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Annihilation of the triplet excitons in the nanoporous glass matrices

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ABSTRACT

The spectra and kinetics of fluorescence decay of 1,2-benzanthracene (1,2-BA) molecular clusters adsorbed in nanoporous borosilicate glasses were investigated. It has been shown that the type of the decay kinetics of delayed fluorescence is determined by the annihilation of triplet excitons in crystalline and percolation clusters. The influence of an external magnetic field on the annihilation rate constant of triplet excitons in the adsorbed 1,2-BA molecules has been studied. The response of the molecular clusters to the magnetic field strongly depends on temperature, pore size and time scale of the observation. Clusters with the crystal structure dominate in the decay kinetics of triplet–triplet annihilation (TTA) and delayed fluorescence in the initial microsecond period of time after excitation. Amorphous clusters determine the form of decay kinetics of delayed fluorescence in the millisecond range. The increase in the pore size and concentration of the adsorbate lead to the dominance of crystalline components. The results presented here can be used to develop techniques for probing the structure of the adsorbed layer in nanoporous systems examining the effect of an external magnetic field on the annihilation delayed fluorescence (ADF) kinetics.

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1. Introduction

Processes of transformation of electronic excitation energy in homogeneous bulk media are well studied, both theoretically and experimentally [1,2]. Effects of the confined space on these phenomena have received less attention, although such objects include porous matrices, colloids, micelles, Langmuir–Blodgett (LB) films and nanoparticles. Common to all of them is the fact that the dimensions of the confined space, in which these processes take place, are comparable to the size of the embedded species and the photoreaction kinetics in such systems cannot be described by classic equations of formal chemical kinetics [3,4]. At present, interest to photoprocesses in confined space at nanoscale is rising owing to the progress in nanotechnology and nanomaterials. One can expect to observe non-traditional kinetics for molecular reactions in small spatial domains of nanostructured systems [5–9].

The reaction of spin-selective triplet–triplet annihilation can influence the optical properties of molecular crystals [10,11], liquid

solutions [12,13], polymers [14], and micellar systems [15]. The role of TTA in deactivation of the excited electronic states of electroluminescent substances was proven [16,17].

Theoretical models of TTA in homogeneous environments were developed in the classic works [10,13,18,19]. In Refs. [20,21] the competitive effect of the magnetic field and the external heavy atom on the TTA in solution was experimentally studied. The theoretical interpretation of the effects of the spin–orbit interaction and magnetic field in the triplet pairs were given in Refs. [22–25]. In Ref. [26], the larger change in the intensity of the annihilation delayed fluorescence in the magnetic field was registered for two-component systems. It was explained by the fact that the annihilation proceeds through the stage of charge transfer [22].

More refined interpretation of experimental data on TTA was presented later [27–30]. The system dimension effects in TTA were studied [4,31,32]. Using the statistical approach and a Monte-Carlo method it was shown that the TTA rate constant depends on the dimension. The nonexponential kinetics of triplet–triplet annihilation delayed fluorescence in LB films was described using a combination of formal-kinetics and percolation models [33,34]. The effect of disorder on the process of TTA and the values of the observed magnetic effects are given in Ref. [35]. Simple analytical

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expressions are given in this article. They allow to estimate the degree of disorder of the structure and total annihilation probability.

It is known that annihilation of triplet excitons proceeds according to the following reaction:

TTA process is sensitive to the external magnetic field [1,10,11]. An external magnetic field effect the evolution of the total spin of triplet pairs. Thus, three of nine possible combinations of the triplet pairs in the zero-field have triplet component and only one combination represents the singlet component. In a magnetic field, at the time of formation of the triplet pair, the spins combine in such a manner that the singlet component is distributed over a larger number of states of the pair and to six spin, combinations can include a singlet component. At high external magnetic field only two spin states of the pair have a singlet component. Thus, the triplet annihilation rate should first increase with increasing field, and then fall in strong fields up to a value less than in zero field.

Stage of spatial separation of excitons unreacted at the first meeting is an important step in the process of spin-selective pair annihilation of triplet excitons. After this stage triplet excitons can migrate separately up to possible repeated interaction. The change of total spin state of a coherent pair of excitons occurs in the meantime. This can lead to the formation of the desired spin component for the occurrence of TTA. At this stage the control of spin dynamics under the influence of an external magnetic field is possible for the implementation of the annihilation reaction. Probability of repeated meeting of reagents may depend on the spatial dimension of the system and efficiency of excitons migration.

The aim of this paper is to study the triplet–triplet annihilation in 1,2-benzanthracene molecules adsorbed on nanoporous glasses. One may expect that the pore size and topology of the inner surface would impose certain restrictions on the geometry

measuring low temperature (77.4 K) nitrogen adsorption–desorption isotherms at relative pressure p/p_0 from 10^{-4} to 0.99 with a Sorptomatic-1990 (Thermo Electron Corporation) adsorption analyser. Before measurements, samples were degassed at $\sim 10^{-3}$ Torr and 130 °C for 6–8 h to remove the surface moisture and other possible contaminants.

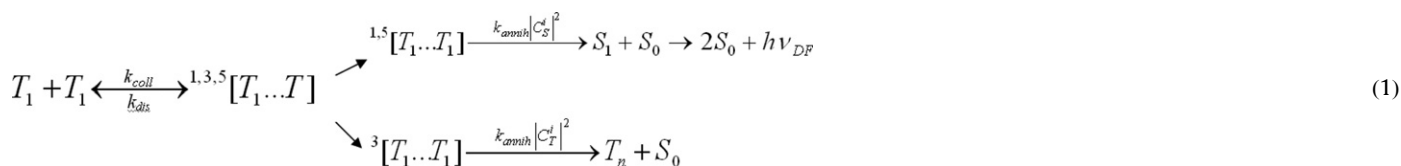
Specific surface area (S_{BET}) was determined by the Brunauer–Emmett–Teller (BET) method [36]. It was 116, 268 and 190 m^2/g for Glass I, II and III, respectively. Pore size distributions (PSD) were calculated using molecular non-local density functional theory (NLDFT) method with the cylindrical pore model [37] (Quantachrome software, version 2.02) (Fig. 1).

Aromatic hydrocarbon molecule 1,2-BA molecules was used as organic additive. The nature of the electron-excited states and spectroscopic properties of the 1,2-BA molecules were studied by various authors [38–41].

Adsorption of 1,2-benzanthracene molecules onto porous glasses was carried out from a hexane solution at concentration $C = 10^{-4} - 10^{-2}$ mol/l. A glass sample was placed in the solution for 1 h, and then it was dried in an oven for 2 h at 100 °C. The amount of adsorbed 1,2-BA molecules was determined from the optical density of the solution before and after sorption.

Photoexcitation of adsorbed 1,2-BA molecules was carried out by the third harmonic of a Nd laser LCS-DTL-374QT ($\lambda_{\text{ex}} = 355$ nm, $\tau = 7$ ns, $E = 5$ μJ). Spectral and kinetic measurements were performed in a photon counting mode. The temperature effects were studied by placing samples in an evacuated optical cryostat.

To determine the effect of the external magnetic field (EMF) the registration of the decay kinetics of delayed fluorescence was carried out with or without the EMF applied. Initially measurements were carried out five–ten times without the field. After that an electromagnet was switched on and the kinetics of the delayed



of the adsorbed molecular systems and the migration behaviour of triplet excitons. Direct contact of migrating triplet excitons at TTA and modulation of its rate by a magnetic field can be used as a sensitive tool for probing the structural features of nanoporous materials and specificity of the reactions in nanodisperse systems.

If the molecules in nanopores glass form clusters with a structure close to that of the crystal, the specificity of walks of triplet exciton in such clusters will be close to the dynamics of exciton migration in molecular crystals. It should lead to the magnetic effects that are characteristic of crystals. However, the structural disorder is present in the molecular clusters. In this case a temperature dependence of ADF and magnetic effects corresponding to locally inhomogeneous structures should be expected.

2. Experimental

Borosilicate glass samples with composition $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ (courtesy of Institute of Glass Chemistry, Russian Academy of Sciences) and three different pore sizes, 2.5, 3.9 and 11.1 nm, were used as the porous matrices denoted as Glass I, Glass II and Glass III, respectively, in the form of square slides, 5×5 mm^2 and 0.5 mm in thickness. Structural characterisation of glasses was carried out by

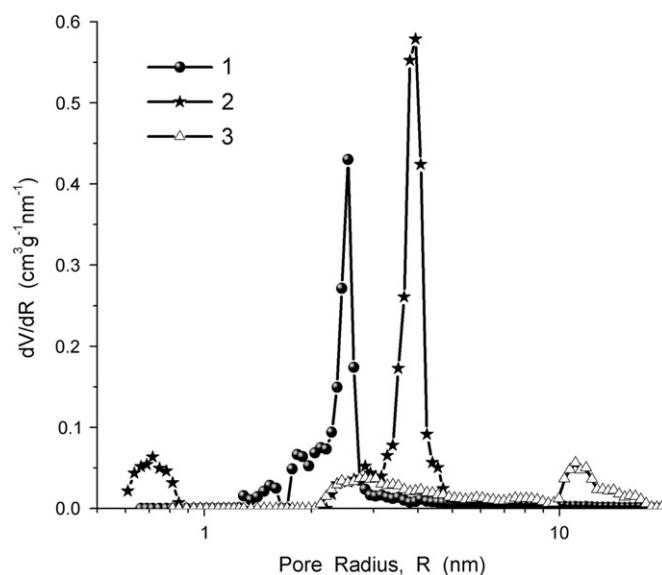


Fig. 1. NLDFT pore size distributions calculated with the model of cylindrical pores using the nitrogen adsorption–desorption isotherms for glasses I (1), II (2) and III (3) at $S_{\text{BET}} = 116, 268$ and 190 m^2/g , and average pore radius 2.5, 3.9 and 11.1 nm, respectively.

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