viscosity) and cation structure.

At ambient temperatures (small viscosity), the ASS fluorescence bands really passes the significant half-width increasing with rise of the acoplanarity and rigidity of initial structure ($\Delta\nu_{a-f} = 3000, 4000, 4500 \text{ cm}^{-1}$ for **III**, **Ib** and **Ia**, respectively). The marked difference in the fluorescence lifetime in the band wavelength range (e.g. $2.41 \pm 0.06 \text{ ns}$ and $2.64 \pm 0.07 \text{ ns}$ at 416 and 385 nm, respectively, for cation **Ia** in isopropanol at 175 K) also testify to the inhomogeneous broadening of the fluorescence band.

Owing to the solvent temperature (viscosity) dependence of the distribution of the emitting acoplanar conformations having different deactivation parameters of the S_1 state along ASR coordinate, the shortwave fluorescence band temperature shift is accompanied by typical variations of the fluorescence band half-width ($\Delta\nu_f^{1/2}$), quantum yield (Φ_f) and observed lifetime (τ_f) values. These values increase in the beginning and then decrease (Figs. 5 and 6). Such an extreme function shape is evidence of the existence of at least two competing relationships. It has been shown earlier [3] that the biphenyl type lowest triplet T^{BP} excited state ($E_T \approx 23\,500 \text{ cm}^{-1}$) of **Ia** is localized on the biphenyl-like moiety with the 4-phenyl substituent which practically does not take part in the ASR. This T^{BP} state can promote

the high intersystem crossing (ISC) rate (small Φ_f) at the low temperature region. However, as the result of the ASR at the sufficiently high temperatures the inversion of the CT (S_1^C, T_1^{CT}) and T_1^{BP} state takes place resulting in the drastic fall in the ISC rate and enhancement of Φ_f in a final fluorescent structure typical for the given temperature (viscosity).

On the other hand, the substantial energy gap (ΔE^{CT}) decrease favours the IC rate increase and the decrease of Φ_f . Thus, the maximum Φ_f value is observed at the intermediate case (Fig. 5b). Just as it has been expected, the only monotonous Φ_f drop due to lowering of the energy gap ΔE^{CT} (IC rate rise) was observed under temperature increase in the model cation **II** having no phenyl ring in the 4th position (Fig. 5b). So, the observed Φ_f dependence on the temperature having extremum (maximum) may be connected with IC–ISC competition in the ASR process with contribution of the T_1^{BP} state localized on the moiety including substituent in the 4th position.

The similar dependence τ_f on temperature with the less distinct maximum in the same region of the fluorescent state energy ($23\,000\text{--}25\,000 \text{ cm}^{-1}$) has apparently an analogous origin (Fig. 6a).

On the other hand, the $\Delta\nu_f^{1/2}$ dependence on the temperature with distinct maximum is typical for both **Ia** and **II** cations (Fig. 5c). Therefore, such a dependence is the direct reflection of the specific change of the emitting acoplanar conformers' distribution only in the angles of the 2,6 ring twist (along the reaction coordinate on the S_1 potential energy surface) probably with the variations of the free volume dimensions depending on viscosity (temperature) and of the cation flattening.

It is necessary to carry out additional study to elucidate the nature of this phenomenon and obtain some quantitative estimations.

4. Conclusions

Under excitation in the absorption band associated with strong charge transfer (CT) transitions from 4, 2, and 6 aryl substituents into the hetero ring in the aryl substituted pyridinium cations the typical fluorescence with anomalous Stokes shift (ASS-fluorescence) arises.

The non-specific cation–solvent interactions stipulate only very small solvent shifts of the absorption and fluorescence bands.

The ASS fluorescence is associated with the adiabatic structural relaxation (ASR) in the S_1 state. The ASR is associated with the 2 and 6 aryl ring rotation to the flattened structure and it proceeds without the intrinsic potential barrier and hence it is well described with help of the continual relaxation model similar to that of the rotational relaxation in the polar solvents.

The ASR proceeds through several main stages. The initial stage does not depend on solvent viscosity. The next

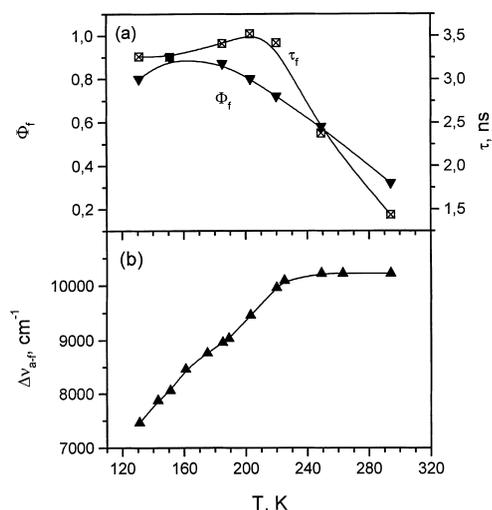


Fig. 6. The fluorescence quantum yield and fluorescence lifetime (a), the Stokes shift (b) dependence on temperature for cation **Ia** in isopropanol.

stage is that in which the ASS and ASR rate values are linear functions of the logarithm of viscosity. In this stage, the dependence of the fluorescence quantum yield, lifetime and the band half-width on viscosity are described by typical functions. This dependence is interpreted qualitatively from the viewpoint of the competition between the ISC and IC processes during the process of ASR.

In the last stage, the significant decrease of the plot-slope (i.e. sensitivity) of the Stokes shift dependence on viscosity is observed.

The dependence of the ASS value on viscosity is a function of both the cation structure and solvent nature. Hence, the microinteractions of the given cation structure with the molecules of the solvent under investigation (microviscosity) can be estimated by ASS values.

Therefore, the ASS dependence on viscosity can be considered as a microviscosity–macroviscosity correlation including the linear function of the logarithm of viscosity within the sufficiently large range of viscosity values.

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