

RELAXATION PROCESSES IN POLAR SOLUTIONS OF THE NAPHTHALIMIDE DERIVATIVES

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Received June 26, 1997*

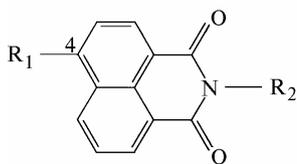
A mechanism of intramolecular conversion of the energy of light excitation by naphthalimides has been studied when their gain and induced absorption spectra have been analyzed with picosecond resolution. It is shown that the TICT state is formed in polar solvents, which affects the fluorescence and lasing spectra. A very fast gain (<2 ps) from the TICT state suggests the occurrence of a complex in the ground state, which precedes the formation of the TICT state.

Naphthalimide derivatives are being increasingly employed in practice as photostable dyes and luminophores¹ and active laser media.²⁻⁴ They also attract more and more attention of researchers. Naphthalimides differ from other organic compounds by a strong dependence of their absorption and fluorescence spectra, duration of fluorescence and its quantum yield (by an order of magnitude or more) on the solvent type. They also possess large Stokes shifts and are highly photostable.

These characteristics change most significantly for polar solvents. Quantum yield of fluorescence of polar solvents sharply decreases and their fluorescence spectra greatly shift toward longer wavelengths. Spectral and luminescent characteristics of naphthalimides depend only weakly on the structure of a substitute attached to nitrogen and are largely determined by a substitute attached to the naphthalene root. It has been found that the long-wave absorption band is connected with intramolecular charge transfer caused by electron interaction of substitutes in 4-naphthalene ring with a system of carbonyl groups.

The present paper is aimed at the study of the mechanism of intramolecular conversion of the energy of light excitation by the naphthalimide derivatives in polar solvents.

The compounds with the common formula



were studied, where R_1 and R_2 are the substitutes, namely, 4-morpholino-N-(o-tolyl)-1,8-naphthalimide

(compound I), 4-(*n*-octylamino)-N-(*n*-hexylphenylene)-1,8-naphthalimide (compound II), and 4-(*n*-benzylamino)-N-(*n*-nitrophenylene)-1,8-naphthalimide (compound III). Ethanol, acetonitrile, and toluene of XC brand as well as N, N-dimethylformamide (DMF) subject to additional drying by the molecular sieve method were used as solvents. The absorption and fluorescence spectra were studied along with the duration of fluorescence and its quantum yield as well as temporally resolved gain and induced absorption spectra and the kinetics of optical density of solutions in a narrow spectral range.

The fluorescence spectra of solutions at room temperature were registered with the SFL-1211A pulsed fluorimeter, the absorption spectra were registered by the Beckman UV-5270 spectrophotometer, and the fluorescence decay times were measured by the PRA-3000 fluorimeter. The quantum yield of fluorescence was calculated from the measured duration of fluorescence and the radiative lifetime⁵ calculated from the absorption spectra. Investigations were performed with picosecond temporal resolution by the standard procedure of excitation and sensing with the use of an automated picosecond spectrometer.⁶

Samples were pumped by pulses of the third harmonic of a neodymium laser on a wavelength of 352 nm with a 3-ps duration. Sensing was carried out by the broadband continuum radiation between 400 and 800 nm of the same duration. The induced absorption and gain spectra were registered with a multichannel analyzer during 100 laser shots. The kinetics of the optical density of samples in a narrow spectral range selected with interference filters was measured with a two-channel power meter interfaced with a microcomputer.

TABLE I. Photophysical characteristics: wavelengths of the maxima in the absorption ($\lambda_{\text{abs}}^{\text{max}}$), fluorescence ($\lambda_{\text{fl}}^{\text{max}}$), and gain ($\lambda_{\text{g}}^{\text{m}}$) spectra, quantum yield (γ) and duration (τ) of fluorescence of the examined naphthalimide derivatives in various solvents with dielectric constant ϵ .

Compound	Solvent	ϵ (from Ref. 7)	$(\lambda_{\text{abs}}^{\text{max}})$, nm	$(\lambda_{\text{fl}}^{\text{max}})$, nm	τ , ps	γ	$(\lambda_{\text{g}}^{\text{max}})$, nm
I	Ethanol	24.55	407	544	0.8; 8.3	0.09	532 (574)
	DMF	36.71	412	542	0.7; 9.6	0.09	570
	Acetonitrile	35.9	397	542	3.1; 5.3	0.23	552
	Toluene	2.38	391	492	7.6	0.59	511
II	Ethanol	24.55	444	547	8.6	0.62	537 (557)
III	Ethanol	24.55	442	530	7.9	0.63	537 (545)

Table I tabulates the spectral and luminescent characteristics and positions of the maxima in the gain spectra of the examined compounds. It should be noted that their spectral and luminescent characteristics are analogous to that of naphthalimides studied earlier.²⁻⁴ The absorption and fluorescence spectra are characterized by the occurrence of wide structureless bands whose positions are determined by the polarity of the medium. The fluorescence spectra of polar solvents are greatly shifted toward longer wavelengths and the duration and quantum yield of fluorescence are significantly decreased. Additional impact of specific interactions is manifested for ethanol solutions through greater shifts of spectra in comparison with acetonitrile and DMF. These properties are most pronounced for compound I. When the ethanol solution is frozen, the mobility of the fragments of the molecule is sharply limited and the fluorescence spectrum is shifted toward shorter wavelengths.⁸

Analogous behavior is typical of the molecule of the type donor-electron acceptor joined by a single bond.⁹⁻¹³ This is connected with the presence of two interconvertible molecules. When the fragments of the molecule can rotate freely, the transition from the excited state to the ground one is competitive in character and the planar (or partly bent) excited molecule with intramolecular charge transfer (ICT) is converted into the bent one (through the turn of the donor and acceptor fragments of the molecule in the orthogonal configuration), which then translates into the ground state with or without photon emission (so-called TICT state). It is common that the long-wave fluorescence band corresponding to this bent state depends strongly on the polar solvent. The compounds examined by us also have electron-donor substitutes joined by a single bond with the residual of the naphthalimide molecule which plays the role of electron acceptor. It is also probable that these substitutes are slightly turned around the molecular carcass already in the ground state.¹⁴

Measuring of the gain and induced absorption spectra with picosecond resolution allows one to study in detail intramolecular processes in polar solutions of naphthalimide derivatives. Figure 1 illustrates the

spectra of the optical density of compound I in excited state dissolved in toluene (*a*), ethanol (*b*), DMF (*c*), and acetonitrile (*d*) as functions of time. High optical density of the sample between 400–480 nm, where the long-wave absorption band lies, results in complete absorption of the sounding continuum radiation and it became impossible to study the behavior of the induced absorption spectrum. An intense positive signal is recorded between 500–600 nm.

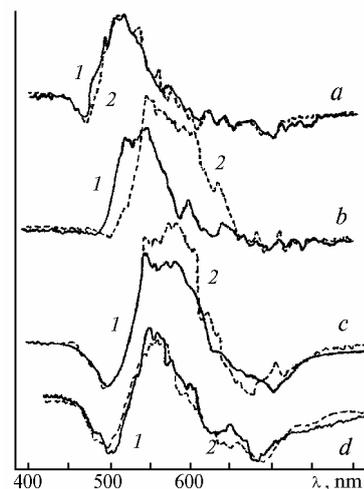


FIG. 1. Gain and induced absorption spectra of compound I dissolved in toluene (*a*), ethanol (*b*), DMF (*c*), and acetonitrile (*d*) 3 (1) and 100 ps (2) after the excitation pulse termination.

The absorption from the ground state is absent in this spectral range, so we attribute this signal to the gain of sensing radiation in the fluorescence band. Then between 600–750 nm, and in some cases in the short-wave part of the gain spectrum, the wide structureless absorption band is recorded. Because it is manifested on both sides of the gain spectrum, we believe that this is a single wide absorption band overlapped with the gain spectrum. This absorption vanishes fast with time. Hence, it can be attributed to the absorption from excited singlet states of the

naphthalimide molecule. The highest intensity of this absorption was recorded for compound I dissolved in DMF or acetonitrile and the lowest one – in the ethanol solution.

The form of temporary resolved gain spectra of compound I dissolved in weakly polar toluene (Fig. 1 *a*) remains practically unchanged with time. The short-wave portion of the gain spectrum is strongly manifested. It has the maximum which coincides with the maximum of the fluorescence spectrum (see Table I) and its rise time coincides with that of the instrumental function (Fig. 2 *a*).

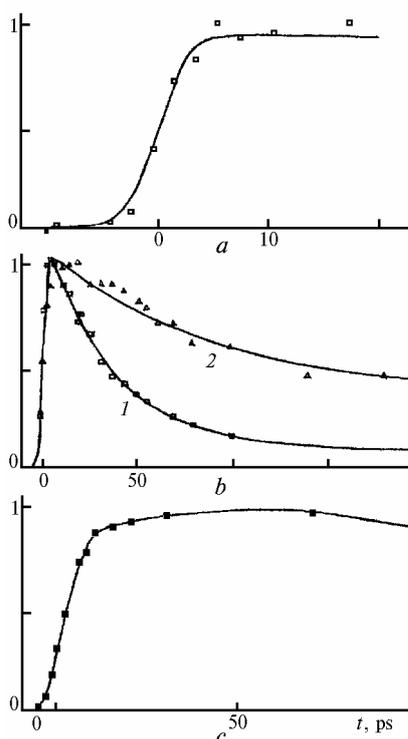


FIG. 2. Kinetics of variations of the optical density for compound I dissolved in toluene (*a*), ethanol (*b*, 1), propanol (*b*, 2), and acetonitrile (*c*).

For ethanol solution (Fig. 1 *b*) the gain spectra recorded at different times after the termination of the excitation pulse differ. First, the short-wave spectrum is recorded, then the long-wave one whose intensity decays with time. Figure 2 *b* shows the kinetics of decay of the short-wave spectrum which, as our measurements show, represents the kinetics of the build-up of its long-wave portion. Moreover, in more viscous propanol this process slows down (the rise time estimated from the results of comparison of the obtained experimental dependence with a model curve increases from 35 ps for ethanol to 90 ps for propanol). The short-wave band is observed immediately after the excitation in ethanol and propanol as well.

The gain spectra of this compound dissolved in polar proton-acceptor DMF and acetonitrile (Fig. 1 *c* and *d*) remain unchanged with time and have only

long-wave portion. Kinetics of its build-up coincides with the instrumental function (Fig. 2 *c*). The positions of the maxima in the gain spectra of compound I dissolved in the examined polar solvents approximately coincide with the maxima of the fluorescence spectra and the fluorescence decay time is much smaller than for nonpolar toluene.

Similar behavior was observed for compounds II and III dissolved in ethanol (Fig. 3); however, the short-wave gain band was less pronounced.

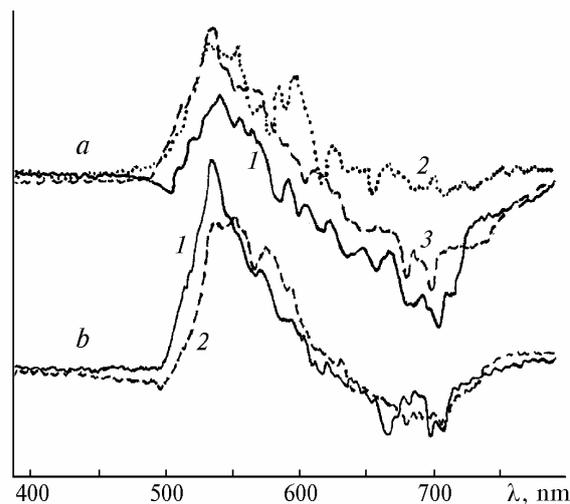


FIG. 3. Spectra of variations of the optical density ΔD of compounds II (*a*) and III (*b*) 3 (1), 150 (2) and 60 ps (3) after the excitation pulse termination.

Our experimental results testify to the formation of the TICT states of polar solutions of naphthalimide derivatives. However, fast gain of the TICT state ($\tau < 2$ ps), which practically coincides with the instrumental function of the spectrometer, for such low-viscous solvents as acetonitrile and DMF is difficult to interpret in the context of classical conception that suggests the planar configuration of the molecule in the ground state and the orthogonal configuration in the excited state. Turning through the large angle should take definite time and should be manifested in the experiments through kinetics. The assumption that the molecular configuration has already been torquated at a large angle (as demonstrated in Ref. 15, the angle of torsion may be as large as 600) leads to the conclusion that the turn into the orthogonal configuration can occur only in sufficiently viscous solvents.

Calculations of Soujanya et al.¹⁶ made for aminophthalimide demonstrated that in acetonitrile the conditions are favorable for torsion of the molecules of this type, because the height of the barrier ΔE between the ICT and TICT states is small (it is equal to 0.06 eV for aminophthalimide). It is shown that as the polarity of the solution increases, the height of this barrier increases, thereby increasing the rate of turn. The time of formation of the TICT state for ethanol solutions is

35 ps, which is much greater than for acetonitrile or DMF, though ethanol has a lower degree of polarity. This is connected with solvation¹⁷ which plays an important role for proton-donor solvents and increases the height of the barrier ΔE .

Thus, application of the methods of picosecond kinetic spectroscopy to the study of dynamics of relaxation processes in naphthalimide derivatives dissolved in various solvents has allowed us to establish that the TICT state is formed in polar solutions of these compounds, which affects the spectra and efficiency of fluorescence and lasing.

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