TEMPERATURE AND SOLVENT VISCOSITY EFFECTS ON THE ABSORPTION AND FLUORESCENCE SPECTRA OF A SERIES OF PYRYLIUM SALTS[†]

VÉRONIQUE WINTGENS, SADHANA TRIPATHI, JOSEPH POULIQUEN and JEAN KOSSANYI

Laboratoire de Photochimie Solaire, Equipe de Recherche 241 du Centre National de la Recherche Scientifique, 2 - 8 rue Henry Dunant, 94320 Thiais (France)

Summary

The excitation and fluorescence spectra and the excited state lifetimes of pyrylium salts were studied in different polar solvents. An emission blue shift is observed when the temperature is lowered from 300 to 77 K. This phenomenon is believed to be due to solvent–solute interactions following changes in the electronic distribution in the excited state. At 77 K the excited state decay is faster than the solvent reorganization and the emission originates from the Franck–Condon state. At 300 K the solvent relaxation is now fast enough (about 50 ps) to allow the excited state to relax before emitting.

---

1. Introduction

Pyrylium salts show strong electrophilic affinities as a result of the positive charge of the aromatic pyrylium nucleus. This important property has received special attention in the electrophotography of poly(*N*-vinyl-carbazole): pyrylium salts can trap electrons and induce the migration of positive holes in the polymer towards a negatively charged electrode [1].

Several compounds of the series show interesting behaviour as laser dyes [2]; in addition, polymethinic pyrylium salts (pyrylocyanines) can also be used as *Q* switches for YAG and ruby lasers [3].

We have already shown that the fluorescence emission of a series of pyrylium salts is shifted to the blue when the temperature is substantially decreased [4]. Effects due to aggregate formation or to the rotation of the phenyl substituent can be disregarded; a relaxed excited state reached by thermal activation from the Franck–Condon state was postulated instead.

With non-rigid molecules, the dependence of the absorption and emission spectra on the solvent, temperature, viscosity or concentration may be
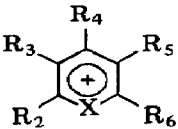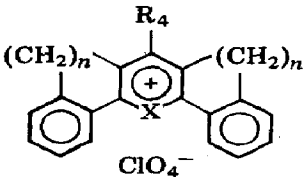

[†] Dedicated to Professor Schulte-Frohlinde on the occasion of his 60th birthday.

reasonably ascribed to the presence of different conformers [5 - 7] or aggregates [8, 9]. Changing the concentration or including the substituents (which can rotate) of the pyrylium ring into a polycyclic structure produced exactly the same shifts of the emission when the temperature was changed from room temperature to 77 K. Owing to their insolubility in non-polar solvents, the spectroscopic measurements of the pyrylium salts were carried out in strongly polar solvents such as acetonitrile. It is well known that the interaction of the molecules of the solute with those of the surrounding polar solvent has a strong influence on the features of the fluorescence spectra as a result of a change in dipole moment [10 - 13]. Since the pyrylium salts are strongly polar molecules, their dipole moments must undergo drastic modification in the singlet excited state.

In this paper we report the results obtained in a study of the spectra and fluorescence efficiencies of pyrylium salts (see Table 1) in butyronitrile solution and in other solvents at various temperatures between 77 and 293 K as well as in a polymeric matrix.

TABLE 1

Formula of the studied pyrylium salts

	X	R_2	R_3	R_4	R_5	R_6
1	O	C_6H_5	H	H	H	C_6H_5
2	O	C_6H_5	H	C_6H_5	H	C_6H_5
3	O	C_6H_5	H	C_6H_5	H	CH_3
4	O	p-$MeOC_6H_4$	H	C_6H_5	H	p-$MeOC_6H_4$
10	S	C_6H_5	H	CO_2H	H	C_6H_5
5	O	C_6H_5	H	p-$MeOC_6H_4$	H	C_6H_5
6	O	p-$MeOC_6H_4$	H	C_6H_5	H	C_6H_5
7	O	C_6H_5	H	p-$NO_2C_6H_4$	H	C_6H_5
8	O	p-$NO_2C_6H_4$	H	C_6H_5	H	C_6H_5
9	O	p-$MeOC_6H_4$	H	C_6H_5	H	p-$NO_2C_6H_4$

	X	n	R_4
11	O	1	H
12	O	2	H
13	O	2	C_6H_5

14    $X \equiv O$

Me = methyl.

2. Experimental details

2.1. Products and solvents

Acetonitrile, methanol, ethanol (all Merck, Uvasol quality), acetic acid, and glycerol (both Prolabo, RP quality) were used as received. 1-Propanol, 1-butanol, 3-methyl-1-butanol, 1,2-ethanediol and cyclohexanol were distilled, 2-methyltetrahydrofuran was filtered over neutral alumina and butyronitrile and n-butyl acetate were distilled and filtered over acidic alumina.

The preparation of the pyrylium salts 1 [14], 2 [15], 3 [16] and 4 - 9 [17] has been described previously. Compound 10 and the rigid products 11 - 14 were prepared according to ref. 18.

2.2. Apparatus

The UV–visible spectra were obtained using a Varian–Cary model 219 apparatus; the emission spectra were recorded using a Perkin–Elmer MPF-44B spectrofluorometer equipped with a DCSU2 correction unit. The singlet excited state radiative lifetime of the pyrylium salts was evaluated with a single-photon counting apparatus (Ortec electronics and an Intertechnique multichannel analyser) which has been described previously [19].

A DN70 low temperature cell and an MTIC temperature control unit, both from Oxford Instruments, were used to carry out the experiments between 293 and 77 K.

2.3. Concentration effects

A saturated solution of known concentration of the pyrylium salt in ethanol–acetic acid (99:1 by volume) was prepared and its UV–visible absorption spectra were recorded employing a cell 0.1 mm thick. The other solutions were prepared from the saturated solution by dilution and the spectra were recorded using cells of various optical pathlengths.

The fluorescence spectra of these solutions were obtained at right angles with a 1 cm × 1 cm cell or using the front surface technique. The excitation spectra were obtained at the emission maximum. These match the absorption spectra for low concentrations (up to 0.0005 M). For more concentrated solutions (0.001 - 0.01 M) a new band appears at longer wavelengths. Excitation at the maximum of this new band gives no additional emission band.

The measurements at 77 K were carried out with a phosphorimeter acessory with its chopper taken out. The solution to be studied was put in a Pyrex tube of internal diameter 6 mm which was then immersed in a Dewar and cooled with liquid nitrogen.

2.4. Fluorescence

The optical density of the various pyrylium salts was adjusted to 0.1 in all the solvents used.

The variable-temperature experiments were carried out by exciting the compounds at the maximum of their long wavelength absorption band. Care

was taken to ensure that excitation at the shorter wavelength bands leads to the same emission spectra. The excitation spectra monitored at the wavelength of the emission maximum or at other emission wavelengths are identical with the absorption spectra.

Experiments at 77 K were carried out following the procedure described above. For the variable temperature experiments between 77 and 293 K, the low temperature device was set up inside the fluorometer. The circulation of liquid nitrogen was adjusted to produce a decrease in temperature of 2 K min^{-1}. The temperature was kept constant for about 10 min at every 10 K in order to record the emission and excitation spectra under stable (± 1 K) temperature conditions. The absence of sample degradation was verified by checking the absorption of the solution after it had returned to room temperature.

2.5. Low temperature lifetime measurements

Singlet lifetime measurements were carried out at 77 K using the single-photon counting technique. A solution of the sample was put into a tube of diameter 6 mm which was immersed in a Dewar containing liquid nitrogen. The measurements between 77 and 293 K were made with the Oxford Instruments device every 15 K. Each measurement was carried out over about 30 min, after the temperature had been stabilized, in order to obtain a sufficient counting rate.

3. Results and discussion

3.1. Absorption

Table 2 gives the position of the long wavelength absorption band for the series of pyrylium salts 1 - 14 at room temperature. This band (described as 1 L$_b$ in Platt's notation) is polarized along the x axis (see Fig. 1) and is attributed to a π,π^* transition [20]. As expected [21], substitution para to the 4-phenyl group induces a slight red shift of the absorption band whether the substituent has electron-attracting (7) or electron-donating (5) properties. The substituent effect is more selective when it involves the 2- (or 6-) position of the pyrylium ring along the polarization axis; now, substitution para to the 2- or 6-phenyl group by electron-attracting groups (8) induces a slight blue shift of the absorption band while substitution with electron-donating groups (4 and 6) shifts the absorption to the red; the effects are not additive, as demonstrated by compound 9 which bears both types of substituents.

More interesting is the increase in rigidity of the phenyl substituents on blocking their rotation by incorporating them in a five- or six-membered ring (11 - 14), resulting in a red shift of the absorption band by 33 - 43 nm (compare 1 with 11 and 12, as well as 2 with 13). As expected from the above discussion, blocking the phenyl group at the 4-position of the pyrylium ring does not produce any important effect since it is not oriented along the polarization axis.

TABLE 2

Position of the long wavelength absorption band, and of the fluorescence emission at 77 K and 293 K and their difference $\Delta\lambda_{em}$

Compound	λ_{abs} at 293 K (nm)	λ_{em} (nm)		$\Delta\lambda_{em}$ $(\lambda_{293} - \lambda_{77})$
		293 K	77 K	
1	402[a]	465	437	28
11	435[a]	478	454	24
12	445[b]	504	470	34
2	408[b]	470	442	28
13	446[b]	498	471	27
3	410[b,c]	469	443	26
14	395[b,c]	424	404	20
5	418[b]	484	449	35
6	450[b]	565	497	68
7	425[b,c]	492	465	27
8	390[a,c]	482	458	24
9	457[b]	558	512	46

[a]Butyronitrile–butyl acetate (95:5 by volume).
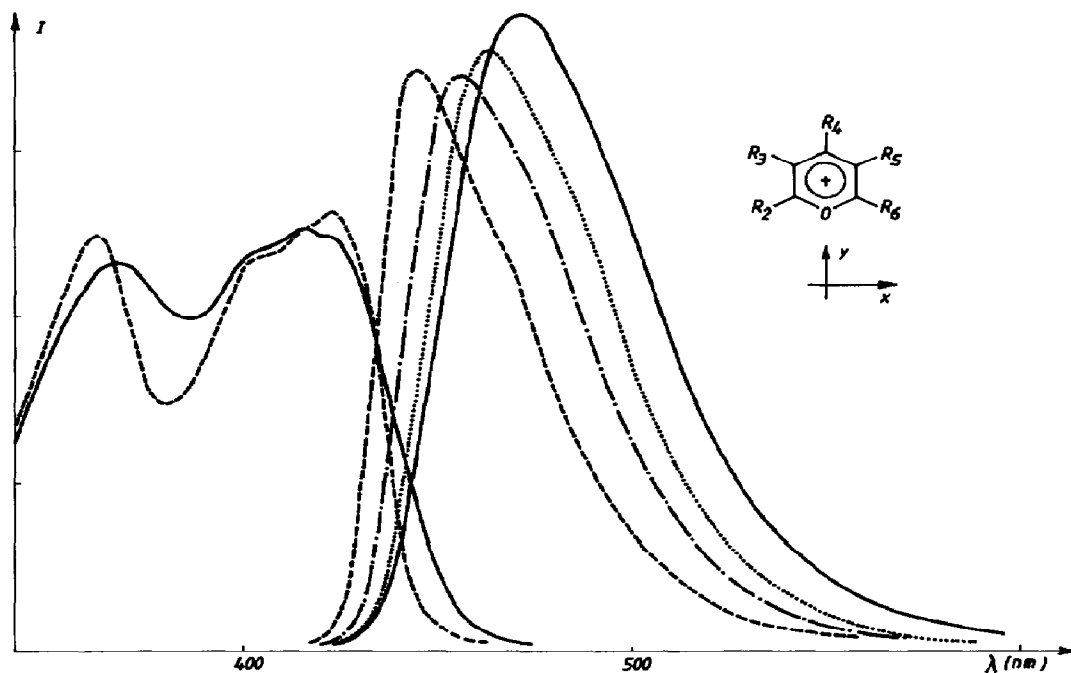[b]Ethanol–acetic acid (99:1 by volume).
[c]Shoulder.

Fig. 1 Change in the emission spectra of compound 2 (in EtOH, λ_{ex} = 410 nm) with decreasing temperature: ———, 290 - 190 K; · · ·, 140 K; — · —, 120 K; — — —, 77 K. The excitation spectra at 290 K (———) and at 77 K (— — —) are given on the left-hand side.

3.2. Fluorescence emission

The fluorescence emission of the compounds studied shows a Stokes shift which is more important as the molecules become less rigid (for instance, 43 nm for 11 compared with 59 nm for 12 and 63 nm for 1); substitution of the phenyl groups by electron-donating groups also increases the Stokes shift but the effect is more pronounced when the substitution is along the polarization axis (115 nm for 6) than perpendicular to it (66 nm for 5) (Table 2).

Increasing the concentration of the fluorophore in the solution shifts both the absorption and emission (Table 3) to longer wavelengths. This can be attributed to trivial reabsorption of the short wavelength emission by ground state molecules; there is no net appearance of a new absorption band, as would have been expected from dimer or aggregate formation. The excitation spectra of the samples reproduce the absorption spectra at low concentrations (10^{-5} M) while at higher concentrations ($10^{-3} - 10^{-2}$ M) a new, narrow and intense band appears at wavelengths longer than the absorption band of the monomer. For this reason, all the measurements on the temperature and viscosity effects were carried out at concentrations lower than 10^{-4} M.

TABLE 3

Concentration effect on the absorption and fluorescence emission bands at 293 K and 77 K

Compound	C^a (mol l^{-1})	T = 293 K		T = 77 K	
		λ_{abs}^b (nm)	λ_{em} (nm)	λ_{abs}^b (nm)	λ_{em} (nm)
2	1×10^{-3}	400, 450	470	400, 440	458
2	3×10^{-4}	400, 440	470	400, 440	455
2	1×10^{-4}	410	468	410	442
4	2×10^{-3}	470, 532	562	470, 510	552
4	2×10^{-4}	470, 510^c	555	472	516
4	2×10^{-5}	470	555	472	512
10	1×10^{-2}	480^c, 506	552	470	508
10	2×10^{-3}	480 (large)	538	420^c, 465	495
10	2×10^{-5}	430	515	430	484

^{a}Ethanol—acetic acid (99:1 by volume).
^{b}The maxima were determined from excitation spectra taken at the emission maximum.
^{c}Shoulder.

3.3. Temperature effects

Decreasing the temperature of the solution from room temperature to 77 K induces a blue shift of the fluorescence maximum of 20 - 68 nm. This modification cannot be attributed to the formation of a dimer or an aggregate as a result of the high concentration of the solution since the emission is red shifted when the concentration is increased (see above). Such an effect

has been observed previously for many non-rigid aromatic molecules in which the aromatic groups are linked to each other by single bonds or polyene chains.

Flexible molecules can undergo the geometrical change that leads to the most stable conformer by internal rotation. Consequently, one can expect a large Stokes shift for the fluorescence. This is the case for hindered stilbenes [22], tetraphenylbutadiene [23] or diphenylmethane dyes [24].

If the rotation is strongly hindered, the emission can arise from the Franck—Condon state or from geometrical intermediates between the latter and the relaxed state, depending on the relative rate constants of the rotational relaxation and the fluorescence decay. In addition, an increase in the quantum yield of the radiative processes can result.

It is tempting to attribute the temperature-induced blue shift of the emission of pyrylium salts 1 - 10 to the blocking of the phenyl substituents in a non-planar configuration which, by internal rotation, relieves the molecules from steric hindrance. This is apparently not the case since the rigid molecules 11 - 14 show the same trend as the molecules in which the phenyl groups can rotate.

Steadily lowering the temperature gives an S-shaped curve for the plot of the fluorescence maximum *versus* temperature (Fig. 2). This type of behaviour has been attributed [10, 25 - 28] to the orientational relaxation processes of the solvent around molecules which undergo a significant redistribution of electron density on electronic excitation; this results in an important change, both in magnitude and direction, of the dipole moment of the molecule during the transition from the ground state to the excited state. The solvent shift method was used to determine dipole moment changes on electronic excitation [29]; we have found that the difference between ground and excited state dipole moments is about 5 debyes for compound 2 and 7.5 debyes for compound 6. Such an effect would be highly sensitive to the polarity of the solvent. That this is effectively the case is shown in Fig. 2,
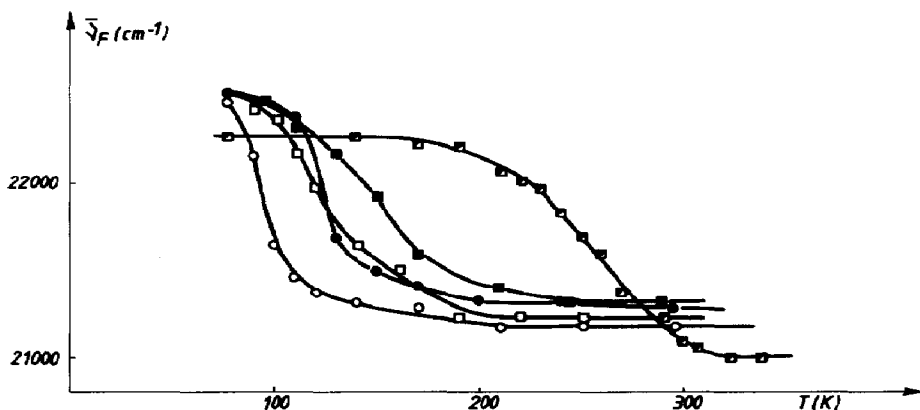

Fig. 2. Plot of fluorescence maximum *vs.* the temperature in various solvents for compound 2: □, ethanol; ■, 1-propanol; ▱, glycerol; ○, 2-methyltetrahydrofuran; ●, butyl acetate—butyronitrile (5:95 by volume).

but it can be noticed already that the form of the S-shaped curves changes only to a small extent with the polarity of the solvent, as demonstrated by 2-methyltetrahydrofuran and butyronitrile, whose dielectric constants are 7 and 37 respectively at room temperature.

At low temperature, the reorientation of polar solvents is slow enough for the decay processes to compete with the solvent relaxation. It is worth noting that (a) there is no change in the excitation spectra when the temperature is decreased from 293 to 77 K, (b) for most solvents (glycerol excepted) the blue shift of the emission begins only when the temperature is lower than 200 K and (c) in the temperature range where the fluorescence is shifted (Fig. 1), the halfwidth of the emission increases steadily with the temperature indicating that the total fluorescence spectrum is composed of many spectra originating from various species having different solvent orientations.

In a polymeric matrix, in which the molecules surrounding the substrate only move with difficulty, one does not expect any important variation in the emission maximum with temperature. This has been verified with compound 2, which was inserted into a poly(methyl methacrylate) matrix. A shift of the emission by about 5 nm is observed [30] when the temperature is decreased from 293 to 77 K, but it is worth noting that the position of the emission varies from one sample to another with the concentration, owing to trivial reabsorption of the emitted light; in any case, its position lies closer to that of the relaxed state than to that of the Franck–Condon state.

3.4. Viscosity dependence

Since the viscosity of the solvent increases as the temperature of the solution is decreased, the shift of the fluorescence maximum might be attributed to such an effect.

When molecules are not rigid and can isomerize, the quantum yield for isomerization decreases with increasing viscosity and this has been attributed to a decrease in free volume, which reduces the space available for the rotation of the substituents during the trans to cis isomerization [31]. The same observation was made in a polymeric matrix where the free volume and the microscopic viscosity are claimed to be critical factors in the rotation of the groups in the molecule.

To separate the dependence of fluorescence on temperature from that on viscosity it is necessary to use data obtained by changing the viscosity alone. These data have been obtained by looking at the shift in the emission in hydroxylated solvents (Table 4). On increasing the viscosity by three orders of magnitude, from methanol (0.6 cP) to glycerol (1430 cP), the emission maximum of 2,4,6-triphenylpyrylium tetrafluoroborate varies by only 4 nm at room temperature, while the absorption maximum is shifted by 7 nm in the same direction. Consequently, the blue shift which occurs when the temperature of the solution is decreased does not result from a viscosity effect but does so from the change in the dielectric constant of the

TABLE 4

Position of the absorption and fluorescence emission bands of 2 at room temperature *versus* the viscosity coefficient of various alcoholic solvents

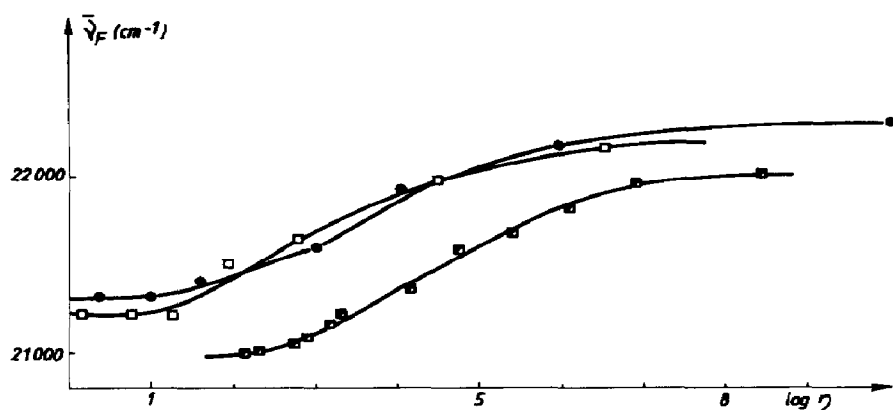| Solvent	η (cP)	$T = 293$ K	
		λ_{abs} (nm)	λ_{em} (nm)
Methanol	0.6	404	469
Ethanol	1.2	410	469
1-Butanol	2.96	409	470
3-Methyl-1-butanol	6.20	410	470
1,2-Ethanediol	19.9	407	474
Cyclohexanol	68	412	472
Glycerol	1430	411	473

Fig. 3. Plot of fluorescence maximum *vs.* the logarithm of the solvent viscosity for compound 2: □, ethanol; ●, 1-propanol; ▨, glycerol.

polar solvent with temperature. This effect is well known and, for instance, the dielectric constant of ethanol [32] increases from 24.3 to 41 when the temperature is decreased from 298 to 213 K. Similarly, methyltetrahydrofuran, which is less polar than ethanol, has a dielectric constant which increases from 7 at 298 K to 9 at 223 K and to 18 at 103 K [33]; furthermore, it has been claimed that it reaches 35 when the temperature is decreased further below 103 K. The curves obtained (Fig. 3) by plotting the change of the position of the fluorescence maximum of 2,4,6-triphenyl-pyrylium perchlorate (2) *versus* the logarithm of the viscosity reflect the solvent reorientation relaxations around the excited molecules as a result of the change in both the dielectric constant of the solvent and the dipole moment of the substrate after excitation in its first excited singlet state.

3.5. Lifetime measurements

The lifetime of the pyrylium salt 2 has been measured at different temperatures and in three solvents: methyltetrahydrofuran, butyronitrile and
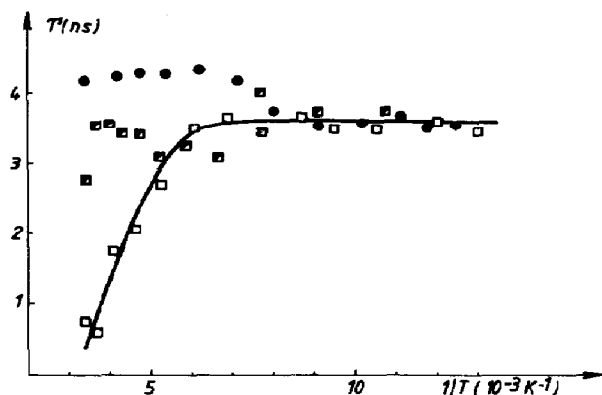
Fig. 4. Plot of the emission lifetime *vs.* $1/T$ in various solvents for compound 2: ◙, glycerol; □, 2-methyltetrahydrofuran; ●, butyronitrile—*n*-butyl acetate (95:5 by volume).

glycerol. In the latter, the variation is weak (about 20%) and not continuous: the lifetime decreases until a minimum is reached at a temperature close to that of the vitreous transition and then it increases back to the starting value (Fig. 4).

The results are more in agreement with a reorientation of solvent molecules around the excited substrate for the case in which 2 is dissolved in methyltetrahydrofuran: the radiative lifetime increases regularly as the temperature decreases, reaching a plateau at about 130 K.

Calculation of the reorientation of the solvent in the solvation sphere of the emitting species is based [34] on the position of the fluorescence band at low and high temperatures corresponding to the short and long wavelength position of the emission maximum on the S-shaped curve. The approximate relationship

$$\tau_r = \frac{\bar{\nu}(T) - \bar{\nu}(h)}{\bar{\nu}(l) - \bar{\nu}(T)} \tau_s$$

has been proposed [26] to determine the time τ_r required for the reorientation of the solvent molecules in the solvation sphere of the excited substrate molecules; τ_s and $\bar{\nu}(T)$ are the lifetime of the excited species and the position of its fluorescence maximum respectively at a temperature T; $\bar{\nu}(l)$ and $\bar{\nu}(h)$ are the position of the maximum of the emission at low and high temperatures respectively, when the band occupies the shorter and longer wavelength position on the S-shaped displacement curve. The values obtained from this relationship are too imprecise to give reliable results; for instance, a shift of 1 nm in the evaluation of the broad structureless band can modify the calculated value by a factor of 5 - 10. Application of the relation for a temperature of 200 K in butyronitrile gives a value for τ_r which corresponds to $\tau_s/5$, while in methyltetrahydrofuran at the same temperature this value is $\tau_s/7$; $\tau_s/6$ is obtained in glycerol at 290 K.

In the temperature range 293 - 160 K, where there is no shift of the fluorescence band, the variation in τ_s with temperature fits the relationship

$$\frac{1}{\tau_s} = \frac{1}{\tau_s^{\,\circ}} + A \exp\left(-\frac{\Delta E}{RT}\right)$$

This expression is composed of a constant value $(1/\tau_s^{\,\circ})$ and of an additional Arrhenius-type component. The activation energy ΔE of the non-radiative processes deduced from the relationship

$$\ln\left(\frac{1}{\tau_s} - \frac{1}{\tau_s^{\,\circ}}\right) = f(1/T)$$

is 13 kJ mol^{-1} and the pre-exponential factor A is found to be 3×10^{11} s^{-1}.

The reorientation of the solvent molecules is slowed down in high viscosity solvents and here the fluorescence decay competes with solvent relaxation; thus, two or more fluorescence decays should be observed with spectral broadening. When isomerizable molecules are in a polymeric matrix, photoisomerization can occur depending on whether the temperature is above or below the glass transition temperature T_g. A kinetic discontinuity thus occurs during the descent near T_g. When the polymer is not homogeneous, complex kinetics are observed below T_g as a result of a multiplicity of different first-order processes. By analogy, one expects a multiexponential fluorescence decay when the temperature varies between 90 and 180 K (Fig. 2), the emission being dominated by that of the unrelaxed species which decays with a subnanosecond lifetime.

Several authors [10, 12, 13, 25, 28] have already characterized, using time-resolved spectroscopy, the emission from both the unrelaxed Franck–Condon state and the relaxed state after solvent orientational relaxation around the excited molecule.

The rotational diffusion time of the substrate can be calculated from the Debye–Stokes–Einstein relationship: $\tau(T) = \eta V/kT$ where η is the viscosity coefficient of the solvent, V is the molecular volume, k is the Boltzmann constant and T is the absolute temperature. A volume of 285 Å^3 has been obtained for 2,4,6-triphenylpyrylium perchlorate (2) using the van der Waals increments [35]. Based on this value, the following results are obtained: $\tau(303\ \text{K}) \approx 70$ ps in ethanol; $\tau(303\ \text{K}) \approx 120$ ps in isopropanol; $\tau(298\ \text{K}) \approx 25$ ps in acetonitrile. Much longer lifetimes are expected in glycerol solution because the viscosity coefficient is increased by almost three orders of magnitude: $\tau(298\ \text{K}) \approx 69$ ns. The time-resolved emission spectra of the unrelaxed and relaxed excited states of several compounds of the series described here were tentatively investigated using a mode-locked YAG laser which delivers a single pulse (duration, 25 ps) coupled to an optical multichannel analyser; the analysing light is a picosecond continuum generated in D$_2$O which extends from 400 to 1000 nm. The experimental set-up has been described previously [36]. Unfortunately, in our case, no variation in the continuum emission was observed except with 6, but then the signal was too weak to be analysed properly and the estimated lifetime in aceto-nitrile solution was of the same order (25 ps) as the pulse duration; this

result agrees with the value calculated from the Debye–Stokes–Einstein equation.

4. Conclusions

Although the dipole moment of the solute is different in the excited state from that in the ground state by about 5 debyes, at low temperature the high viscosity of the polar solvent prevents any relaxation of the solute–solvent system; consequently, the solvent relaxation time is longer than the lifetime of the pyrylium-ion singlet excited state, so that the emission originates from the unrelaxed (Franck–Condon) state.

At room temperature, the solvent–solute system undergoes a rapid reorientation process (in less than 50 ps) and the fluorescence emission now arises from the relaxed state at longer wavelengths.

Acknowledgment

References

1 V. Wintgens, J. Pouliquen, M. Simalty, J. Kossanyi, F. K. Justesen and J. Eriksen, *J. Photochem.*, *26* (1984) 131.
2 D. Bastin, F. P. Schafer and B. Steyer, *Appl. Phys.*, *3* (1974) 81.
3 J. L. R. Williams and G. A. Reynolds, *J. Appl. Phys.*, *3* (1968) 5327.
4 V. Wintgens, J. Kossanyi and M. Simalty, *Bull. Soc. Chim. Fr. II*, (1983) 115.
5 E. Haas, G. Fischer and E. Fischer, *J. Phys. Chem.*, *82* (1978) 1638.
6 Y. B. Sheck, N. P. Kovalenko and M. V. Alfimov, *J. Lumin.*, *15* (1977) 157.
7 J. B. Birks, G. Bartocci, G. G. Aloisi, S. Dellonte and F. Barigelletti, *Chem. Phys.*, *51* (1980) 113.
8 E. Fischer, *J. Phys. Chem.*, *84* (1980) 403; *Bull. Soc. Chim. Belg.*, *88* (1979) 889.
9 C. Goedicke, H. Stegemeyer, G. Fischer and E. Fischer, *Z. Phys. Chem. N. F.*, *101* (1976) 181.
10 T.-I. Lai, B. T. Lim and E. C. Lim, *J. Am. Chem. Soc.*, *104* (1982) 7631.
11 J. Drew, P. Thistlethwaite and G. Woolfe, *Chem. Phys. Lett.*, *96* (1983) 296.
12 V. Sundstrom, T. Gillbro and H. Bergstrom, *Chem. Phys.*, *73* (1982) 439.
13 A. Declemy, C. Rulliere and P. Kottis, *Chem. Phys. Lett.*, *101* (1983) 401.
14 M. Simalty, *Bull. Soc. Chim. Fr.*, (1961) 538.
15 M. Simalty, *Bull. Soc. Chim. Fr.*, (1965) 1944.
16 H. Strzelecka, M. Dupre and M. Simalty, *Tetrahedron Lett.*, (1971) 617.
17 J. Carretto, *Ph.D. Thesis*, University of Paris, France, 1967.
18 S. Tripathi, M. Simalty, J. Pouliquen and J. Kossanyi, *Bull. Soc. Chim. Fr.*, accepted for publication.
19 J. Kossanyi, G. Daccord, S. Sabbah, B. Furth, P. Chaquin, J. C. Andre and M. Bouchy, *Nouv. J. Chim.*, *4* (1980) 337.
20 J. R. Wilt, G. Reynolds and J. A. Van Allan, *Tetrahedron*, *29* (1973) 795.

21 H. Khedija, H. Strzelecka and M. Simalty, *Bull. Soc. Chim. Fr.*, (1972) 1398, 3173.
22 U. Mazzuccato, *Pure Appl. Chem.*, *54* (1982) 1705.
23 M. A. El Bayoumi and F. M. Abdul Halim, *J. Chem. Phys.*, *48* (1968) 2536.
24 G. Oster and Y. Nishijima, *J. Am. Chem. Soc.*, *78* (1956) 1581.
25 T. Okamura, M. Sumitani and K. Yoshohara, *Chem. Phys. Lett.*, *94* (1983) 339.
26 V. S. Pavlovich, L. G. Pikulik and P. P. Pershukevich, *Zh. Prikl. Spektrosk.*, *31* (1979) 998.
27 T. Azumi, K. Itoh and H. Shiraishi, *J. Chem. Phys.*, *65* (1976) 2550.
28 S. K. Chakrabarti and W. R. Ware, *J. Phys. Chem.*, *55* (1971) 5494.
29 J. Waluk, B. Pakula and C. Balakier, *Chem. Phys. Lett.*, *94* (1983) 58.
30 V. Wintgens, J. Pouliquen, J. Kossanyi, J. L. R. Williams and J. C. Doty, *Polym. Photochem.*, *6* (1985) 1.
31 D. Gegiou, K. A. Muszkat and E. Fischer, *J. Am. Chem. Soc.*, *90* (1968) 12.
32 *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 61st edn., 1980, p. E56.
33 T. Tamamura, M. Yokoyama, S. Kusabayashi and H. Mikawa, *Bull. Chem. Soc. Jpn.*, *47* (1974) 442.
34 N. G. Bakhishev, Y. Maruzenko and I. V. Piterskaya, *Izv. Akad. Nauk S.S.S.R., Ser. Fiz.*, *32* (1968) 1360.
35 J. T. Edwards, *J. Chem. Educ.*, *47* (1970) 261.
36 C. Rulliere, A. Declemy and P. Pee, *Rev. Phys. Appl.*, *18* (1983) 347.