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Spectral broadening and red edge excitation effect in liquid and viscous solutions of DMABN

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ABSTRACT

Effect of intensity redistribution of two fluorescence bands of N,N'-Dimethylaminobenzonitrile in polar solutions of the different viscosity was studied using selective UV irradiation over the red edge of the main absorption band. The effect being depends on temperature and viscosity, indicated eloquently strong inhomogeneous spectral broadening appearing at the red edge excitation. The conformational broadening exists for electronic transitions in the range of the local excited short wavelength band with weak change of electric dipole moments of the solutes. It was found that the spectral conformational broadening may exists independently on the orientational broadening which is due to the change of solute electric dipole moments in polar media and of thermal environmental fluctuations. When different conformers are excited into upper singlet levels, there is no fast dissipation of excitation energy over different conformational sublevels compared to the charge transfer reaction rates. In this case fluorescence and the charge transfer reaction occur from Franck-Condon sublevels with different rates.

1. Introduction

Excitation of molecules is usually accompanied by considerable redistribution of their electron density in the process of electronic transitions. In some systems, this process continues in the excited state due to a geometry change of a molecule, which leads to a change in its characteristics, including electric dipole moments, and relates to the intramolecular charge transfer (CT) and formation of new conformations. The excited-state CT processes in organic compounds and their complexes belong to the most frequently observed primary photoreactions [1–10]. These processes manifest themselves in pure form or they are directly related to other photoreactions, preceding them or occurring at the final stage. Typical examples are the intramolecular proton transfer in the 3-hydroxyflavone derivatives and in numerous other chemical compounds [5–7].

Understanding CT processes is of fundamental importance in chemistry and biology since they play a key role in major photosynthetic reactions of plants and in the functioning of various biological organisms. Today, these processes are also extensively used for various molecular probes techniques for investigating the local characteristics of samples in the region of probe penetration as CT- intramolecular reactions occurring in individual molecules strongly change their physical - chemical parameters. Therefore, the CT states may exhibit efficient emission, in particular, the so-called dual fluorescence [2–7]. The study of the properties of the dual fluorescence allows a researcher to get detailed information not only about CT characteristics, but also about the most important properties of the very close environment on the nanometer scale.

Therefore, the dual fluorescence is an efficient method of investigating numerous molecular systems, including the most important biological molecules and cells.

The foregoing explains the great attention which was paid in recent decades to intense study of the primary CT - reactions in numerous systems, both models and natural objects.

Organic chemists have learned to synthesize efficient systems with CT and proton transfer using substitution by electron–acceptor and electron–donor groups. These systems are widely used as light converters, laser elements, fluorescent molecular probes, and as devices for conversion of light energy into electric energy.

Usually, the donor–acceptor systems can exhibit dual fluorescence

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Abbreviations: CAN, acetonitrile; ASIGM, the asymmetric double sigmoid function; CB, the conformational broadening; CT, the intramolecular charge transfer; DMABN, *N,N′*-dimethylaminobenzonitrile; ESIPT, the excite state internal proton transfer; F, C transition - Franck-Condon transition; IB, the inhomogeneous broadening; LE, the local excited state; ME_2 group, dimethylamino group; OB, the orientational broadening; PICT, the planar intramolecular charge transfer; REE spectroscopy, the red-edge excitation spectroscopy; TICT, the twisted intramolecular charge transfer.

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Nomenclature

λ_a, λ_{LE} and λ_{CT}	are maximum positions of absorption, LE and CT bands, respectively
$\Delta\lambda = \lambda_{CT} - \lambda_{LE}$	is the band separation
λ_{ex} and are λ_{reg}	are the excitation and the registration wavelengths, respectively
I, w	the maximum band intensity and its full width at the half maximum (FWHM), respectively
$R_I = I_{LE}/I_{CT}$	is the intensity ratio of the LE and CT bands
R_p	is the ratio of the integral intensities of the LE and CT bands (the ratiometric parameter)
τ	is the lifetime
μ	is the electric dipole moment
φ	is the twist angle
k	is the reaction rate
τ	is a lifetime
μ	is the electric dipole moment
φ	is the twist angle
k	is a reaction rate
T_S	is the effective Stepanov's temperature

in polar solvents; i.e., their fluorescence spectra contain, in addition to the local excited state (LE), the second band shifted towards the red part of the spectrum. This band belongs to the CT structure. In benzontriles LE and CT band are referred to the transitions from ^1L_b and ^1L_a states, respectively [4].

The archetype of the molecules which manifest dual emission is N,N′- dimethylaminobenzonitrile (DMABN). Its dual fluorescence was firstly described by [5] and until now this object attracts a lot of attention [4]. The origin of the CT band is still under discussion [4]. The twisted intramolecular charge transfer (TICT) [11] and the planar intramolecular charge transfer (PICT) [12] models are most frequently discussed.

The TICT model suggests that the short-wavelength band is emitted by a LE - Franck–Condon (FC) state with an intermediate polarity. At the same time, the long-wavelength band belongs to spontaneous emission of the strongly polar CT state, which is formed due to adiabatic reaction. In the polar environment CT state is stabilized due to the rotation of the $(ME)_2$ group by 90° around the single bond between this group and benzonitrile (twist state).

This concept put forward by Grabowski et al. [11] is generally recognized [4].

CT state is separated from the LE state by a large energy barrier and it is not populated in low-polarity environment. Since in the polar solvent the energy of the polar CT state decreases, due the solvent-induced stabilization the barrier between the LE and CT states also decreases. As a result, the CT level begins to be populated which leads to fluorescence. If the polarity increases then the barrier between these states decreases and the long-wavelength fluorescence band becomes more intense. The most important feature of the planar CT model is the planarization of the $(ME)_2$ group due to the efficient vibronic coupling between two excited states.

The features of the energy states in DMABN and its derivatives has been carefully studied, but has not yet been unambiguously identified [4].

An essential addition to the traditional methods is the red-edge excitation (REE) spectroscopy, which allows researcher to detect the heterogeneity of spectral centers. For example, it has been found [13] that the REE at absorption wings of samples of some derivatives of benzonitriles in polymer matrix significantly increases efficient emission from the CT states. This effect was explained both by existence of conformers in the ground, so-called, pretwisted state with different twist angles, and by the polymer structure. This structure contains free volumes allowing realization of the TICT mechanism responsible for the CT fluorescence band [13]. Similar effect was observed for molecules of pyrrolidine derivatives of benzonitrile in propanol solutions. It was explained using the stochastic diffusion model [14].

Although the REE spectroscopy is efficient method of investigation of complex molecules in solutions and other heterogeneous media, it did not find wide practical applications in photochemistry.

In this context, further study of CT - molecular systems [1–10] is of a great significance for better understanding of the CT mechanism and of the properties of these systems.

The goal of this study is a thorough and systematic investigation of absorption, dual fluorescence and its excitation in DMABN solutions which viscosity is changed with temperature variation. As a working tool, the REE spectroscopy has been used.

For a better understanding of the problem, the following remarks should be made.

It was found [16,17] that in liquid non-viscous acetonitrile (ACN) solvent decrease in the excitation photon energy in the region of the long wavelength tail of the main absorption does not change the shape of individual bands in emission spectra. However, the intensity ratio of the bands is noticeably redistributed in favor of the CT band. These effects clearly manifest themselves within the temperature range 274–353 K. Therefore, the spectral characteristics indicate the REE effects, which were previously observed as a rule, in viscous media or in the case of induced lifetime shortening of the excited state.

Therefore, we choose those experimental conditions which best meet our needs to demonstrate the REEE and fine details of the band broadening.

Two solvents which polarity close to each other but the viscosity is different, ACN and viscous glycerol were taken. The experiments were performed in the temperature range of 274–353 K.

It was found that REE effects in glycerol manifest themselves more emphatically showing strong spectral broadening in emission and excitation spectra. Main features of the band broadening were found using newly developed decomposition algorithms of electronic spectra [17,18].

It is unusual that REE effects were observed in the non-solvatochromic LE band within above temperature range. This observation confirms our suggestion based on the conception of conformational mechanism of spectral inhomogeneity [15,16].

Also it has been confirmed that the conformational broadening (CB) of electronic spectra presents additional mechanism apart on the fluctuational spectral broadening which depends on the change of constant dipole moments of solutes electronic states in polar media. In turn, the CB is possible only in the framework of solute models that admit the possible existence of conformers or rotamers differing in their spectral properties.

2. Experimental

We used solutions of DMABN (Aldrich Chemicals) (the concentration was 10^{-5} M) which was additionally purified by recrystallization and by thin-layer chromatography.

The fluorescence emission and the fluorescence excitation spectra were measured by Hitachi F 2500 spectrofluorimeter. The absorption spectra were measured by Hitachi U-2810 spectrophotometer. The solvents (Aldrich Chemicals, spectroscopic purity grade) had negligible emission of impurities for the excitation in the wavelength range 280 – 320 nm. The measurements were performed at the temperature range 274–333 K (with accuracy ± 0.5 K). The luminescence was recorded using common scheme: the excitation beam was in a 90° angle with the detector. Spectra were obtained by averaging of 3 repetitions of each