Local Temperature of Fluorescent Centres in Polymer Films Determined from Universal Kennard–Stepanov Relation between Absorption and Fluorescence Spectra

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Based on the Kennard–Stepanov relation between the extinction coefficient and fluorescence intensity in their overlapping region, local temperatures T^* are determined for several dyes and stilbene derivatives in PVA and PVC polymers. It is found that excitation energy excess for $\tilde{\nu}_{\text{exc}} > \tilde{\nu}_{0\text{-}0}$ causes local heating in a rigid polymer, and the temperature difference $\Delta T = T^* - T$ holds during the emission process. Such a behaviour results from slow geometrical relaxation in a polymer. Excitation energy excess is also evidenced by the fact that the intensity distribution in the emission band depends slightly on the excitation wavelength. This effect is stronger for higher energy excess.

Key words: Universal Relation between Absorption and Fluorescence Spectra; Local Temperature; Polymer Fluorescent Solutions.

1. Introduction

In [1] we determined local temperatures T^* of luminescent molecules (Erythrosin B in water, 4-dimethylamino-ω-diphenylphosphinyl-trans-styrene (2a) in *n*-hexane, *n*-hexadecane and 4-dimethylamino-ω-methylsulphonyl-trans-styrene (3a) in *n*-hexane, *n*-decane and *n*-hexadecane) of short lifetimes from 7 to 77 ps, based on the universal Kennard–Stepanov relation [2, 3] between the extinction coefficient and fluorescence intensity in their overlapping region. It was found that the local temperatures T^* of the above luminescent molecules in solvents of low viscosity exceed distinctly the ambient temperature T.

In the case of long living molecules (above 1 ns) in liquid unpolar and polar solvents it is always observed that T^* (within the error limits ± 10 K) is equal to the ambient temperature T. This means that in this case thermal equilibrium prevails between the luminescent molecule and its surrounding (solvent molecules). Appropriate literature is listed in [1, 4]. According to Bakhsiev et al. [5], the universal relationship of Kennard–Stepanov is for four level systems in liquid solutions only fulfilled if there exist suitable conditions for full relaxation, i.e., $\tau_f \gg \tau_R$ (τ_f is the mean fluorescence lifetime and τ_R is the relaxation time of the reaction field). However, for unpolar luminescent molecules in unpolar liquid solutions it is also observed that $T^* = T$, which means that absorption and emission processes are described by a two level system (only weak interactions of dispersive nature appear [4, 6] [1].

The Kennard–Stepanov relation is visibly broken in the case of viscous and frozen systems [7–10]. For example, for 4-amino-N-methylphtalimid and 4-aminophtalimid in glycerol Stepanov obtained $T^* = 610$ K and $T^* = 550$ K, respectively [3]. It has also been found that in the case of rigid polymeric solutions, as for example for 9,10-dichloroantracene (DCA), 9,10-dibromoantracene (DBA), 9,10-diphenylantracene (DPA), 2,5-di(4-biphenyl)oxazole (BBO), rhodamine B and rhodamine 6G in polymethylmetacrylate (PMAM), it is always true that $T^* > T$ [4, 6].

The problem of local temperatures of fluorescent centres is still of great interest, which is evidenced by numerous papers (cf. Review article [12]). In the present work local temperatures T^* are determined for several organic dyes: Na-fluorescein, erythrosin B, rhodamine S and rhodamine 6G as well as stilbene derivatives: 4-dimethylamino-4′-nitrostilbene (DNS), 4-amino-4′-nitrostilbene (ANS) and 4,4′-diphenylstilbene (DPS) in poly(vinyl alcohol) (PVA) and poly (vinyl chloride) (PVC) polymers.

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[1] In [6], Table 1, fourth columns, second line: there is 360 K instead of 296 K.

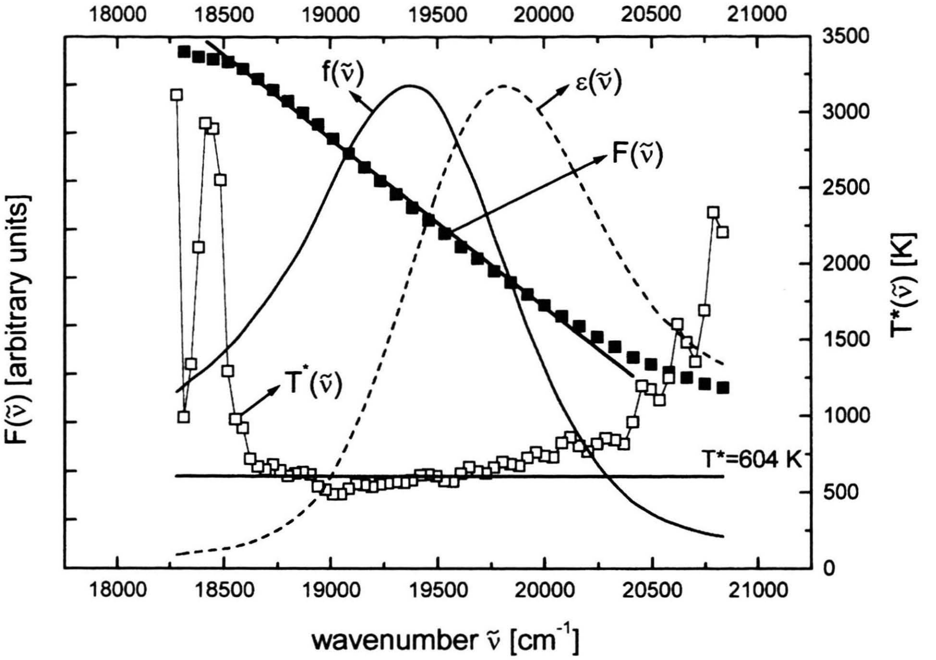

Fig. 1. Absorption, fluorescence and $T^*(\tilde{\nu})$ spectra of Na-Fluorescein in PVA (unheated) as well as the corresponding $F(\tilde{\nu})$ function. $f(\tilde{\nu})$ = spectral distribution of the fluorescence intensity, $\varepsilon(\tilde{\nu})$ = extinction coefficient.

2. Experimental

Isotropic poly(vinyl alcohol) (PVA) and poly(vinyl chloride) (PVC) films were prepared by the method described in [13–15].

Absorption and fluorescence as well as emission anisotropy spectra were measured with the apparatus described in [16–18].

3. Results and Discussion

If in the excited state the population density of vibrational levels does not correspond to the temperature T of the solution studied but to a higher "vibrational temperature" T^*, the universal Kennard–Stepanov relationship between the extinction coefficient and fluorescence intensity [2, 3] can be written in the modified form [19]

$$F(\tilde{\nu}, T^*) \equiv \ln \frac{f(\tilde{\nu}, T^*)}{\tilde{\nu}^3 \cdot \varepsilon(\tilde{\nu}^3, T^*)} = -\frac{hc\tilde{\nu}}{kT} + \text{const}, \quad (1)$$

where $f(\tilde{\nu})$ is the spectral distribution of the fluorescence intensity, $\varepsilon(\tilde{\nu})$ the extinction coefficient, h and k are Plancks and Boltzmanns constants, and c is the velocity of light.

Figures 1–4 show absorption and fluorescence spectra as well as the course of $F(\tilde{\nu}, T^*)$ for Na-fluorescein, rhodamine S, erythrosin B and DNS in PVA. As for liquid solutions, a linear dependence of $F(\tilde{\nu})$ given by (1) is observed for PVA. Figure 1 gives additionally the course of the function

$$T^*(\tilde{\nu}) = -\frac{hc}{k}\left(\frac{\mathrm{d}F(\tilde{\nu})}{\mathrm{d}\tilde{\nu}}\right)^{-1} \quad (2)$$

obtained by differentiating (1) [12, 20]. We can see that strong deviations of $T^*(\tilde{\nu})$ from the straight line parallel to the $\tilde{\nu}$ axis corresponding to the mean temperature T^* of the luminescent centres appear only at the tails of the absorption and fluorescence bands, where the experimental error is distinct. The temperatures T^* determined by (1) are collected in Table 1. In the same table the wavenumbers of the exciting light and 0-0 transitions are given.

Among the studied stilbene derivatives in PVA and PVC films only DNS and ANS in PVA and DPS in PVC fulfill the essential assumption under which (1) is valid. Relation (1) should hold true universally as long as the system contains only one absorbing species. The above linear molecules with one double bond embedded in PVA films exhibit unusual behaviour as far as their ab-

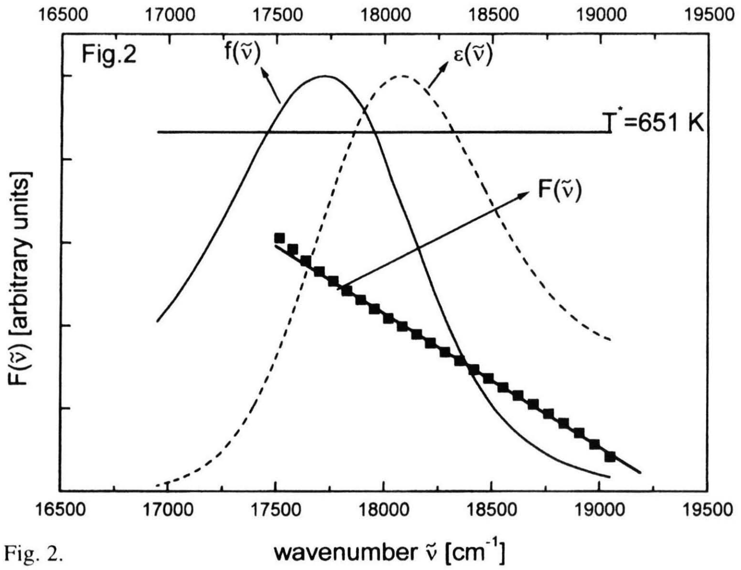

Fig. 2.

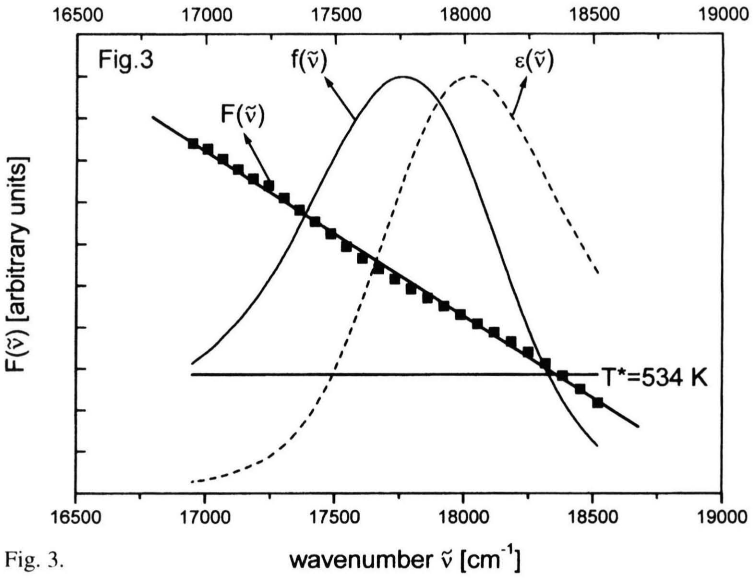

Fig. 3.

Fig. 2–4. Absorption and fluorescence spectra of Rhodamine S in PVA (heated) (Fig. 2), erythrosin B in PVA (unheated (Fig. 3), and DNS in PVA (heated) (Fig. 4), respectively, and the corresponding $F(\tilde{\nu})$ function. The temperatures T^* given in Figs. 2 and 4 are incorrect and there are: $T^* = 431$ K (Fig. 2) and $T^* = 753$ K (Fig. 4).

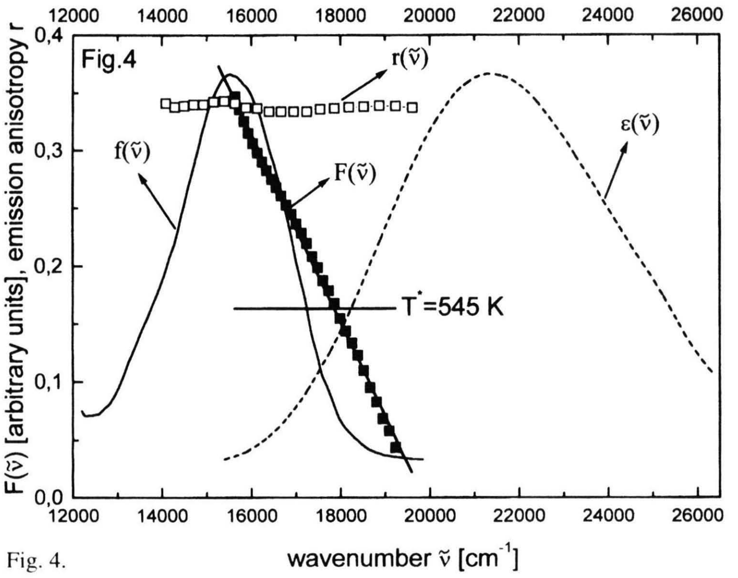

Fig. 4.

Table 1. Spectral properties and local temperatures of compounds studied in polymer films.

Compound	Solvent	$\tilde{\nu}_{exc}$ [cm^{-1}]	$\tilde{\nu}_{0\text{-}0}$ [cm^{-1}]	$\Delta\tilde{\nu}$ [cm^{-1}]	T^* [K]	T ambient [K]	ΔT [K]
Na-fluorescein	PVA unheated	22727	19583	3144	604	297	307
	PVA heated	21739	19550	2189	607	297	310
Rhodamine 6G	PVA heated	20000	18382	1618	468	297	171
Rhodamine S	PVA unheated	20000	17953	2047	872	297	575
	PVA heated	20000	17867	2133	431	297	135
Erythrosin B	PVA unheated	20000	17900	2100	534	297	237
	PVA heated	20000	17906	2094	489	297	192
DNS	PVA heated	21277	18109	3168	753	296	457
ANS	PVA unheated	23256	18176	5080	1262	296	966
	PVA heated	23256	19130	4126	862	296	566
DPS	PVA unheated	29412	24850	4562	817	296	521
	PVA heated	29412	26136	3276	715	296	419
DPS	PVC heated	28169	26726	1443	475	296	179

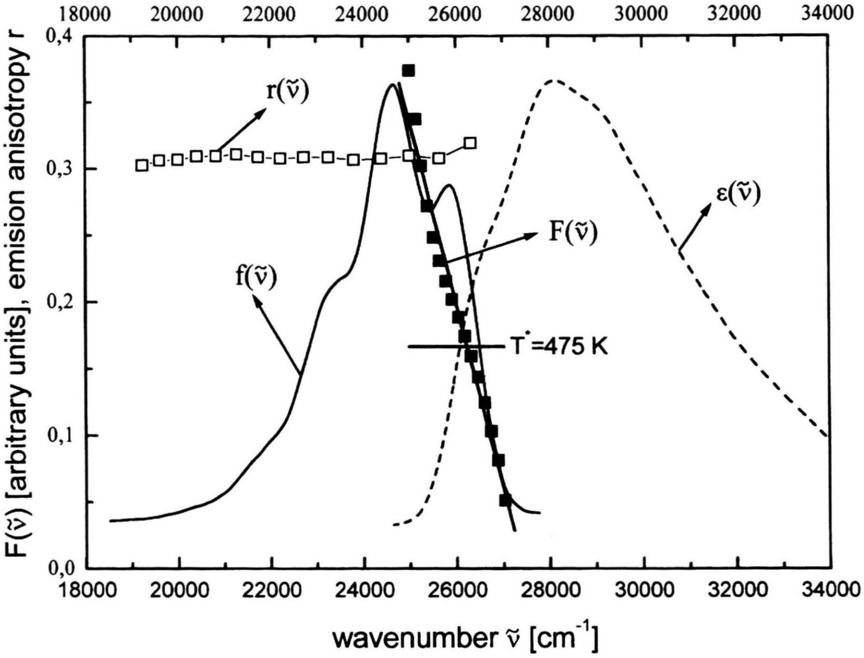

Fig. 5. Absorption, fluorescence and emission anisotropy $r(\tilde{\nu})$ spectra of DPS in PVC (heated) and the corresponding $F(\tilde{\nu})$ function.

sorption and fluorescent properties at different temperatures (296 K – 423 K) are concerned [21]. It should be emphasized that in the temperature range 296 – 358 K, i.e. up to the glassy transition temperature, the optical density of the molecules studied does not change. Only above the glassy transition temperature an increase in optical density appears (1.6 – 3 times) which is much less than that for diphenylpolyenes. On heating, conformational changes occur in the ground state of the molecules and the transition from cis[2] to the fluorescent form trans takes place according to the energy diagram shown in Fig. 4 in [22].

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[2] If the cis form is capable of emitting fluorescence, then the ratio of the intensity of this form to that of the transform should be not more than 1 : 600.

It results from Table 1 that for heated PVA films the local temperature T^* is lower than that for unheated films for all the compounds studied except Na-Fluorescein. Simultaneously, the emission anisotropy, r, remains constant in the emission band (within the error limit) and it is distinctly higher for the heated PVA films. The unusual absorption and fluorescence properties at different temperatures is, however, not observed both for unheated and heated (up to 393 K) PVC films [23]. The absorption, fluorescence and emission anisotropy in PVC films measured at room temperature are the same for unheated and heated films. Figure 5 shows the results for the unpolar molecule DPS in PVC.[3]

The excitation energy excess ($\tilde{\nu}_{\text{exc}} > \tilde{\nu}_{0\text{-}0}$) in the case of molecules studied in a rigid polymer causes the local heating and the temperature difference $\Delta T = T^* - T$ during the emission process, due to the slow geometrical relaxation in the polymer. The excess of excitation energy is also evidenced by the fact that the intensity distribution in the fluorescence band depends slightly on the excitation wavelength. This effect is more visible for higher energy excess.

In view of the low emission anisotropy observed in the polymers studied it can be assumed that the luminescent molecules are in polymer caves and are in part free. The fluorescence depolarization is caused by rotations of the molecules. In unheated PVA polymer the emission anisotropy r is distinctly lower than for rigid (heated) films [21]. Since T^* behaves completely reverse to r, it can be assumed that the transfer process of excitation energy excess from the molecule to its vicinity (polymer) is made difficult. However, in the PVA polymer rigidified by heating the empty spaces are getting smaller, which restricts the process of fluorescence depolarization. Stronger coupling between the luminescent molecules and the polymer leads to partial dissipation of excitation energy excess and hence it lowers the local temperature T^*.

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[3] The strongly polar compounds ANS and DNS in PVC films are not suitable for our studies, because of the appearance of two different fluorescent centres in this polymer with different microenvironments around the ANS and DNS molecules [23]

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