The Local Temperature Dependence of Fluorescent Centres in PVA Films on the Excitation Wavenumber

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The temperature difference $\Delta T = T^* - T$ (where T^* is the local temperature and T the ambient temperature) is studied as a function of the excitation wavenumber $\tilde{\nu}_{\mathrm{exc}}$ in the longwave region of the absorption band of 4-amino-4′-nitrostilbene (ANS) and 4-dimethylamino-4′-nitrostilbene (DNS) as well as rhodamine S, rhodamine 6G and Na-fluorescein in poly(vinyl alcohol) (PVA) films heated up to 403 K. Local temperatures T^* are determined by a universal Kennard-Stepanov relation. A linear dependence of ΔT on $\tilde{\nu}_{\mathrm{exc}}$ has been found for all investigated luminescent compounds. For dyes, due to the big spectral overlaps between the absorption and fluorescence bands, it was possible to excite also in the anti-Stokes region. In this case for $\Delta T = 0$, i.e. when $T^* = T$, one has $\tilde{\nu}_{\mathrm{exc}} = \tilde{\nu}'_{0-0}$. In view of the slow geometrical relaxation of excitation energy excess in PVA polymers, the relaxation time τ_{R} for thermal equilibration between the luminescent molecule and the vicinal polymer exceeds distinctly the mean fluorescence lifetime τ_{F}.

Key words: Kennard-Stepanov Universal Relation; Local Temperature; PVA Fluorescent Films.

1. Introduction

In [1], local temperatures T^* have been determined based on a universal Kennard-Stepanov relation [2, 3] for a series of luminescent molecules in unheated and heated PVA films. For unheated and heated films of the same luminescent compound different values of T^* were obtained. Reproducible results can only be obtained for rigidified films heated above the glassy transition temperature $T = 358$ K. In a freshly prepared unheated PVA film there exist regions of a different degree of polymerization, and such an unrigidified film forms an inhomogeneous environment.

For the luminescent molecules studied in [1], in the PVA polymer heated up to 403 K a local heating takes place which is characterized by a temperature T^* distinctly higher than the ambient temperature T. Higher temperature T^* evidences excitation energy excess, and this is the reason of the observed subtle dependence of fluorescence band peak location on the excitation wavelength in the longwave absorption band. A particularly strong shift of the fluorescence band is observed for the strongly polar molecules 4-amino-4′-nitrostilbene (ANS) and 4-dimethylamino-4′-nitrostilbene (DNS) in heated PVA films.

Therefore it is necessary to study the difference $\Delta T = T^* - T$ as a function of the excitation wavenumber $\tilde{\nu}_{\mathrm{exc}}$ in the longwave absorption band. In the present paper the following molecules are studied: ANS, DNS, rhodamine S, rhodamine 6G, and Na-fluorescein only in heated up to 403 K PVA films.

2. Experimental

Isotropic poly(vinyl alcohol) films (PVA) were prepared by the method described in [4, 5]. Absorption and fluorescence spectra were measured with the apparatus described in [6, 7].

3. Results and Discussion

The temperatures T^* were determined by the universal Kennard-Stepanov relation between the extinction coefficient $\varepsilon(\tilde{\nu})$ and the fluorescence intensity $f(\tilde{\nu})$ [2, 3], written in the modified form [8]

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

where h and k are the Planck and Boltzmann constants, respectively, and c is the velocity of light.

Figures 1 and 2 present experimental data for ANS and DNS in heated PVA films for three selected wavenumbers of the exciting light $\tilde{\nu}_{\mathrm{exc}}$. A distinct dependence of the fluorescence band location on $\tilde{\nu}_{\mathrm{exc}}$ is observed. The

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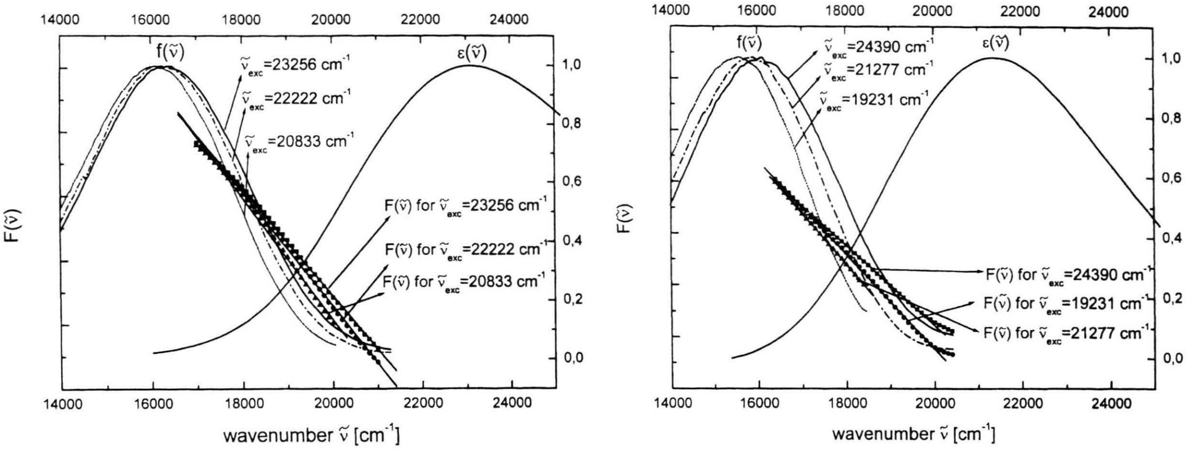


Figs. 1 and 2. Absorption $\varepsilon(\tilde{\nu})$, fluorescence, $f(\tilde{\nu})$, spectra and the corresponding $F(\tilde{\nu})$ functions at different excitation wavenumbers, $\tilde{\nu}_{\text{exc}}$, for ANS (Fig. 1) and DNS (Fig. 2) in PVA films.

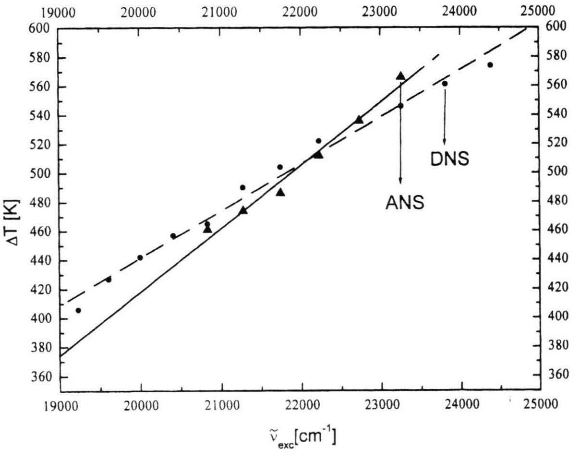


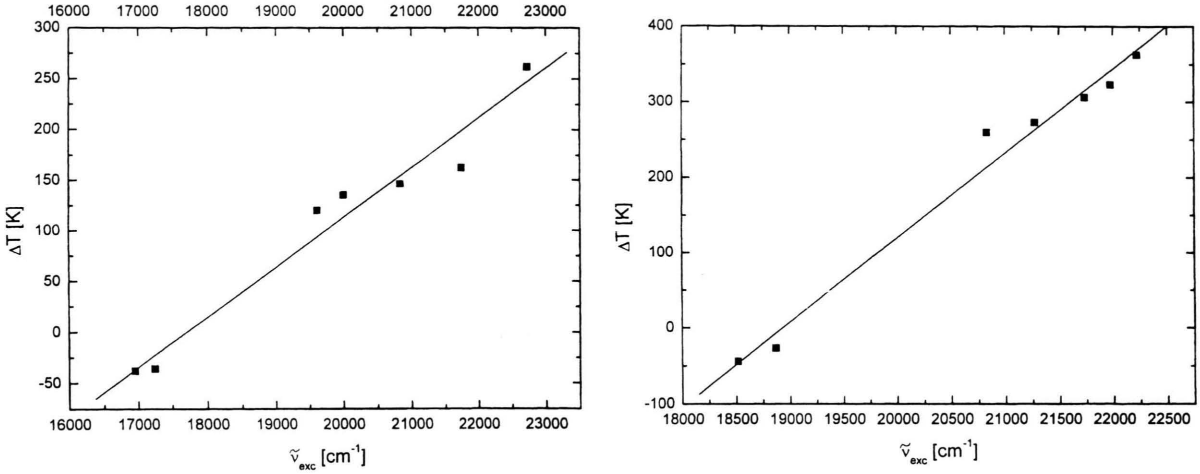
Fig. 3. The increments of temperatures, $\Delta T = T^* - T$, at different excitation wavenumbers $\tilde{\nu}_{\text{exc}}$ for ANS and DNS in PVA films.

Table 1. Excited state local temperatures of stilbene derivatives in PVA films determined for different wavenumbers of exciting light.

Compound	$\tilde{\nu}_{\text{exc}}$ [cm^{-1}]	$\tilde{\nu}_{0-0}$ [cm^{-1}]	$\Delta\tilde{\nu}$ [cm^{-1}]	T^* [K]	ΔT [K]
ANS	23256	19130	4126	862	566
	22727	19080	3647	832	536
	22222	19020	3202	808	512
	21739	18920	2819	782	486
	21277	18890	2387	770	474
	20833	18820	2013	757	461
DNS	24390	18384	6006	856	560
	23809	18335	5474	836	540
	23255	18271	4984	813	517
	22727	18238	4489	795	499
	22222	18206	4016	777	481
	21739	18173	3566	761	465
	21276	18109	3167	753	457
	20833	18070	2763	715	419
	20408	18034	2374	705	409
	20000	18000	2000	682	386
	19607	17930	1677	657	361
	19230	17860	1370	625	329

temperatures T^* listed in Tables 1 and 2, based on the linear dependence of $F(\tilde{\nu})$ given by (1), exceed for different $\tilde{\nu}_{\text{exc}}$ the ambient temperature T similarly as for complex molecules in gaseous phase [9].

For $\tilde{\nu}_{\text{exc}} > \tilde{\nu}'_{0-0}$ the temperature difference is positive, $\Delta T = T^* - T > 0$, which means that excited molecules possess an excess of vibrational energy compared to the equilibrated energy characterized by the ambient temperature T. Figure 3 shows the dependence of ΔT on $\tilde{\nu}_{\text{exc}}$ for ANS and DNS. Similar linear dependencies have been found for rhodamine S, rhodamine 6G, and Na-fluorescein in heated PVA films (Figs. 4 and 5). In the latter cases the samples could also be excited in the anti-Stokes region due to the large overlap between the absorption and fluorescence spectra. For the anti-Stokes region, the reverse relation $\tilde{\nu}_{\text{exc}} < \tilde{\nu}'_{0-0}$ holds and $\Delta T \leq 0$, which means that the supply of vibrational energy of excited molecules is smaller or equal to the equilibrated energy corresponding to T. From the Table 2 and Figs. 4 and 5 it is seen that for $\Delta T = 0$, which means that temperature T^* of the excited molecules is equal to the ambient temperature T, the relation $\tilde{\nu}_{\text{exc}} = \tilde{\nu}'_{0-0}$ holds true. Tables 1



Figs. 4 and 5. The increments of temperatures, $\Delta T = T^* - T$, at different excitation wavenumbers $\tilde{\nu}_{exc}$ for rhodamine S (Fig. 4) and Na-fluorescein (Fig. 5) in PVA films.

Table 2. Excited state local temperature of dye molecules in PVA films determined for different wavenumbers of exciting light.

Compound	$\tilde{\nu}_{exc}$ [cm^{-1}]	$\tilde{\nu}_{0-0}$ [cm^{-1}]	$\Delta\tilde{\nu}$ [cm^{-1}]	T^* [K]	ΔT [K]
Rhodamine S	22727	17844	4883	558	262
	21739	17861	3878	458	162
	20833	17871	2962	442	146
	20000	17867	2133	431	135
	19608	17844	1764	416	120
	17241	17738	–497	260	–36
	16949	17711	–762	258	–38
Rhodamine 6G	22222	18242	3980	493	197
	20833	18242	2591	469	173
	20000	18242	1758	450	154
	19607	18239	1368	430	134
	17241	18138	–897	288	–8
	16949	18147	–1198	267	–29
Na-fluorescein	22222	19567	2655	659	363
	21978	19576	2402	619	323
	21739	19550	2189	602	306
	21277	19567	1710	569	273
	20833	19556	1277	556	260
	18868	19392	–524	269	–27
	18519	19269	–750	252	–44

Table 3. Values of wavenumbers $\tilde{\nu}'_{0-0}$ obtained from interpolation of experimental dependencies $\Delta T(\tilde{\nu}_{exc})$ for $\Delta T = 0$ K.

Compound		
Rhodamine 6G	Rhodamine S	Na-fluorescein
17170 cm^{-1}	17700 cm^{-1}	18935 cm^{-1}

and 2 show apart from T^* the values of $\tilde{\nu}_{0-0}$ obtained from the location of absorption and fluorescence peaks for different $\tilde{\nu}_{exc}$. The best agreement between the values of $\tilde{\nu}_{0-0}$ (Table 2) and $\tilde{\nu}'_{0-0}$ (Table 3) was obtained for rhodamine S.

The excitation energy excess for $\tilde{\nu}_{exc} > \tilde{\nu}_{0-0}$ causes in the rigid PVA polymer local heating during the emission process. Having in mind the slow geometrical relaxation of this energy excess, the relaxation time, τ_R, for thermal equilibration between the luminescent molecule and the surrounding polymer exceeds distinctly the mean fluorescence lifetime τ_F.

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