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TIME-RESOLVED SPECTRA OF AN INTRAMOLECULAR EXCIPLEX

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Summary

The intramolecular exciplex formed from N,N-methylphenyl 2-ethyl-(2-naphthoyl)amine was studied by time-resolved emission spectroscopy using a cavity-dumped argon ion laser (wavelength, λ = 257.25 nm) and single-photon counting detection. The spectra, taken at several time delays after excitation, show that the excited amine (lifetime, τ_f = 1.78 ns) contributes to the exciplex formation. The excited naphthoate (τ_f = 7.98 ns) is the major species observed in the late-gated spectrum (31 ns after excitation), its lifetime being larger than that of the exciplex (τ_f = 4.27 ns).

The results obtained are explained on the basis of the existence of a static quenching and a slow dynamic quenching.

1. Introduction

Time-resolved emission spectroscopy has been used in studies concerned with the solvent relaxation of excited states [1]. In particular, Ware *et al.* [2] have used the technique to study the temperature-dependent spectral shifts of the aminophthalimides in alcoholic solvents.

The method of single-photon counting has also been used to measure the rate constant for exciplex formation [3, 4]. It is now well established that an exciplex may be formed by exciting either partner of a given electron donor–acceptor pair [5, 6].

We have reported [7] that, in the aminoester (I) shown in Fig. 1, the exciplex/monomer intensity ratio varies with excitation wavelength, and the ratio increases when the excitation is essentially in the aniline chromophore.

In order to obtain more information regarding the excited state responsible for exciplex formation in this compound, we used the technique of time-resolved emission spectroscopy, and found that the excited amine is effective in forming the exciplex.
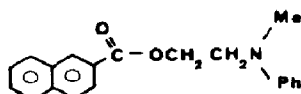
Fig. 1.

2. Experimental

The time-resolved fluorescence spectrometer used has been described previously [8] and consisted of a frequency-doubled and cavity-dumped argon ion laser for excitation and for single-photon counting detection. Excitation was at a wavelength of 257.25 nm and the fluorescence resolution was 0.5 nm.

The sample (I) was dissolved in cyclohexane (purified by passing three times through a silica column) such that the absorbance was 0.1 at a wavelength of 280 nm. The solution was thoroughly degassed by the freeze–pump–thaw technique.

Lifetimes were fitted to single- or double-exponential decay schemes using a non-linear least-squares convolution procedure on an ICL 1900 series computer.

3. Results and discussion

The total fluorescence spectrum of (I) is shown in Fig. 2. The time-resolved spectra, recorded 0,10.5 and 31 ns after excitation, are shown in Fig. 3. The lifetimes of the major emitting species at each wavelength are given in Table 1.

Using steady state fluorescence techniques [7], no emission of the aniline chromophore could be detected in this compound. However, using the experimental conditions described here, the total fluorescence spectrum showed a broad band lying under the emission of the naphthoate ester. This broad band could be assigned to the aniline chromophore and was consistent with the lifetimes measured and listed in Table 1. These indicate that there are three major emitting species present in solution: (1) that emitting at 315 nm corresponds to the amine moiety with a lifetime of 1.78 ns; (2) the well-structured emission centred at 350 nm has a lifetime of 7.96 ns and is attributed to the naphthoate chromophore; and (3) the broad structureless emission appearing at 440 nm should be due to the intramolecular exciplex with a lifetime of 4.27 ns.

At the excitation wavelength of 257.25 nm both the aniline and the naphthoyl chromophores will be excited, although the excitation is mainly localized on the amine. Energy transfer from the amine to the naphthoyl is possible and might be operating, given the fluorescence intensity of the naphthoate group at this wavelength.
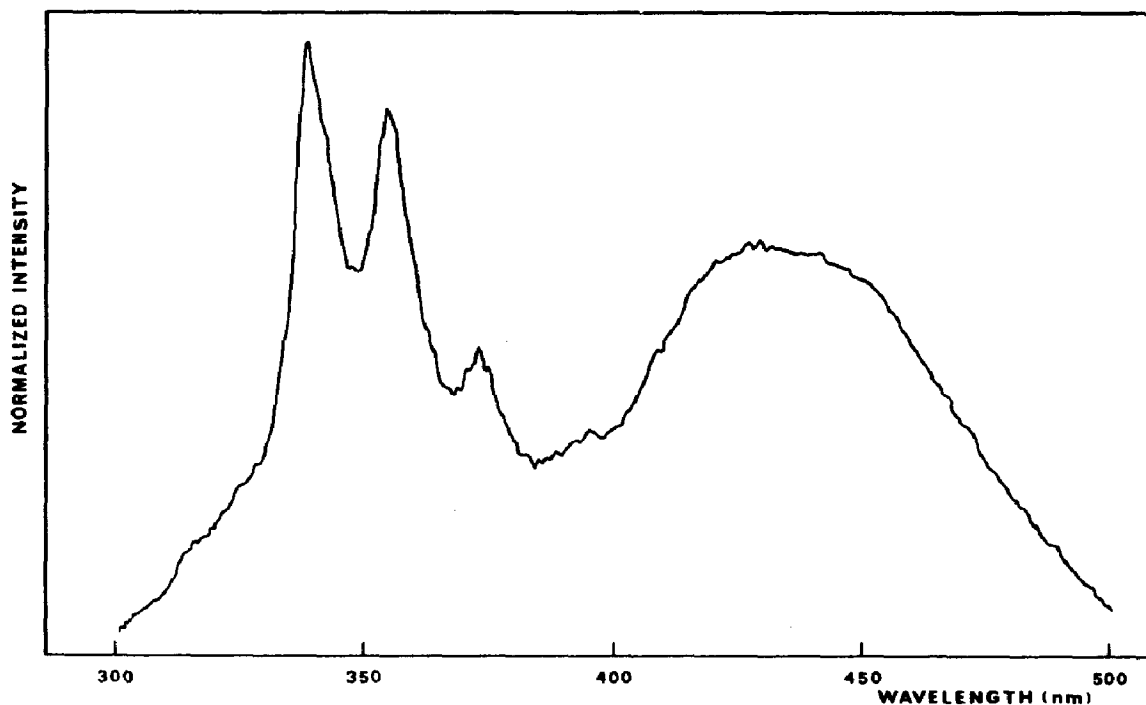
Fig. 2. The total fluorescence spectrum of (I) in cyclohexane. Resolution, 5 Å; λ_{exc}, 257.25 nm.

An early-gated time-resolved spectrum, with the gate positioned on the leading edge of the pump pulse and with a narrow gate width, is expected to discriminate in favour of emission from the unrelaxed system, and indeed the spectrum displays large amine and exciplex components superimposed on the naphthoate emission. After 10 ns (middle-gated spectrum) the amine and exciplex emissions have reduced in intensity leaving a noticeable naphthoyl fluorescence. The late-gated spectrum shows mainly naphthoyl emission with little evidence for exciplex emission.

Assuming that the quenching is purely dynamic when both chromophores are initially excited the exciplex could originate from either the donor (amine) or the acceptor (ester), but in both cases bimolecular formation of the exciplex must compete with the radiative and non-radiative decay of the chromophore. Since the amine lifetime is very short, exciplex formation from the longer-lived naphthoate would be favoured on the basis of this argument. However, the spectra obtained suggest that when the excitation is essentially localized in the amine chromophore the exciplex is preferentially formed from the excited amine and not from the excited naphthoate, since a significant exciplex component would be expected in the late-gated spectrum if the naphthoate chromophore were involved in a dynamic intramolecular exciplex formation. The magnitude of the lifetime of the exciplex supports this conclusion.

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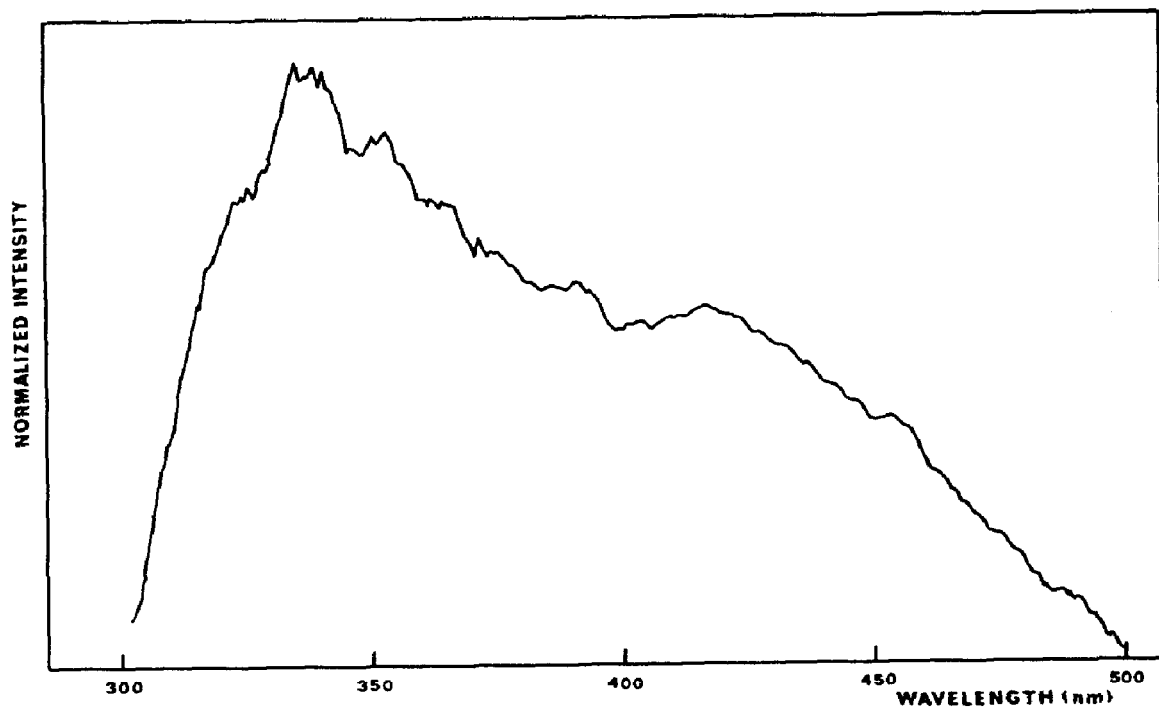
(a)
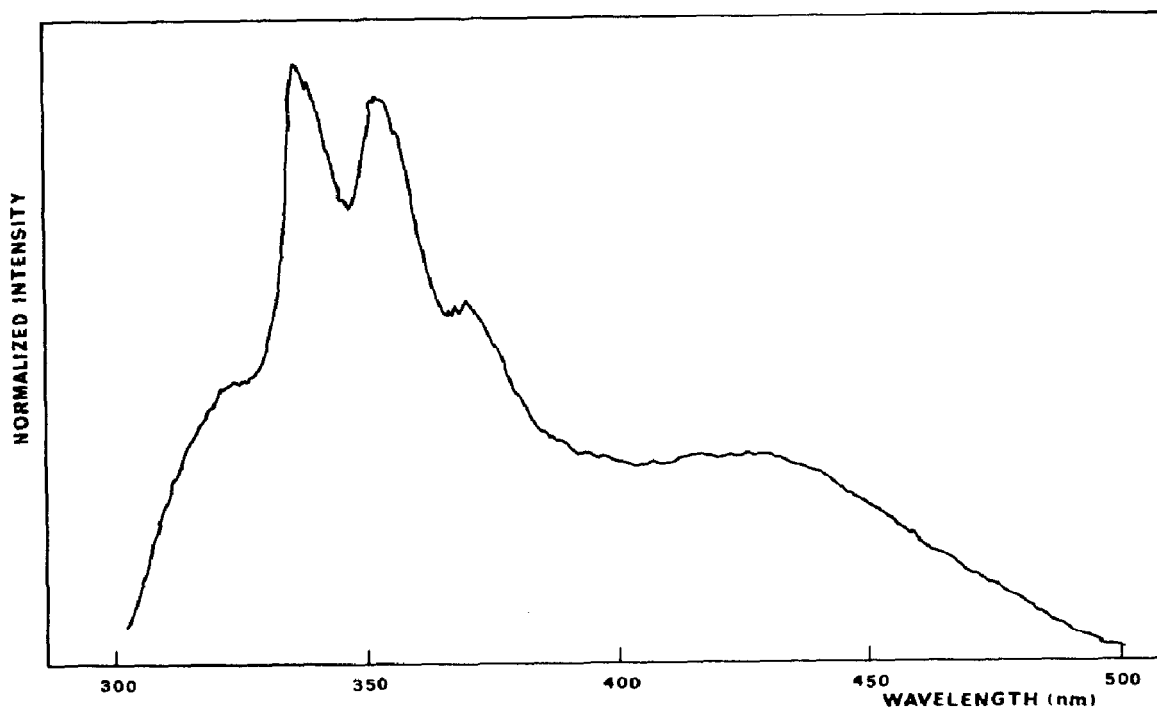
(b)
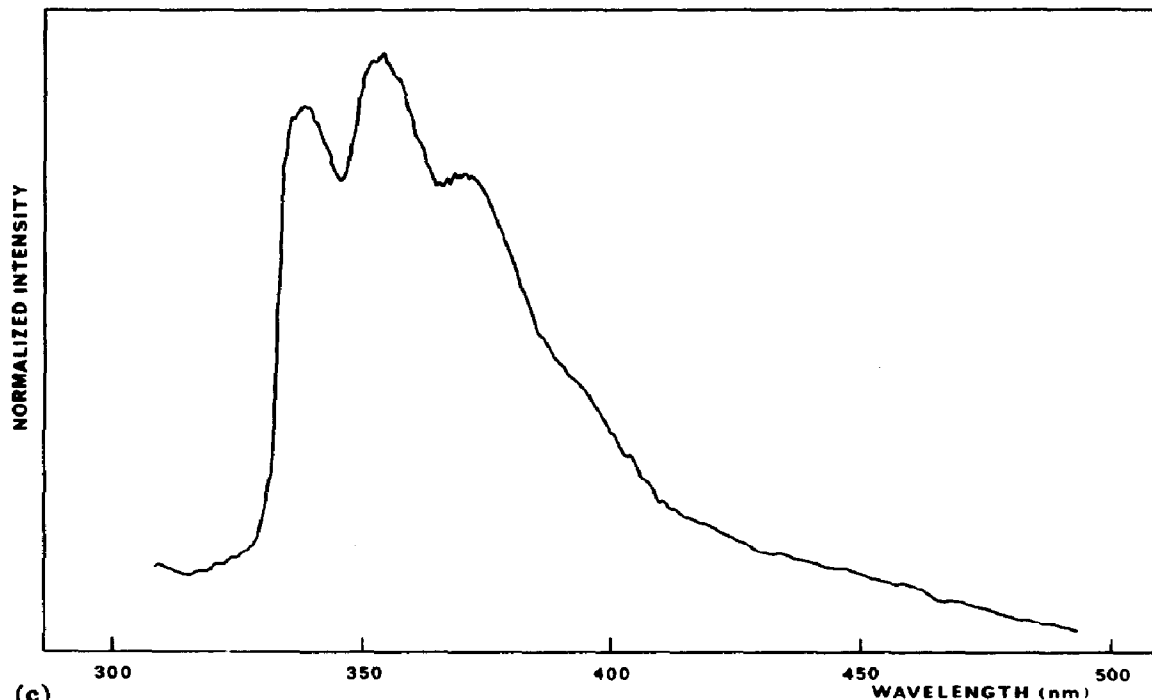
(c)

Fig. 3. (a) Early-gated spectrum: Δt (time delay) = 0, δt (gate width) = 3.8 ns; (b) middle-gated spectrum: Δt = 10.5 ns, δt = 1.5 ns; (c) late-gated spectrum: Δt = 31 ns, δt = 3 ns.

The results obtained do not exclude the possibility of exciplex formation from the excited naphthoate but imply that the excited amine, in spite of its shorter lifetime, is more effective in forming the exciplex. On the basis of a dynamic quenching, the data obtained are consistent with the transfer of excitation to the naphthoate following a mechanism

$$\text{Aniline}^*\!\sim\!\!\sim\!\!\sim \text{naphthoate} \longrightarrow (\text{D}^+\text{A}^-) \longrightarrow \text{Aniline} \sim\!\!\sim \text{naphthoate}^*$$

since in this case the exciplex emission as an intermediate species would not contribute to the late-gated spectrum and the lifetime of the exciplex would be shorter than that of naphthoate, as is observed.

TABLE 1

Lifetimes of (I) measured at different wave-lengths

$\lambda_{emission}$ (nm)	A^a	τ_f (ns)
315	0.060	1.78 ± 0.02
338	0.031	7.96 ± 0.02
440	0.044	4.27 ± 0.02

$^aF(t) = A\,e^{-t/\tau}$

However, the foregoing mechanism implies exciplex reversibility which, as has been pointed out in ref. 7, can be ruled out both on thermodynamic grounds and from the observed exponential naphthoate decay. Moreover the ratio ϕ_0/ϕ (≈ 250) is much larger than the ratio τ_0/τ (≈ 1.7) (ϕ_0 and τ_0 refer to the methyl naphthoate).

Therefore it seems necessary to invoke the existence of a static interaction, in agreement with our earlier reports [7]. The exciplex observed in the early-gated spectrum essentially originates from a static quenching and this explains the efficiency of the amine for the exciplex formation. While the naphthoyl fluorescence emission is observed in the late-gated spectrum, the absence of a significant exciplex emission may be explained as follows:

(1) the steady state measurements indicate a very low exciplex quantum yield;

(2) the approach of both chromophores, implying the bending of a molecular chain, is slow [9, 10] and the unimolecular deactivation pathways from the excited naphthoate are very competitive in this case.

Nanosecond emission spectroscopy thus supports our earlier observations that the interaction in this system has both static and dynamic contributions.

Further support for our conclusions will be provided by kinetic studies of this and similar systems which will be reported in a full paper.

Acknowledgments

References

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