Journal of Luminescence 165 (2015) 174–178

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

The concentration dependence for X-ray excited luminescence in liquid phosphors

V.Ya. Degoda, V.G. Pivovarenko, I.M. Moroz *, D.Yu. Shilov

Taras Shevchenko National University of Kyiv, 01033 Kiev, Ukraine

ARTICLE INFO

Article history:
Received 18 September 2014
Received in revised form
1 April 2015
Accepted 22 April 2015
Available online 30 April 2015

Keywords:
3-Hydroxyflavone (3HF)
Luminophores
Concentration
Liquid phosphors
X-ray luminescence
Photoluminescence

ABSTRACT

An analytical form of concentration dependence of photo- and X-ray luminescence intensity in liquid phosphors is presented in this paper. Theoretically obtained dependences were compared with experimental results that were obtained for 3-Hydroxyflavone in toluene and acetonitrile solutions. The value of density of electronic excitations occurring in liquid phosphor after the absorption of X-rays was estimated. The results show that the solution of 3-Hydroxyflavone in toluene is not only an effective photo-luminophore but also an efficient X-ray luminophore, which make it possible to choose the optimal concentration of impurity molecules in order to obtain maximal scintillation impulse in practical applications of liquid scintillators.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Concentration dependences of optical absorption and photoluminescence (PL) quantum yield have been thoroughly investigated and as a result liquid phosphors [1] are widely used as scintillators [2,5]. However, a low intensity of X-ray luminescence (XRL) compared to very intensive PL remains the main problem that many researchers of liquid phosphors face. In general, the transfer mechanism of electronic excitation energy from the matrix (solvent) of liquid luminophore to luminescence centers (luminophore groups) remains poorly understood. Unfortunately, there is lack of information on analytical dependence of XRL intensity from concentration of photochromic groups, while concentration dependence of PL is well-understood, which was studied and documented in such reports as [1,6].

The dyes of the 3-Hydroxyflavone (3HF) group emit radiation in two bands. These bands are observed in fluorescence as two emission bands are allowed in dipole approximation: the blue–green and yellowish red bands. This property is associated with the reaction of Excited State Intramolecular Proton Transfer (ESIPT [2,7,8]) peculiar to 3HF in the excited state. The reaction scheme and Jablonski diagram for singlet transitions in the molecules of 3HF group are shown in Fig. 1.

When the exciting light irradiates the molecule, it becomes excited and reaches the excited state and the hydroxyl proton of the molecule transfers to the acceptor, another adjacent oxygen atom of the molecule, through intramolecular H-bond. The molecule transforms from the excited state of the normal form (N*) into the excited state of form T* and decays to the ground state, which is accompanied by the emission of fluorescence or by with a nonradiative transition, and then returns to the ground state of the normal form (N). Time-resolved studies have shown that this process of ESIPT is exceedingly fast, less than a picosecond or even on the time scale of a subpicosecond [2].

In this paper we propose a model for calculating concentration dependence of XRL intensity. The model is based on two probabilistic conceptions. The first is the equiprobable distribution in space of luminescent molecules; the second conception implies that the electronic excitations are generated after absorption of X-ray quantum. The Obtained theoretical equation describing the concentration dependence of XRL was compared with experimental results measured with usage of liquid luminophore: 3-Hydroxyflavone in toluene.

2. Materials and methods

The main difference between liquid and crystal luminophores is an equiprobable distribution of luminescent centers in the solvent (matrix). The concentration dependence of PL intensity is in direct proportion to the intensity of excited radiation when the quantum yield of luminescence (η) is constant

* Corresponding author. Tel.: +380 930697618.
E-mail address: inna.moroz1990@gmail.com (I.M. Moroz).

http://dx.doi.org/10.1016/j.jlumin.2015.04.019
0022-2313/© 2015 Elsevier B.V. All rights reserved.

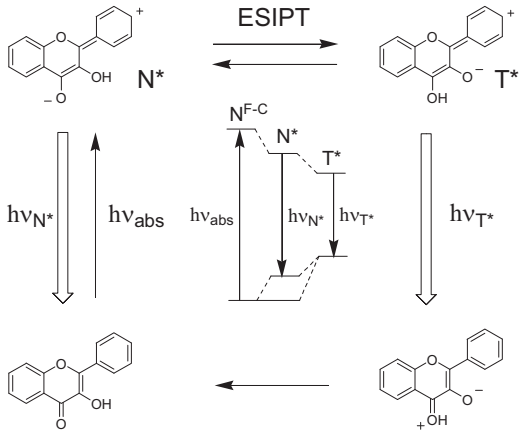

Fig. 1. Cycle of ESIPT reaction for molecule of 3HF group.

$$I_{excite} = I_0(1-R)\left(1-e^{-C\sigma d}\right) \tag{1}$$

where I_0 is the intensity of excited radiation, R is the reflection coefficient of excited radiation, C is the concentration (the number of luminescent molecules in cm^3), σ is the absorption cross section of excited radiation of luminescence centers, and $d$is the thickness of liquid phosphor.

Respectively, the intensity of luminescence (I_{PL}) that will be registered is [9,11]

$$I_{PL} = I_{excite}\cdot\Omega\eta \tag{2}$$

Parameter Ω defines the part of luminescent radiation which is registered by experimental facilities. The quantum yield of luminescence depends on the root-mean-square distance between the neighboring centers of luminescence. We obtain the PL intensity as a function of concentration by taking into account the decrease of luminescence intensity as a function of concentration (C)

$$\frac{J_{PL}(C)}{J_{max}} = \frac{1-e^{-\sigma Cd}}{1+\frac{C}{C_0}} \tag{3}$$

where the denominator from formula (3) describes the concentration extinction of luminescence $\left(1+\frac{C}{C_0}\right)^{-1}$ [3,4]. In the absence of self-absorption of PL in the sample, the concentration dependence of PL is determined by the absorption of the exciting radiation.

The concentration of 3HF molecules is smaller than the concentration of solvent molecules. Therefore, we can assume that all the absorption of X-ray radiation is a result of absorption by the solvent molecules. The function of XLR intensity concentration of luminescent molecules was found for constant value of excitation intensity by introducing a new parameter ΔV, which is the volume around one luminescent molecule filled with the solvent molecules. If the exciting light comes into this volume, the luminescent molecule is excited and as a result the luminescent quantum is emitted. In order to perform the calculations we should determine the population level (γ) of the solvent by the luminescent molecules depending on the concentration. Assuming that the distribution of luminescent molecules in the solvent is equiprobable therefore the changes of population level when the concentration of luminescent molecules decreases, can be found from the following equation

$$\frac{d\gamma}{dC} = \Delta V(1-\gamma) \tag{4}$$

The integration over C gives the general population level of the solvent by luminescent molecules

$$\gamma = \left(1-e^{-\Delta V\cdot C}\right) \tag{5}$$

The population level is proportional to the concentration of luminescent molecules when their concentration is very low and in general is determined by Eq. (5). The absorption of one X-ray quantum in condensed matter under the action of high-energy photoelectrons generates a significant number of electronic excitations.

The number of excitations N_0 is determined by phenomenological relations [6,10,12–14] and depends on the energy of X-ray quantum $(h\nu_X)$ and ionization potential (I) of the solvent molecules

$$N_0 = \frac{h\nu_X}{3I} \tag{6}$$

The total energy needed for generating one electronic excitation is $\sim 3I$ [6,10,12–15] (for liquids I is potential of ionization and is the band gap for dielectric), i.e. two-third of this energy is transformed into heat. Here was considered that the processes of elastic and inelastic scattering of high energy electrons on atoms almost does not depend on the state of condensed matter. This is performed for solid state materials, which are composed of light elements (diamond (C) and silicon carbide (SiC)), like solvents in liquid phosphors. The estimation shows that the diameter of a high-energy electron field is about 15–20 times smaller than the straight stopping length [15]. By introducing a new parameter (V_0) – the volume of absorbing one X-ray quantum and generating N_0 electronic excitations we can estimate the density of electron excitations$\left(\frac{N_0}{V_0}\sim 10^{18}\ cm^{-3}\right)$. Assume in the first approximation that the electronic excitations are generated evenly in volume V_0.

In order to obtain the XRL concentration dependence we use probabilistic model. In analogy to the population level (γ) we derive the ratio of excitations (i) in the volume of luminescent molecules to the total number of generated excitations. The probability of excitation occurrence in volume ΔV is

$$\frac{di}{dN} = 1-e^{-\frac{\Delta V}{V_0}(V_0C-i)} \tag{7}$$

This equation follows from correlation (4). The integration of Eq. (7) from 0 to N_0 yields dependence $i(C)$

$$i(C) = CV_0 - \frac{V_0}{\Delta V}\ln\left[1+\gamma e^{-\frac{\Delta V}{V_0}(N_0-V_0C)}\right] \tag{8}$$

The XRL intensity is directly proportional to the portion of excitations(N_0/V_0) occurring in the volume of luminescent molecules. Taking into account the concentration decrease of luminescence intensity we obtain

$$I_{XRL}(C) = \frac{I_0' C}{1+\frac{C}{C_0}}\left\{1-\frac{1}{\Delta VC}\ln\left[1+\gamma e^{-\Delta V\left(\frac{N_0}{V_0}-C\right)}\right]\right\}, \tag{9}$$

where I_0' includes all the constant values. The theoretical relation (9) can be used for verifying the experimental data.

The next step is analysis of Eq. (9) by applying the varied parameters which provides the field in which it can be applied. Eq. (9) includes three parameters: ΔV, N_0, V_0 and two of them are presented by ratio N_0/V_0. When we modify these parameters the dependence behaves as described in the following way.

The concentration decrease of luminescence intensity is described by the known relation (4) and is independent from the parameters. For investigation we use function$Y(C)$, which does not depend on the concentration decrease

$$Y = C\left(1+\frac{1}{\Delta VC}\ln\left[1+\gamma\cdot e^{-\Delta V\left(\frac{N_0}{V_0}-C\right)}\right]\right) \tag{10}$$

Download English Version:

https://daneshyari.com/en/article/5398869

Download Persian Version:

https://daneshyari.com/article/5398869

Daneshyari.com