

TRANSIENT LOCAL HEATING EFFECTS RESULTING FROM RADIATIONLESS DEACTIVATION OF ELECTRONICALLY EXCITED MOLECULES IN RIGID MEDIA

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Summary

The fate of the energy lost through radiationless deactivation of electronically excited molecules in rigid matrices has been investigated by the observation of the excitation wavelength dependence of their fluorescence spectra. It is concluded that any local heating is sufficient to mobilize only such solvent molecules which are linked to the solute by specific associations (e.g. hydrogen bonds) and that true local melting of the solid matrix does not take place.

When an electronically excited molecule undergoes *radiationless* deactivation from a state S_n to a state S_m , the energy difference $E_n - E_m$ eventually becomes heat in the surrounding medium. This heat is generated locally, and it may therefore appear as a relatively strong transient local heating of the solvent shell in the immediate vicinity of the deactivated molecule. There are speculations that such local heating may result in "local melting" of rigid matrices, which would explain, for example, some sterically demanding photoinitiated isomerizations of cation radicals in such media [1]. It also raises the possibility of "pseudophotochemical" reactions in which the thermal activation energy would be supplied by the local heating, leading to "hot" ground state reactivity.

In this communication we report our preliminary findings concerning the evidence for local heating phenomena, based on the observation of the excitation wavelength dependence of the fluorescence spectra of dipolar molecules in polar rigid media. Figure 1 illustrates the principle of our experimental approach.

A molecule of ground state (S_0) and dipole moment μ_0 dispersed in a solvent of static dielectric constant ϵ is excited by absorption of a photon of energy $h\nu_e$ to a state S_i . It then undergoes a very rapid radiationless deactivation to its lowest singlet excited state S_1 from which it will eventually fluoresce. If the fluorescence lifetime is sufficiently long, the fluorescence occurs from the thermally equilibrated excited state S_1 at the temperature T of the solvent. Should the dipole moment μ_1 of the molecule in this

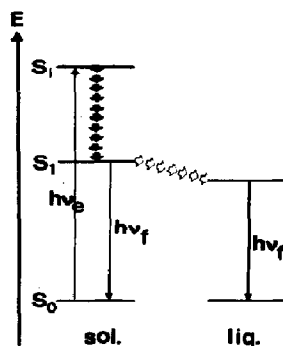


Fig. 1. Energy level diagram for the transient local heating experiment. The line of black arrows corresponds to the excess energy available in the form of heat for local softening of the matrix shell and the line of white arrows corresponds to the dipole dielectric stabilization due to solvent relaxation around the excited molecule.

state S_1 be larger than μ_0 , then the (liquid) solvent rearranges to stabilize the new dipole and the fluorescence spectrum shows a red shift with increasing solvent dielectric polarity. (The solvent dielectric polarity is defined by the function $f(\epsilon) = 2(\epsilon - 1)/(2\epsilon + 1)$, ϵ being the static dielectric constant of the solvent [2].)

If the solvent is frozen around the fluorescing molecule, then this rearrangement cannot take place and the fluorescence spectrum is blue shifted compared with that observed in the same solvent in the liquid state. However, if transient local melting of the solid solvent shell can occur, then this "liquefied" or "softened" shell may rearrange to stabilize the excited state dipole μ_1 and then freeze in this new situation as the heat is lost to the bulk of the matrix. If local melting is essentially complete, the fluorescence spectrum should be similar to that observed in the liquid solvent at the same temperature [2]. Since the heat given off to the surroundings is $h\nu_e - E(S_1)$, the softening of the matrix shell should increase with increasing excitation energy and therefore a correlation (antiparallel) between emission (red shift) and excitation energy is expected.

In the present experiments we have used 1-naphthylamine (1-NA) and 4-aminophthalimide (4-AP) as fluorescers on account of their long fluorescence lifetimes and the strong solvent polarity dependence of their fluorescence spectra. Their relevant photophysical properties are summarized in Table 1.

We find that in most solid polar non-protic solvents such as dimethylformamide (DMF), acetonitrile, tetrahydropyran etc. near (*i.e.* 5-10°C below) their melting point there is either no shift or a *blue shift* of the fluorescence spectra with shorter excitation wavelength. Figure 2 shows 1-NA and 4-AP in DMF and acetonitrile as examples. The blue shift observed for many highly dipolar solvents is readily accounted for by the process of site selection which is an unavoidable complicating feature of these experiments. Site selection occurs because the excitation light close to the long wavelength edge of the absorption spectrum of the solute is absorbed mostly

TABLE 1

Photophysical properties of 1-naphthylamine and 4-aminophthalimide

	Fluorescence lifetime (ns) in the following solvents ^a				Maximum fluorescence wavelength (nm) in the following solvents			
	C ₆ H ₁₂	THF	DMF	EtOH	C ₆ H ₁₂	THF	DMF	EtOH
1-NA	6	—	—	20	375	400	410	422
4-AP	—	19	17	10	386	447	468	519

The fluorescence lifetimes were measured from the decay kinetics following nitrogen laser excitation.

^aTHF, tetrahydrofuran; DMF, dimethylformamide.

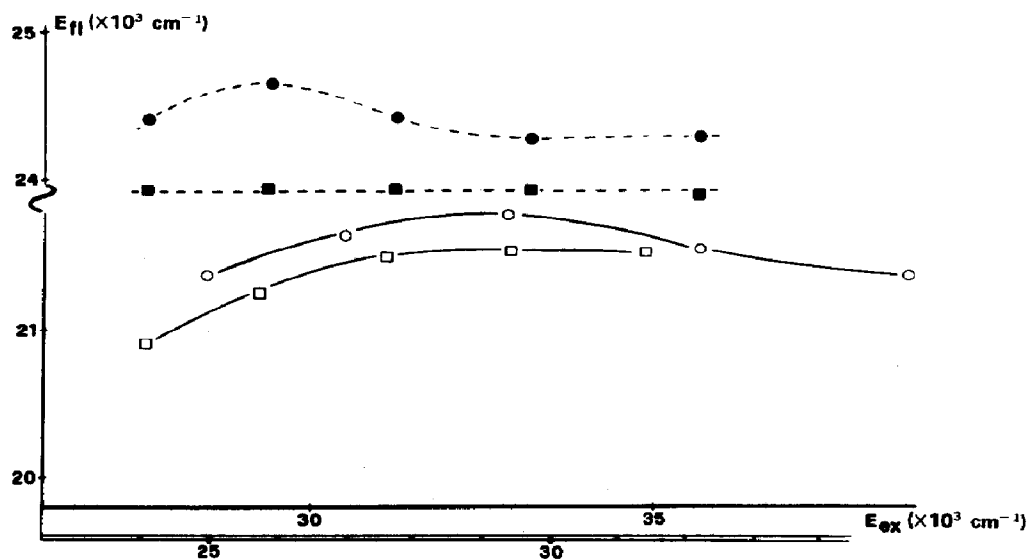


Fig. 2. Dependence of the fluorescence emission maximum on the excitation frequency (on the abscissa the upper scale and lower scale refer to 1-NA and 4-AP respectively): ■, 1-NA-acetonitrile (at -65°C); □, 4-AP-DMF (at -76°C); ●, 1-NA-EtOH (at -120°C); ○, 4-AP-EtOH (at -118°C).

by those molecules frozen in the energetically most favourable matrix cage configurations; this results in the *parallel shift* (i.e. the fluorescence frequency shift is parallel to the excitation frequency) also observed in some polymeric systems [3]. This shift covers only a narrow wavelength region, leading eventually to a region where the fluorescence spectrum shows no further change with excitation wavelength. Hence, for all these cases there is no clear-cut evidence for local melting of the matrix, even with excess energies up to 2 eV.

However, a different result is obtained in polar protic matrices such as 1-NA-EtOH or 4-AP-EtOH; the above parallel shift due to site selection is followed clearly by a *red shift* with increasing excitation frequency, also leading eventually to a wavelength-independent region (Fig. 2). Although

a spectroscopic origin (*e.g.* modified site selection) of this antiparallel shift cannot be excluded at this stage of the work, we are inclined to conclude that it truly reflects local matrix softening since it disappears as the temperature of the matrix is lowered far below its melting point.

It is noticeable that this red-shift region has been found only for solute-solvent systems characterized by a strong specific association in the form of hydrogen bonding. Even here, however, it falls far short of anything attributable to extensive local melting, since the fluorescence spectrum stays considerably blue shifted from its position in the liquid solvent.

To summarize, the results obtained so far indicate the following.

(i) In general, there is no detectable rearrangement of the matrix shell attributable to local heating due to the release of energy during radiationless deactivation, even when this energy is in excess of 2 eV.

(ii) In systems characterized by specific solute-solvent associations, indications of a slight rearrangement of the solvent shell are found.

(iii) In no case has a true local melting been found in the sense that the situation in the liquid solvent is realized.

For specific associations such as hydrogen bonding it may be that the energy is conducted from the solute to the solvent specifically through that link resulting in a high energy concentration in a limited space around the solute. In the absence of specific associations all the molecules of the solvent shell are essentially equivalent, the excess energy being distributed over a much larger space. Nowhere is its density high enough to produce mobilization of the solvent molecules. It may be noted that the general conclusion of the *absence* of local heating effects in solute-solvent systems free of specific associations agrees qualitatively with the result of recent investigations [4] aimed at the observation of photoinduced structural relaxation and isomerization of ion radicals in rigid matrices at 77 K. Here, however, the observation of local melting effects was even more unlikely, since the temperature of the matrix was well below its melting point. Some important questions remain concerning the general fate of the energy liberated during radiationless deactivation in the condensed phase, in particular the time scale of its conduction from the first solvation shell to the bulk of the solvent.

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