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On the choice of proper average lifetime formula for an ensemble of emitters showing non-single exponential photoluminescence decay

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Abstract

In this paper, we investigate non-single exponential photoluminescence decays in various disordered condensed-matter systems. For such materials, two formulas for the average lifetime of system's excited state are commonly used in the analysis of experimental data. In many cases, the choice of formula is arbitrary and lacks a clear physical justification. For this reason, our main goal is to show that the choice of correct mathematical formula should be based on the interpretation of measured photoluminescence decay curve. It is shown that depending on the investigated system, after appropriate normalization, photoluminescence decay curve can represent either a survival probability function or a probability density function of lifetime and for this reason two different formulas for the average lifetime are required. It is also shown that, depending on luminescence quantum yield, some information on the probability density function of lifetime can be lost in the process of measurement, which results in underestimated values of average lifetime. Finally, we provide an interpretation of total decay rate distributions which are frequently obtained by phenomenological modeling of non-single exponential photoluminescence decays.

Keywords: average lifetime, mean lifetime, luminescence decay, photoluminescence decay, energy transfer efficiency, lifetime distribution, non-exponential

(Some figures may appear in colour only in the online journal)

1. Introduction

There are many examples of modern luminescent materials showing non-single exponential photoluminescence decay, including colloidal quantum dots embedded in photonic crystals [1, 2], lanthanide-doped phosphors [3, 4] and crystals [5–7], as well as some semiconductor alloys [8, 9], superlattices [10, 11], quantum wells [12] or epitaxial quantum dots [13]. The non-single exponential decay dynamics of excited states reflects the microscopic heterogeneity of these complex condensed-matter systems. For such materials,

photoluminescence decay measurement is an effective tool, which allows us not only to study the relaxation phenomena but also to determine different macroscopic material parameters, which are important in the context of possible applications. Many of such averaged quantities, characterizing an ensemble of emitters, are calculated based on average lifetime during which collection of emitters remain in their excited states. This includes, for example, the efficiency of energy transfer between lanthanide ions in solids [5, 14] or the average absorption cross-section of semiconductor nanocrystals [15, 16]. For such materials, excited state of each single emitter can decay with its own characteristic rate and for this reason to

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characterize a large ensemble of such heterogeneous emitters it is usually necessary to define one macroscopic parameter which describes the average amount of time the whole system spends in the excited state. Taking this into account, it is clear that accurate determination of different macroscopic material properties requires correct calculation of the average lifetime of system's excited state. This, in turn, depends not only on accurate measurement of the photoluminescence decay curve but also on the equation describing the average lifetime which is used in calculations.

There are two alternative mathematical formulas for the average lifetime which are very commonly used in the analysis of kinetic experiments involving the relaxation of complex materials. Both formulas have the same origin in the statistical methods of survival analysis. The first average lifetime formula is given as:

$$\langle \tau \rangle_1 = \int_0^\infty I_{\text{PL}}(t) / I_{\text{PL}}(0) dt \quad (1)$$

where $I_{\text{PL}}(t)$ denotes the measured photoluminescence decay curve. The second average lifetime formula is given as:

$$\langle \tau \rangle_2 = \int_0^\infty t I_{\text{PL}}(t) dt / \int_0^\infty I_{\text{PL}}(t) dt. \quad (2)$$

It is clear that equations (1) and (2) give the same results only in the case of single-exponential photoluminescence decays. For non-single exponential decay curves, equations (1) and (2) are not equivalent and yield different results. As we shall show in this paper, the problem with equations (1) and (2) is that both average lifetimes can have exactly the same physical meaning of the average amount of time a complex system spends in its excited state but the two formulas are applicable in a completely different situations, which depends on the statistical interpretation of the normalized photoluminescence decay curve. This means that for a specific material only one of the above equations correctly describes the average lifetime of a system in an excited state, and while for some materials this could be equation (1), for other materials this could be equation (2). For this reason, the choice of equation should be based on specific physical criteria and cannot be made without justification. Taking this into account, it is surprising that such criteria have not been broadly discussed in recent literature, especially in the context of condensed-matter luminescent materials. To our knowledge, similar issue has been addressed only by Sillen *et al* [17] from a very specific perspective of biological systems, such as fluorescent proteins. This, however, has not exhausted the subject and it is very interesting to investigate the applicability of equations (1) and (2) in the context of problems typical for solid-state physics. Such discussion should be useful for researchers interested in a proper analysis of experimental data and could help to decide which equation is appropriate to calculate the average lifetime of system's excited state in a particular situation.

In this paper, we consider the relaxation phenomena of a macroscopically large ensemble of emitters. We use distributions of radiative and non-radiative recombination rates to describe the heterogeneity of emitters or their environment,

which then results in non-single exponential photoluminescence decays. Based on some examples of published experimental data, we analyze different scenarios and discuss which equation [equations (1) or (2)] allows for correct calculation of the average lifetime of system's excited state. In this context, it is shown that the choice of suitable formula depends on the underlying physical mechanism behind the non-single exponential character of a photoluminescence decay curve. Finally, we discuss the interpretation of total decay rate distributions which are frequently obtained by phenomenological modeling of non-single exponential photoluminescence decays. This last result could be useful for proper interpretation of experimental data obtained by maximum entropy method.

2. Definitions and assumptions

Let us consider an ensemble of emitters (also referred to as donors) in their excited state, surrounded by static acceptors (i.e. defects) which act as non-radiative recombination centers. In our model, an emitter can either recombine radiatively or transfer excitation to a nearby acceptor which dissipates the energy. For this reason, each emitter is characterized by a total recombination rate which accounts for both the radiative and non-radiative events. We assume that the ensemble in question is large enough to use a continuous approximation in the calculation of photoluminescence (PL) decay of the excited emitters. Consequently, the total recombination rate is regarded as a continuous random variable whose value is k and whose probability density function (pdf) is $\Psi(k)$.

The survival probability $S_T(t)$ describes the probability that system of emitters remains in the excited state beyond time t , that is $S_T(t) = \Pr\{T > t\}$, where T is time to recombination. For an ensemble of emitters whose total rates are described by density function $\Psi(k)$, we can write [18]:

$$S_T(t) = \int_0^\infty \Psi(k) \exp(-kt) dk \quad (3)$$

In this equation, $S_T(t)$ describes the macroscopic behavior of the whole excited system consisting of many individual emitters which often cannot be observed individually but each of them contribute to the average response of the material. The average (or expected) lifetime which such system of emitters remains in the excited state can be calculated using $S_T(t)$ as [19]:

$$\langle \tau \rangle = \int_0^\infty S_T(t) dt. \quad (4)$$

Equation (4) has the same form as the experimental equation (1) since by definition $S_T(0) = 1$. Because $S_T(t)$ describes the probability that the excited state survives past time t , the probability of recombination is simply $\Pr\{T \leq t\} = 1 - S_T(t)$. The rate of recombination events per unit time can be therefore calculated as [19]:

$$f_T(t) = \frac{d}{dt} [1 - S_T(t)] = -\frac{d}{dt} S_T(t). \quad (5)$$

The above function $f_T(t)$ is also known as the probability density function of the lifetime distribution and can be used to

calculate the same average lifetime as previously in equation (4) but with different formula [19]:

$$\langle \tau \rangle = \int_0^\infty t f_T(t) dt. \quad (6)$$

Clearly, equation (6) has the same form as equation (2), since by definition of pdf $\int_0^\infty f_T(t) dt = 1$. Here, it should be emphasized that equation (5) is the pdf that describes the rate of recombination events due to both radiative and non-radiative recombination processes. Since only radiative events can be measured in photoluminescence decay experiment, we have to decompose equation (5) into two contributions: the rate of radiative recombination events and the rate of non-radiative recombination events.

Let us now assume that the radiative recombination rate and the non-radiative recombination rate are independent random variables whose values are k_R and k_{NR} , respectively. In general, it is not a trivial assumption and its applicability to a given material system should be always carefully analyzed. In many situations, we have to use *a priori* knowledge about the investigated material to decide whether or not the random variables are independent. For example, if there is a physical interaction which somehow relates k_R and k_{NR} the two variables will be correlated. Nevertheless, in most of the real-world situations, it is enough to assume that only one of the two variables is truly stochastic while the distribution of the other one can be approximated by the Dirac delta function. For this reason and to avoid unnecessary discussion, in the following sections we assume that only one of the variables, either k_R or k_{NR} , is described by a truly stochastic pdf while the second one is described by the Dirac delta function. It should be emphasized that such approach allows us to cover a variety of interesting examples reported in the literature. In this section, however, we keep our equations more general.

Having said that, we can now define $\gamma(k_R)$ and $\phi(k_{NR})$ as the probability density functions of radiative and non-radiative rates, respectively. It follows from the probability theory that the sum of two independent random variables whose value is $k = k_R + k_{NR}$, is itself a random variable with pdf $\Psi(k)$ given by the convolution of $\gamma(k_R)$ and $\phi(k_{NR})$ pdfs:

$$\Psi(k) = [\gamma * \phi](k). \quad (7)$$

Substituting equation (7) to (3) and using the basic property of the Laplace transform of a convolution, we can now write $S_T(t)$ as a product of two survival probabilities:

$$S_T(t) = \int_0^\infty \Gamma(t, k_R) dk_R \int_0^\infty \Phi(t, k_{NR}) dk_{NR} \quad (8)$$

where $\Gamma(t, k_R) = \gamma(k_R) \exp(-k_R t)$ and $\Phi(t, k_{NR}) = \phi(k_{NR}) \exp(-k_{NR} t)$.

In equation (8), the first integral represents the survival probability with respect to radiative events, while the second integral describes the survival probability with respect to non-radiative events. Finally, after calculating the derivative in

equation (5), we can write:

$$f_T(t) = \int_0^\infty k_R \Gamma(t, k_R) dk_R \int_0^\infty \Phi(t, k_{NR}) dk_{NR} + \int_0^\infty \Gamma(t, k_R) dk_R \int_0^\infty k_{NR} \Phi(t, k_{NR}) dk_{NR}. \quad (9)$$

Clearly, the rate of recombination events due to the radiative process (emission of photons) is represented only by the first term in equation (9), while the second term in equation (9) represents the rate of recombination events solely due to non-radiative processes [2]. Integrating the first term of equation (9) between $t = 0$ and $t \rightarrow \infty$ gives the probability of photon emission at all times, which is equal to the luminescence quantum yield (QY):

$$QY = \int_0^\infty \left[\int_0^\infty k_R \Gamma(t, k_R) dk_R \int_0^\infty \Phi(t, k_{NR}) dk_{NR} \right] dt. \quad (10)$$

It follows from all of the above that the measured PL decay $I_{PL}(t)$ which represents the histogram of the arrival times of photons is described as:

$$I_{PL}(t) = C \int_0^\infty k_R \Gamma(t, k_R) dk_R \int_0^\infty \Phi(t, k_{NR}) dk_{NR} \quad (11)$$

where C is an experimental constant. It should be emphasized that the second term of equation (9) is missing from equation (11) since it represents the non-radiative process which does not result in the emission of photons [2]. For this reason, as a rule, equation (11) does not represent neither $f_T(t)$ pdf nor $S_T(t)$. This implies that for strongly non-single exponential PL decays equations (1) and (2) give completely different outcomes. However, as it is shown in the following sections, in many cases it is possible to normalize the measured $I_{PL}(t)$ so that it is brought to either $S_T(t)$ or $f_T(t)$. This, in turn, allows for proper calculation of the average lifetime using either equations (1) or (2).

It should be further emphasized that, for the sake of simplicity, we did not include the rate of internal non-radiative relaxation of the emitter in the above model. The non-radiative processes described by $\phi(k_{NR})$ are due to the coupling to external non-radiative centers. Nevertheless, as long as all radiative and non-radiative processes are independent, the contribution from any internal non-radiative decay can always be included in the survival probability by simple multiplication [20]. For example, if there is only one additional internal non-radiative process whose rate is k_{iNR} we can define its distribution as the Dirac delta function $\varphi(k_{NR}) = \delta(k_{NR} - k_{iNR})$ and calculate pdf of the total recombination rate as the convolution of three densities:

$$\Psi'(k) = [\gamma * \phi * \varphi](k). \quad (12)$$

The modified survival probability $S'_T(t)$, which includes the internal non-radiative decay rate k_{iNR} , is now simply given by the product:

$$S'_T(t) = S_T(t) \exp(-tk_{iNR}) \quad (13)$$

where $S_T(t)$ is defined by equation (8). In general, since the survival probability has been modified, we have to calculate the new pdf $f'_T(t)$ and resulting $I'_{PL}(t)$.

3. Discussion and examples

3.1. Single radiative rate and distribution of non-radiative rates

Let us consider an ensemble of identical donors (e.g. lanthanide ions) characterized by a single lifetime τ_{SD} which describes the decay of donor in the absence of acceptors. The decay rate is given by $1/\tau_{SD} = k_{RD} + k_{iNR}$ where k_{RD} is the rate of spontaneous radiative decay and k_{iNR} is the rate of internal non-radiative decay of donor. The distribution of radiative rates is $\gamma(k_R) = \delta(k_R - k_{RD})$ and the quantum yield of isolated donor is $QY_0 = k_{RD}\tau_{SD}$. Assuming that emitters are randomly surrounded by acceptors which results in non-radiative rate distribution $\phi(k_{NR})$, using equations (13) and (8) we can define $S_T(t)$ as:

$$S_T(t) = \exp(-t/\tau_{SD}) \int_0^\infty \phi(k_{NR}) \exp(-k_{NR}t) dk_{NR}. \quad (14)$$

With equation (14) we calculate $f_T(t)$ in a similar manner as in the previous section:

$$f_T(t) = k_{RD} \exp(-t/\tau_{SD}) \int_0^\infty \phi(k_{NR}) \exp(-k_{NR}t) dk_{NR} + \{NR(t)\} \quad (15)$$

where $\{NR(t)\}$ denotes the terms related solely to all non-radiative recombination processes [see equation (9)], including also the internal non-radiative decay of donor. Since $\{NR(t)\}$ cannot be measured in a PL decay experiment, excluding this term from equation (15) allows us to define $I_{PL}(t)$ as:

$$I_{PL}(t) = C_0 \exp(-t/\tau_{SD}) \int_0^\infty \phi(k_{NR}) \exp(-k_{NR}t) dk_{NR}. \quad (16)$$

We easily notice that experimental $I_{PL}(t)$ [equation (16)] differs from $S_T(t)$ [equation (14)] only by the constant $C_0 = k_{RD}A_0$, where A_0 is a constant related to the concentration of initially excited donors and some other experimental factors. Since $I_{PL}(0) = C_0$ we can readily obtain $S_T(t)$ from the measured curve. For this reason, to be consistent with the stochastic definition of average lifetime, we have to calculate $\langle\tau\rangle$ as:

$$\langle\tau\rangle = \int_0^\infty S_T(t) dt \equiv \int_0^\infty I_{PL}(t) / I_{PL}(0) dt = \langle\tau\rangle_1. \quad (17)$$

Clearly, equation (1) has to be used to calculate average lifetime if we can safely assume that an ensemble of emitters is characterized by a single radiative rate k_{RD} and the non-single exponential character of PL decay results entirely from the non-radiative contribution due to the distribution $\phi(k_{NR})$. Here, it should be emphasized that in this case it is not possible to use $I_{PL}(t)$ to calculate $f_T(t)$ given by equation (15) because $\{NR(t)\}$ is not measured in photoluminescence decay experiment. For this reason, equation (2) does not allow to correctly calculate the average lifetime of system's excited state as it is based on equation (6) and requires complete information about the pdf.

The above conclusion is consistent with the results of Sillen *et al* [17], who considered systems of interacting fluorophores

and showed that in most cases equation (1) should be used instead of equation (2). The methodology presented by Sillen was, however, different and somewhat more sophisticated, as he did not use the survival analysis method. Here, it is important to underline that our approach allowed to shed new light on the actual reason why equation (1) has to be used in many situations. Apparently, it is not uncommon that after appropriate normalization the experimental PL decay reflects the theoretical survival probability function $S_T(t)$ rather than the corresponding pdf $f_T(t)$, which is somewhat unexpected. As a matter of fact, in many theoretical models that describe the statistical aspects of non-radiative energy transfer from donor to acceptor, the survival probability has the form of equation (14) which is the product of two survival probability functions. There are many examples of such models [20–22], including the famous Inokuti–Hirayama model [23], where the first term of decay function is $\exp(-t/\tau_{SD})$ and describes the survival probability with respect to intrinsic radiational and radiationless decay, while the second term, which usually has much more complicated form, describes the survival probability with respect to energy transfer processes.

Next, we shall demonstrate that using an improper definition of the average lifetime results in significant errors when PL decay is strongly non-single exponential. For this purpose, we use the experimental values reported by Fernandez-Gonzales [5], who investigated $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ garnets doped with Ce^{3+} and Er^{3+} ions. In this work, it has been shown that co-doping the garnets with Ce^{3+} – Er^{3+} ions results in energy transfer processes from Ce^{3+} to Er^{3+} that occur via dipole–dipole interactions between donors (Ce^{3+}) and acceptors (Er^{3+}). It has been also demonstrated that in the presence of Er^{3+} ions, the PL decay measured for Ce^{3+} ions becomes non-single exponential and can be fitted very well with the famous equation derived by Inokuti–Hirayama.

The Inokuti–Hirayama model [23] assumes that initially excited donor can either decay radiatively or non-radiatively, transferring energy to nearby acceptors by multipolar interactions. For this reason, the non-radiative transfer rate k_{NR} depends on the distance between donor and acceptor. In this model, the non-single exponential decay of donor is a result of parallel relaxations via many non-radiative channels and a hierarchy of donor–acceptor distances. To put this in other words, PL decay becomes non-single exponential only when measured for an ensemble of different donors because each and every donor is surrounded by a random configuration of acceptors that provide many possible paths for non-radiative decay. This, on the other hand, results in the distribution of non-radiative rates, which reflects the system complexity. In the case of dipole–dipole interactions reported by Fernandez-Gonzales [5], this distribution has a particularly simple form (see appendix A for derivation):

$$\phi(k_{NR}) = \frac{Q}{2k_{NR}\sqrt{\pi k_{NR}\tau_{SD}}} \exp\left[-\frac{Q^2}{4k_{NR}\tau_{SD}}\right] \quad (18)$$

where $Q = \sqrt{\pi}C/C_0$, C is acceptor concentration and C_0 is so called critical transfer concentration. Since Inokuti–Hirayama model has the form of equation (16) it follows from our earlier

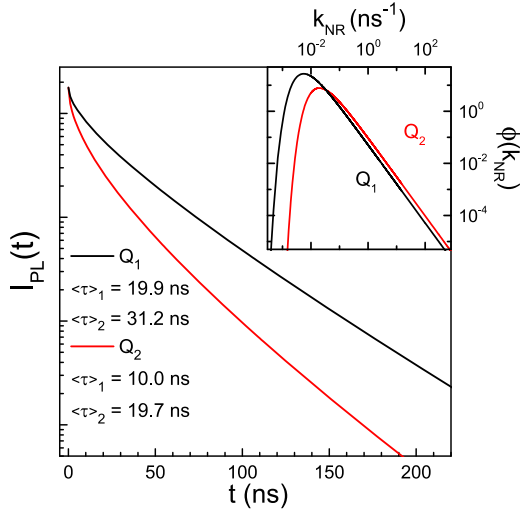


Figure 1. PL decay curves of Ce^{3+} ions in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ garnets co-doped with Ce^{3+} and Er^{3+} . These decay curves correspond to the distributions of non-radiative recombination rates which are displayed in the inset and labeled as Q_1 and Q_2 . The average lifetimes $\langle\tau\rangle_1$ and $\langle\tau\rangle_2$ were calculated according to equations (1) and (2). The presented data is based on the experimental PL decays reported in reference [5].

discussion that the correct formula for the average lifetime is given by equation (1).

Figure 1 shows PL decay curves of Ce^{3+} ions and respective $\phi(k_{\text{NR}})$ distributions calculated according to equation (18) with $\tau_{\text{SD}} = 56.0$ ns as reported in reference [5]. To recover the experimental average lifetimes and decay curves reported by Fernandez-Gonzales [5], the model parameters were set to $Q_1 = 1.37$ (sample with a lower Er^{3+} concentration) and $Q_2 = 2.57$ (sample with a higher Er^{3+} concentration). It can be seen in figure 1 that both PL decays are non-single exponential with fast decay at low times. Moreover, $\phi(k_{\text{NR}})$ distributions show the power-like property for large k_{NR} , which is typical for stretched-exponential PL decays and has been discussed in details elsewhere [18]. Based on that data, we calculated that for $Q_1 = 1.37$ the correct and incorrect average lifetimes [equations (1) and (2), respectively] are $\langle\tau\rangle_1 = 19.9$ ns and $\langle\tau\rangle_2 = 31.2$ ns while for $Q_2 = 2.57$ we obtained $\langle\tau\rangle_1 = 10.0$ ns and $\langle\tau\rangle_2 = 19.7$ ns. Clearly, there is a huge difference between the respective values of average lifetime and the correct value is always the shorter one.

It should be underlined that incorrect calculation of the average lifetime can seriously affect other calculated quantities. To show this, let us first integrate the first term of $f_T(t)$ in equation (15) to obtain luminescence QY:

$$\text{QY} = k_{\text{RD}} \int_0^\infty \left[\exp(-t/\tau_{\text{SD}}) \int_0^\infty \phi(k_{\text{NR}}) \exp(-k_{\text{NR}}t) dk_{\text{NR}} \right] dt. \quad (19)$$

The integrand in square brackets is easily recognized as $S_T(t)$ defined by equation (14). Since we already noticed that $S_T(t)$ and $I_{\text{PL}}(t)$ differ here only by a multiplication constant, we can rewrite the above equation in the following simpler form:

$$\text{QY} \stackrel{\text{def}}{=} k_{\text{RD}} \int_0^\infty I_{\text{PL}}(t) / I_{\text{PL}}(0) dt = k_{\text{RD}} \langle\tau\rangle_1. \quad (20)$$

It should be strongly underlined that despite equation (20) is valid for the specific case discussed in this section, it is not valid as a rule. The general definition of QY is given by equation (10). Nevertheless, our derivation of equation (20) unambiguously shows which formula for the average lifetime should be used for luminescence QY calculation. Since luminescence QY is proportional to other quantities, like for example the steady-state luminescence intensity [17], it is important to use the correct formula for average lifetime in equation (20). Moreover, what follows from equation (20) is that to calculate the energy transfer efficiency η_{ET} from donor to acceptor, we have to write:

$$\eta_{\text{ET}} = 1 - \text{QY}/\text{QY}_0 = 1 - \langle\tau\rangle_1/\tau_{\text{SD}}. \quad (21)$$

Although the general form of equation (21) is well known and has been used in many papers [5, 24], we have the impression that for many authors it has not been clear which formula for the average lifetime should be used to calculate η_{ET} . Our derivation unambiguously proves that the average lifetime in equation (21) has to be calculated according to equation (1) since in this case this is the quantity related to the luminescence QY of donor. This confirms the former conclusion of Sillen [17], who examined similar problem using a different methodology. Here, it should be emphasized that up to now many authors [3, 4, 6, 7, 14, 25–30] have used equation (2) to calculate the average lifetime used in equation (21). Most probably, they followed the definition arbitrarily proposed in the original paper of Inokuti and Hirayama which refers to the ‘mean duration’ of donor luminescence [23]. It should be underlined that such quantity was not used in Inokuti–Hirayama paper to calculate η_{ET} . On the contrary, η_{ET} was calculated based on luminescence QY defined as in our equation (19) [see equation (10) in reference [23]]. In view of the above, it can be stated that using equation (2) in the context of Inokuti–Hirayama model is inconsistent with the assumptions of this model as long as we need to calculate the average lifetime of the excited state of the system and related quantities. This statement remains valid also in the context of much more sophisticated models which account for different donor–donor interactions, including the model of Yokota–Tanimoto [21] or the model of Allinger–Blumen [20]. This is because all of these models assume a single decay rate $1/\tau_{\text{SD}}$ of separated donor and regard this decay channel as independent of the energy transfer processes [20]. Here, it is very important to emphasize that η_{ET} values derived with the incorrect formula for average lifetime are always underestimated. In our example, the correct (incorrect) η_{ET} is 0.65 (0.44) for Q_1 and 0.82 (0.65) for Q_2 . It is also worth to mention that in some cases values of η_{ET} reported by different authors for the same material-system cannot be directly compared because of the inconsistency in the formula for average lifetime which has been used to obtain η_{ET} . From a purely technological perspective, it is essential to use the proper formula for average lifetime to calculate η_{ET} , as only in this case material parameters can be determined correctly and the evaluation of a particular technological approach for material synthesis can be made.

3.2. Distribution of radiative rates

In this section, we consider an ensemble of emitters with different radiative recombination rates described by a distribution $\gamma(k_R)$. We assume that non-radiative recombination in this system is very low and can be disregarded. Taking this into account, the survival probability has a very simple form which can be written as:

$$S_T(t) = \int_0^\infty \gamma(k_R) \exp(-k_R t) dk_R. \quad (22)$$

Like previously, we use equation (5) to derive pdf:

$$f_T(t) = \int_0^\infty k_R \gamma(k_R) \exp(-k_R t) dk_R. \quad (23)$$

Since non-radiative events were excluded from consideration, equation (23) describes the rate of purely radiative recombination events. It means that equation (23) differs from the measured PL decay curve only by an experimental constant A_0 and we can write:

$$I_{PL}(t) = A_0 f_T(t). \quad (24)$$

It is clear that in this case, the experimental $I_{PL}(t)$ has to be normalized to the probability density function. For this reason, the correct formula for the average lifetime in this case is given by:

$$\langle \tau \rangle = \int_0^\infty t f_T(t) dt \equiv \int_0^\infty t I_{PL}(t) dt / \int_0^\infty I_{PL}(t) dt = \langle \tau \rangle_2. \quad (25)$$

To put this in other words, if for some reason the non-radiative events can be neglected, after appropriate normalization the measured PL decay curve represents theoretical pdf $f_T(t)$, as could be expected. This is exactly the opposite of what was discussed in the previous section, where the experimental PL decay curve was normalized to $S_T(t)$. Here, the non-single exponential character of $I_{PL}(t)$ is caused entirely by the distribution of radiative rates and therefore we have to use equation (2) to calculate the average lifetime in order to be consistent with the statistical definition given by equation (6). In practice, such a situation is expected to occur when non-radiative recombination is inefficient with regard to photon emission (i.e. for an ensemble of emitters characterized by a very high emission quantum yield).

There are many reasons why an ensemble of emitters could exhibit a distribution of radiative rates. The most typical example is a collection of semiconductor nanocrystals characterized by size distribution, where the radiative recombination rate depends on the nanocrystal size [16]. In this case, however, it should be mentioned that nanocrystal size usually influences also the emission wavelength and for proper calculation of the average lifetime it is necessary to measure PL decay for the whole excited population of nanocrystals. Another interesting example is the exponential distribution of radiative rates occurring for localized indirect excitons in different semiconductor alloys [8, 9]. This kind of distribution is caused by random potential fluctuations seen by electrons, due to the compositional disorder of the alloy [9]. Despite slightly different origins, this kind of distribution describes also radiative

rates of excitons in some semiconductor superlattices [10, 11] and quantum wells [12]. Here, it is worth to mention that the exponential distribution of radiative rates results in power-law PL decay which does not have finite average lifetime when $QY = 1$. Nevertheless, in most practical situations, there is also an internal non-radiative process present (i.e. due to phonons) [9] and in such case the average lifetime can be calculated. This interesting example is, however, outside of the scope of this section.

To explore the differences between results of equations (1) and (2), let us consider an ensemble of identical emitters randomly distributed over different sites of an inhomogeneous dielectric medium. In this case, we deal with a distribution of radiative rates since the rate of spontaneous emission is proportional to the local radiative density of optical states to which the emitters couple. For our calculations, we take the experimental example of colloidal CdSe/ZnSe quantum dots randomly embedded in a three-dimensional photonic crystal (inverse opal) [1]. It has been demonstrated experimentally that an ensemble of colloidal quantum dots distributed in this kind of photonic material can be described by the log-normal distribution of radiative recombination rates [1, 2, 31],

$$\gamma(k_R) = B_0 \exp(-\ln^2(k_R/k_{MF})/w^2) \quad (26)$$

where k_{MF} is the most frequent rate, B_0 is a normalization constant to pdf and w corresponds to the distribution width Δk at $1/e$:

$$\Delta k = 2k_{MF} \sinh(w). \quad (27)$$

Similarly as in the previous section, we would like to compare the differences in average lifetimes calculated from equations (1) and (2). For this purpose, we use distributions corresponding to two different values of k_{MF} and Δk , which were obtained experimentally and reported by Nikolaev *et al* [1]. In this section, however, we omit the contribution of internal non-radiative decay in CdSe/ZnSe quantum dots. This approximation is justified for two reasons. First, CdSe/ZnSe quantum dots are characterized by a very high luminescence quantum yield [32] and exhibit a single-exponential PL decay when measured outside of the photonic crystal [1]. Second, it has been shown by Nikolaev *et al* [1] that the log-normal distribution of rates is entirely caused by the distribution of radiative rates caused by the spatial and orientational variation of the local radiative density of optical states.

Figure 2 shows two different distributions $\gamma(k_R)$ characterized by $k_{MF} = 0.0154 \text{ ns}^{-1}$, $\Delta k = 0.0511 \text{ ns}^{-1}$ (γ_1) and $k_{MF} = 0.0148 \text{ ns}^{-1}$, $\Delta k = 0.0991 \text{ ns}^{-1}$ (γ_2) together with corresponding PL decays calculated from equation (24). The average lifetime obtained for the first PL decay is $\langle \tau \rangle_2 = 43.1 \text{ ns}$ when we use the correct formula [here, equation (2)] and $\langle \tau \rangle_1 = 19.0 \text{ ns}$ when we use the incorrect formula [in this case equation (1)]. For the second PL decay curve, we obtained $\langle \tau \rangle_2 = 26.8 \text{ ns}$ and $\langle \tau \rangle_1 = 4.2 \text{ ns}$ for the correct and incorrect average lifetimes, respectively. Once again, the differences between respective average lifetimes calculated with different equations are significant, but this time the correct value is always higher. It should be also pointed out that the ratio $\langle \tau \rangle_2 / \langle \tau \rangle_1$ depends

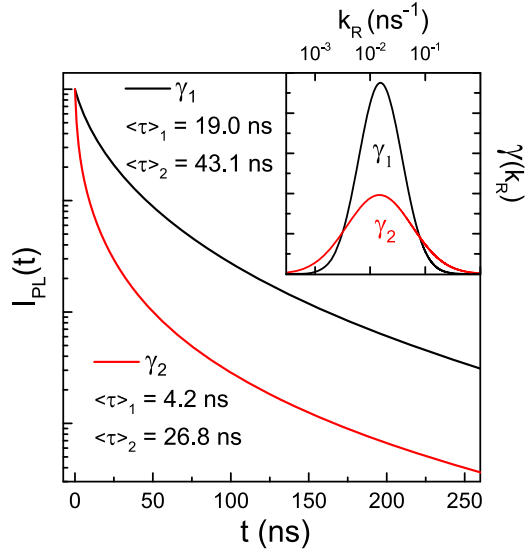


Figure 2. PL decays of colloidal CdSe/ZnSe quantum dots randomly embedded in a three-dimensional photonic crystal. These PL decays correspond to the log-normal distributions of non-radiative recombination rates which are displayed in the inset and labeled as γ_1 and γ_2 . The average lifetimes $\langle\tau\rangle_1$ and $\langle\tau\rangle_2$ were calculated according to equations (1) and (2). The presented data was calculated based on the experimental distributions reported in reference [1].

on the width of the radiative rate distribution: for γ_1 it is approximately 2.3, while for γ_2 it is around 6.4. This last result is not surprising at all, since PL decay corresponding to γ_2 shows much stronger deviation from single-exponential decay than the curve corresponding to γ_1 . In other words, the more non-single exponential PL decay curve, the higher the difference between outcomes of equations (2) and (1). It is worth to mention that such a property could be useful for the quantitative assessment of the extent to which a PL decay curve is non-single exponential, simply by calculating the relative difference between the outcomes of equations (2) and (1).

3.3. Distribution of radiative rates and single internal quenching rate

Let us now consider an ensemble of emitters characterized by the distribution of radiative rates $\gamma(k_R)$ and a single non-radiative process whose rate is k_{iNR} and therefore the resulting distribution is $\varphi(k_{NR}) = \delta(k_{NR} - k_{iNR})$. Once again, we consider the previously mentioned example of CdSe/ZnSe quantum dots embedded in a photonic crystal [1], where the distribution of radiative rates $\gamma(k_R)$ is log-normal (equation (26)). This time, however, we take into account the additional rate of non-radiative recombination which is due to the internal non-radiative decay occurring in CdSe/ZnSe quantum dots. Clearly, this is a more realistic example, since we can now obtain $QY < 1$ simply by altering the value of k_{iNR} .

Taking into account all of the above, using equation (8) we can write the survival probability for the ensemble of excited emitters as:

$$S_T(t) = \exp(-k_{iNR}t) \int_0^\infty \gamma(k_R) \exp(-k_R t) dk_R. \quad (28)$$

The corresponding pdf which describes the rate of recombination events per unit time [see equation (9)] is:

$$f_T(t) = \exp(-k_{iNR}t) \int_0^\infty k_R \gamma(k_R) \exp(-k_R t) dk_R + k_{iNR} \exp(-k_{iNR}t) \int_0^\infty \gamma(k_R) \exp(-k_R t) dk_R. \quad (29)$$

As discussed in section 2, only the first term of the sum in equation (29) is related to recombination events where photons are emitted. Using equation (10), we can define the luminescence QY as:

$$QY = \int_0^\infty \left[\exp(-k_{iNR}t) \int_0^\infty k_R \gamma(k_R) \exp(-k_R t) dk_R \right] dt. \quad (30)$$

The experimental PL decay curve is now given as:

$$I_{PL}(t) = C_0 \exp(-k_{iNR}t) \int_0^\infty k_R \gamma(k_R) \exp(-k_R t) dk_R \quad (31)$$

where C_0 is a constant related to the detection system and to the concentration of excited emitters.

The above equations have very important consequences as they put limits on the quantum yields for which the average lifetime can be accurately calculated based on the experimental data. It is apparent that in general, it is not possible to divide the experimental $I_{PL}(t)$ by a constant to normalize it to either $f_T(t)$ given by equation (29) or $S_T(t)$ given by equation (28), like we did in the two previous sections. Strictly speaking, the integrand in equation (31) is different than integrand in equation (28), so the normalization of experimental $I_{PL}(t)$ to recover $S_T(t)$ is not possible. Furthermore, $I_{PL}(t)$ cannot be normalized to the exact form of pdf given by equation (29) because the second term of equation (29) is always lost in the process of measurement [2]. It follows from the above that, except in specific cases which are discussed below, the average lifetime cannot be precisely calculated neither from equations (1) nor (2). This is a somewhat unexpected result and to our knowledge it has not been discussed before.

To investigate this problem in more details, we calculated the average lifetime as a function of the luminescence QY. The calculations were conducted for the two log-normal distributions of radiative rates which were used also in the previous section. The luminescence quantum yield has been gradually decreased from 1 to almost 0 by increasing the non-radiative rate k_{iNR} . In this way, we inspected different real-world scenarios where quantum dots are characterized by luminescence $QY < 1$. The theoretical values of average lifetime have been calculated according to equation (4) using $S_T(t)$ given by equation (28). This definition gives us the correct values of average lifetime $\langle\tau\rangle_{REF}$ which are used here as a reference. Since in this case we cannot normalize $I_{PL}(t)$ to neither $S_T(t)$ nor $f_T(t)$, we calculated also the average lifetime from the experimental $I_{PL}(t)$ using both equations (1) and (2). These results represent the estimation of theoretical average lifetimes which can be made based on the experimental data.

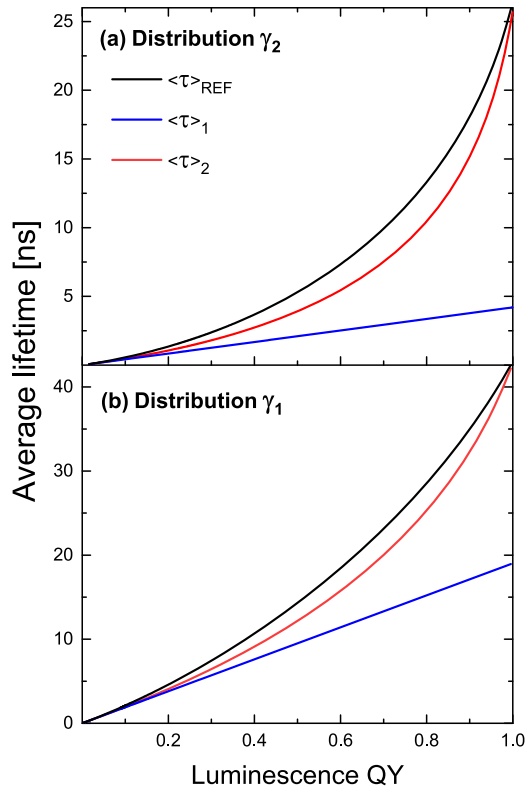


Figure 3. The average lifetime calculated as a function of luminescence quantum yield. The average lifetimes $\langle\tau\rangle_1$ and $\langle\tau\rangle_2$ were calculated according to equations (1) and (2). The average lifetime $\langle\tau\rangle_{\text{REF}}$ was calculated according to equation (4) and represents the reference value. The calculations were made for two distributions of radiative rates labeled as γ_2 (a) and γ_1 (b). These distributions are based on experimental data reported for CdSe/ZnSe quantum dots in photonic crystal [1], as discussed in section 3.2.

The results of our calculations are shown in figure 3(a) as a function of luminescence QY. It can be seen that besides some specific points, equations (1) and (2) yield different values from the theoretical line denoted as $\langle\tau\rangle_{\text{REF}}$. The first exception from this rule is when $\text{QY} = 1$ and the outcome of equation (2) is exact by definition, as discussed in section 3.2. For intermediate values of QY, equations (1) and (2) generally underestimate average lifetimes and equation (1) always underestimates more. It is clear that in this range of QY, equation (2) is always much closer to the theoretical value $\langle\tau\rangle_{\text{REF}}$ and, if only QY is sufficiently high, it gives very good estimates of the average lifetime. This is not surprising in the context of our results from section 3.2 and we can conclude that equation (2) is preferred also in this case, provided that QY is sufficiently high or PL decay is not strongly non-single exponential. Finally, we can see in figure 3(a) that when QY is very low, all of the calculated lines come very close to each other and converge to a common value. This is an expected result, as in the region of very low QY the non-radiative recombination dominates and PL decay converges to single-exponential function.

It is noteworthy that in this section we investigated strongly non-single exponential PL decays, like those reported in reference [1]. Obviously, the closer PL decay is to

single-exponential, the more accurate is the average lifetime calculated from equation (2). In figure 3(b) we showed results of the same calculations obtained for the narrower distribution γ_1 . It is clear that while the effects discussed above are still present in figure 3(b), the differences between the theoretical line $\langle\tau\rangle_{\text{REF}}$ and the line obtained from equation (2) are smaller compared to figure 3(a).

In conclusion to this section, we have to emphasize that although equation (2) can be used to calculate the average lifetime of emitters characterized by an unknown distribution of radiative rates and a single non-radiative rate, it should be used with caution. This remark applies especially to a situation where average lifetime is used to calculate other quantities, like for example absorption cross-section of semiconductor nanocrystals characterized by non-single exponential PL decay [15, 33]. In this case, it is important to remember that equation (2) might yield underestimated results, which should be taken into account when such experimentally derived quantities are compared with theoretical predictions.

4. Implications for maximum entropy methods

It happens very often that the function which describes the distribution of radiative or non-radiative rates is unknown. In such circumstances, modeling of non-single exponential PL decays is usually based on simplified equation [34],

$$I_{\text{PL}}(t) = \int_0^\infty \sigma(k) \exp(-kt) dk \quad (32)$$

where $\sigma(k)$ is a distribution of total decay rates related to the phenomenological distribution of decay times τ as $\kappa(\tau) = (1/\tau^2) \sigma(1/\tau)$. This phenomenological model has been successfully used in many papers [2, 16, 35, 36].

There are different methods of finding the distribution $\sigma(k)$ which fits the experimental data, including the well-known maximum entropy method [37, 38], which allows to find the distribution of total rates without any *a priori* assumptions about a particular form of this distribution. Regardless of the method used to fit the experimental data, the interpretation of the obtained distribution $\sigma(k)$ is often problematic. This is because $\sigma(k)$ includes information about both radiative and non-radiative relaxation processes. Although the form of equation (32) is similar to equation (3), it should be underlined that equation (32) does not describe the survival probability function but only the measured $I_{\text{PL}}(t)$ and for this reason the interpretation of $\sigma(k)$ is generally different than the interpretation of $\Psi(k)$ discussed in section 2. Nevertheless, given some physical intuition on the relaxation processes occurring in the investigated material, it is possible to express $\sigma(k)$ in a simple form, which might be helpful in a proper interpretation of the experimental data. Below, we show the interpretation of $\sigma(k)$ only in the context of relaxation processes considered in section 3, but the described methodology can be used also for more complicated systems under the assumption that the considered relaxation processes are independent.

First, we consider the example from section 3.1. In this case, we deal with a single spontaneous rate $1/\tau_{SD}$ and some distribution of non-radiative rates $\phi_{NR}(k)$. Comparing equations (16) and (32), we can therefore write:

$$\sigma(k) = A_0 k_{RD} [\delta(k - 1/\tau_{SD}) * \phi_{NR}(k)]. \quad (33)$$

The above relation can be easily validated after substitution of $\sigma(k)$ to equation (32), which represents the Laplace transform of $\sigma(k)$. It is enough to say that we have to use the basic property of Laplace transform of a convolution, which states that $\mathcal{L}[f(k) * g(k)] = F(t)G(t)$, where $F(t)$ and $G(t)$ are transformed functions $f(k)$ and $g(k)$. Using the above property, we can transform equations (32) to (16). What follows from equation (33) is that if a given material system fulfills the requirements described at the beginning of section 3.1, the distribution of total rates $\sigma(k)$ represents the distribution of non-radiative rates shifted by $1/\tau_{SD}$ towards higher rates and multiplied by a constant. It should be emphasized that if $\sigma(k)$ was determined in a proper way and no information has been lost in the process, the shape of this distribution reflects the basic properties of $\phi_{NR}(k)$.

Next, we skip the example from section 3.2, and we focus our attention on the more general example discussed in section 3.3. In this case, we have a distribution of radiative rates $\gamma_R(k)$ and a single internal non-radiative process described by the rate k_{iNR} . Using similar arguments as above, we can write for the distribution of total rates:

$$\sigma(k) = C_0 [(k\gamma_R(k)) * \delta(k - k_{iNR})]. \quad (34)$$

It follows from equation (34) that in this case, under assumptions described in section 3.3, apart from the trivial factor C_0 , $\sigma(k)$ represents the distribution of radiative rates weighted by the corresponding radiative rates and shifted by k_{iNR} towards higher rates. It should be pointed out that a similar interpretation has been given first by van Driel *et al* [2], but our equation (34) has a simpler and more useful form. Finally, it is interesting to mention that in general, the shape of distribution $\sigma(k)$ can be different from the original shape of $\gamma_R(k)$ due to the weighting process. However, for some distribution functions, including log-normal distribution described by equation (26), the weighting process does not change the general shape of $\gamma_R(k)$ and results only in an additional shift of the most frequent rate.

5. Conclusions

In this paper, we closely reviewed two formulas for the average lifetime of system's excited state which are frequently involved in the analysis of non-single exponential PL decays. It has been shown that, despite their common statistical origin, these formulas are not equivalent when applied to experimental data and for this reason one must carefully choose the appropriate equation for the average lifetime calculation. We pointed out that the choice of a suitable formula depends on the physical mechanism responsible for the non-single exponential character of PL decay curve. First of all, if PL decay is

non-single exponential due to a complex non-radiative recombination process, i.e. radiationless energy transfer between lanthanide ions in different solids, equation (1) should be used. This is because in such cases, appropriately normalized PL decay curve usually represents the survival probability function of excited donors, as discussed in section 3.1. Second, if PL decay is non-single exponential owing to a distribution of radiative rates, like in the case of certain photonic materials or semiconductor alloys, equation (2) is always more applicable. It has been shown that in this situation, appropriately normalized PL decay curve represents the probability density function of the lifetime distribution, although the accuracy of this representation depends on luminescence quantum yield. This, in turn, can result in underestimation of average lifetimes, especially in the case of strongly non-single exponential PL decays, as discussed in section 3.3.

Finally, in section 4, we discussed the interpretation of total decay rate distributions which are frequently obtained by phenomenological modeling of non-single exponential PL decays. It has been shown that such phenomenological distributions reflect properties of the more fundamental distributions of radiative and non-radiative recombination rates. Our discussion could be useful for proper interpretation of lifetime distributions obtained by various methods that involve Laplace transform inversion, including maximum entropy method.

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Appendix A

It is well-known that the ensemble averaged survival probability of a donor in the presence of static acceptors is given as [39, 40]:

$$S_{NR}(t) = \exp \left[-\Gamma(1 - 3/s) (C/C_0) (t/\tau_{SD})^{3/s} \right] \quad (35)$$

where $\Gamma(x)$ is Euler's gamma function and $s = 6, 8, 10$ for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively. Equation (35) describes only the decay due to the excitation transfer; the other, internal radiative and non-radiative decay channels of the donor are to a good approximation independent of the energy transfer processes, and their effect is incorporated into the final survival probability function by multiplication with $\exp(-t/\tau_{SD})$. Taking this into account, the distribution of non-radiative recombination rates is given by the inverse Laplace transform:

$$\phi(k_{NR}) = \mathcal{L}^{-1}[S_{NR}(t)]. \quad (36)$$

The distribution of non-radiative rates reported in section 3.1 was obtained using equation (36), for the specific case of $s = 6$. We confirmed our result computing equation (36) numerically, using Stehfest algorithm. It is clear that with equation (18) the analytical solution of equation (16) has the

form of Inokuti–Hirayama model for $s = 6$. This was not mentioned in section 3.1 in order to underline that conclusions of section 3.1 are valid for many different distributions of non-radiative rates.

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