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Non-isolated pair model for upconversion energy transfer processes

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The description of the temporary evolution of upconversion energy transfer processes in solid samples including doped luminescent centers is revised using a simple but non-restrictive pair model. The formalism is related to upconversion processes between a collective of donor and acceptor optical centers, and leads to analytic expressions for the temporary behavior of the emission intensities from the intermediate excited states and the up converted excited state. From a microscopic viewpoint, the results of the model are compared with numerical solutions of the system of differential equations and with those obtained from kinetic type equations, showing the limits of directly using the latter in the analysis of upconversion processes. The proposed model makes it possible to obtain average macroscopic solutions, explicitly dependent on the concentration of dopant luminescent centers in the crystalline lattice, and permits an adequate prediction of the shapes of the decay curves. It would improve the determination of the upconversion energy transfer rates from experimental data.

Keywords: Upconversion; energy transfer processes.

Se desarrolla un modelo para la descripción de la evolución temporal de los procesos de transferencia de energía por upconversion en materiales de estado sólido, dopados con centros ópticos luminiscentes. El modelo de pares, sencillo aunque no restrictivo, aplica para procesos de upconversion en un colectivo de centros ópticos donores y aceptores y conduce a expresiones analíticas para la evolución temporal de las intensidades de emisión desde los estados excitados intermediarios y el estado excitado superior. Desde un punto de vista microscópico, se comparan los resultados del modelo con las soluciones numéricas del sistema de ecuaciones diferenciales y con aquellas obtenidas desde ecuaciones de tipo cinético, demostrándose las limitaciones de utilizar directamente estas últimas en el análisis de los procesos de upconversion. El modelo habilita establecer soluciones macroscópicas promedio, que son explícitamente dependientes en la concentración de centros luminescentes dopantes en la matriz cristalina, y que permiten una adecuada predicción de la forma de las curvas de decaimiento desde los estados excitados. El modelo podría mejorar la determinación de las velocidades de transferencia de energía por upconversion desde los datos experimentales.

Descriptores: Procesos de transferencia de energía; upconversion.

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1. Introduction

Since Auzel [1-3] referred to the possibility of energy transfer mechanisms of the upconversion type, much experimental evidence has been reported in different types of systems[4-14, *inter alia*]. Upconversion processes have been the subject of important research in the last decades due to their use in luminescent devices in which photons having energies higher than that of excitation are produced, such as upconversion lasing[15], quantum counters and temperature sensors[16] and improved solar cells [17]. An updated review on this topic has been recently published by Auzel[18].

In previous work [19-25], we tried different approaches to modeling energy transfer phenomena in solid state, both crystalline systems as well as vitreous materials, focusing on the macroscopic observables (rate constants, shape of decay curves, etc.), but connecting these results with the details of the interactions at a microscopic level. We proposed and developed a model that has been used to study energy transfer processes such as cross-relaxations via electric multipolar and exchange interactions, and it has made possible the rationalization of the macroscopic processes and rates involved in terms of the actual crystallographic structure of crystalline systems and explicit details of the interaction. The formalism is general in nature and could be applied to any crystalline matrix containing optical centers such as Ln^{3+} or transition metal ions. It has been successfully tested in systems like elpasolite type crystals [19-22], reproducing qualitatively and quantitatively some observables such as the shapes of the decay curves from excited states, and also in LnX_3 (X = F, Cl)[23], proposing alternative formalisms to rationalize exchange interactions and, in laminar type perovskite crystals, explaining the quenching-concentration dependence in terms of their quasi-bidimensional luminescent ion substructures[24]. In recent work, some of the ideas underlying this formalism have been useful in improving the understanding of the upconversion regime in amorphous solids containing optical centers[25].

In the literature, one finds simplified theoretical analyses of upconversion processes with macroscopic kinetic type equations, which allow a reasonable qualitative description of the phenomenon. This type of analysis permits the fitting of the experimental data using adjustable parameters, but discrepancies between the shapes of the theoretical and experimental curves normally lead to errors in the determination of the magnitude of the upconversion energy transfer rates.

Following Prasad [26], upconversion processes could be separated into two broad classes; 1) a namely excited state absorption (ESA) process, in which a single optical center reaches a high-energy excited level through sequential absorption of two photons and cooperative transition processes, which include upconversion energy transfer (UPET) between two optical centers, one of them already in an intermediate excited state, and reaching the up-converted excited state by energy transfer from the donor center; and 2) cooperative emission between two ions, both in an excited state and emitting from an upper virtual state or cooperative sensitization (where two excited ions transfer energy to a third one). More recently, Andrews and Jenkins [27] have proposed a three-center quantum electrodynamic model, performing a more general treatment for the upconversion energy transfer processes.

From the very beginning, Auzel pointed out that the UPET processes have a better quantum efficiency than other processes such as ESA, cooperative sensitization or cooperative luminescence [3], and some time after Auzel's first reference[1], Vial and Buisson [13,14] proposed a simple two-center model of isolated ion pairs to explain temporal behavior of UPET processes. Examples of this kind of process have been reported in crystals of $CsCdBr_3$:Pr^{3+}, LaF_3:Pr^{3+}, $LaCl_3$:U^{3+}, $Gd_3Ga_5O_{12}$:Er^{3+}, among others.

Assuming a two-center and three energy level system for the interacting centers (conventionally labeled as donor d and acceptor a), initial state for the pair $|i\rangle = |d*, a*\rangle$ (both donor d and acceptor a excited optical centers are in an intermediate excited level), and a final state $|f\rangle = |d^o, a^{up}\rangle$ (in which the donor center transfers energy to the acceptor, relaxing to the ground state and the acceptor center reaches the$|a^{up}\rangle$ higher energy state), the macroscopic temporal evolution of both states is:

$$N_i(t) = N_i(0)e^{-(\gamma_1+\gamma_2+k_o^{up})t},$$

for the initial state and

$$N_f(t) = \frac{N_f(0)\;k_o^{up}}{\gamma_1+\gamma_2-\gamma_3+k_o^{up}}\left[e^{-\gamma_3 t} - e^{-(\gamma_1+\gamma_2+k_o^{up})t}\right],$$

for the final state.

The simplicity achieved in the isolated pair model contrasts, however, with the fact that it is restricted only to the pair population, that it does not consider the effect of isolated centers (which will always contribute to the decay and will be recorded in the experiment), that there is a chance to have donors surrounded by more than one acceptor (*i.e.* pairs not strictly isolated), and that the macroscopic rates of energy transfer are always dependent on the doping of the sample, an experimental fact that is not reflected in these results either.

This paper reports a study that incorporates the scheme of previous work into this type of process and presents a different formal description of the decay curves from the upconversion state. A cubic system of the elpasolite type with two different Ln^{3+} lanthanide ions has been chosen as an example of a model system, although the formalism is rather general in nature and could be applied to any system doped with optical centers to establish better figures for the upconversion rates from experimental data.

2. Model

This section reviews some general aspects of our model in view of previous work and subsequently develops a non-isolated pair model for upconversion.

Some general remarks on the formalism

The decay of an optical center in an excited state can include, among other things, intra-center deactivation processes and energy transfer processes such as cross-relaxation processes with other surrounding centers in the ground state. Under these considerations, the differential equation to be solved for the jth donor ion and its resulting microscopic probability to remain excited at time t is [19,20]:

$$\rho'_j(t) = \left\{-\gamma\rho_j(t) - \sum_i w_{ij}^{cr}\rho_j(t)\right\} \longrightarrow \rho_j(t) = e^{\left\{-\gamma-\sum\limits_i w_{ij}^{cr}\right\}t}, \quad (1)$$

where γ is the rate of intra-center decay (including both radiative and non-radiative paths), and $w_{ij}^{cr}$is the rate of energy transfer for the cross-relaxation between the jth donor and the ith acceptor. Addition over the population of acceptors that surround the donor leads to the total interaction contribution $\sum\limits_i w_{ij}^{cr}$.

Averaging over the acceptor and donor population, the formalism leads to macroscopic solutions of the following type:

$$\bar{\rho}(t) = \frac{1}{N_D}\sum_j e^{-(\gamma+\sum\limits_i w_{ij}^{cr})t} = \Delta_{stat}(X,t)\times e^{-(\gamma+\bar{W}_{eff}^{cr}(X))t}, \quad (2)$$

where $\bar{W}_{eff}^{cr}(X)$ is the effective rate of the cross-relaxation, which depends on matrix elements of the interaction Hamiltonian, which may be electric multipolar, magnetic dipolar or exchange and both terminal states of the transition, composition X and crystallographic characteristics of the sample. In addition, $\Delta_{stat}(X,t)$ is a polynomial term that is a function of time and of the statistical fluctuations in the acceptor population for a given concentration of optically active centers in the crystal matrix. Within this formalism, the connection and difference between the microscopic details and the macroscopic averages is clear, since it retains the exponential form considering an effective rate $\bar{W}_{eff}^{cr}(X)$, but including the term $\Delta_{stat}(X,t)$, which leads to some changes that modify the shape of the evolution of the states in time. The search for agreement between the experimental data and the model and the subsequent estimation of the rates of energy transfer is done by comparing the decay curves to $\bar{\rho}(t)$.

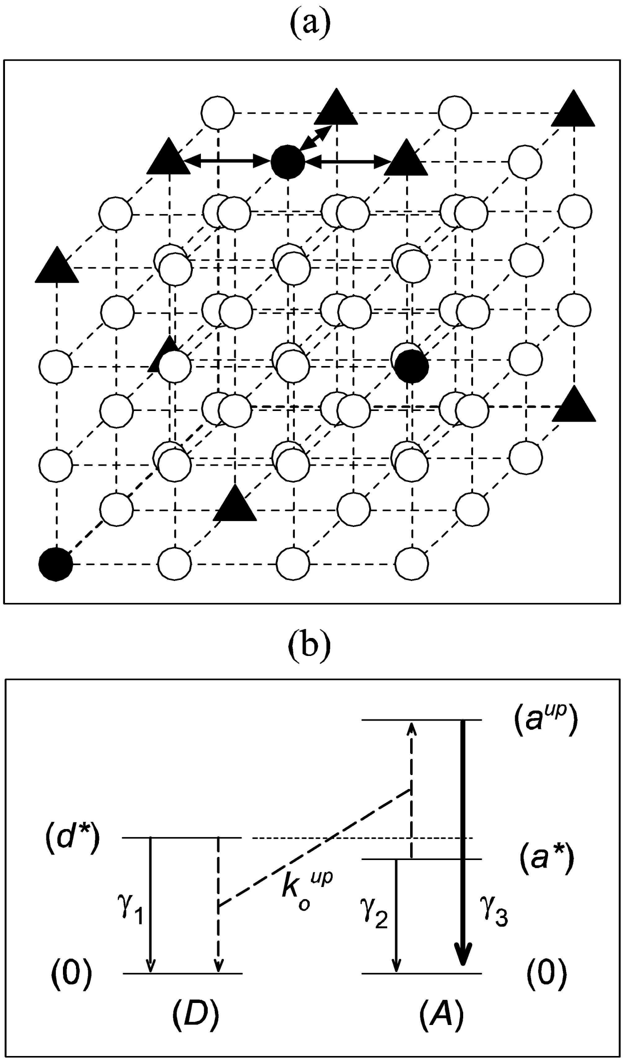

FIGURE 1. a) Cubic lattice, showing only those sites that can be doped by luminescent centers. To the left of the upper face, one donor (black circle) is surrounded by three acceptors (black triangles). The remaining excited centers are isolated (both donors and acceptors) and the white spheres represent non luminescent centers; b) energy level diagram for a simple UPET process. γ_1 is the intrinsic decay rate for the donor center, γ_2 and γ_3 analog rates for the acceptor center (intermediate and upconversion states, respectively) and k_o^{up} is the upconversion energy transfer rate.

Non-isolated pair model for upconversion

Although the donor-acceptor distance of the pair may be any, in previous papers and in reports by other authors it has been shown that the interactions between pairs separated by the minimum distance in the lattice account for about 90% of the energy transfer effect[19,22]. Therefore, in this paper we shall consider only nearest neighbour pairs, making it easier to deal with the macroscopic equations. Let us consider a cubic lattice in which local environments contain a donor ion that may be isolated or may have one or more nearest neighbour acceptors (see Fig. 1a). At the microscopic level, and for a particular donor, the differential equations to be solved are:

$$\begin{aligned}
\rho_i'(t) &= -\gamma_1\rho_i(t) - p\,k_o^{up}\rho_i(t)\rho_j(t)\\
\rho_j'(t) &= -\gamma_2\rho_j(t) - qk_o^{up}\rho_i(t)\rho_j(t)\\
\rho_f'(t) &= -\gamma_3\rho_f(t) + qk_o^{up}\rho_i(t)\rho_j(t).
\end{aligned} \tag{3}$$

Here, i is the donor in an initial intermediate excited state $|d*\rangle$, j is the acceptor, in a different initial intermediate excited state $|a*\rangle$, f is the acceptor in the final up-converted state $|a^{up}\rangle$ (see Fig. 1b), and p is the number of nearest neighbour acceptors in the $|a*\rangle$ state, surrounding the generic donor and forming pairs. In correspondence, there are also q donors in $|d*\rangle$ state, surrounding a generic acceptor. In Eq. (3), it has been assumed that there is independence in the interactions, an aspect that is not strictly true at high concentrations of luminescent centers, where more complex interaction mechanisms must be considered. However, a general deduction will be made first, and then we will validate results finding the proper concentration regime.

Equations (3) may be written as

$$\rho_i(t) = e^{\{-\gamma_1 t\}}e^{\left\{-pk_o^{up}\int\limits_0^t \rho_j(t)dt\right\}} \tag{4}$$

$$\rho_j(t) = e^{\{-\gamma_2 t\}}e^{\left\{-qk_o^{up}\int\limits_0^t \rho_i(t)dt\right\}}; \tag{5}$$

both fulfill the initial condition $\rho_i(0) = \rho_j(0) = 1$.

Since Eqs. (4) still retain an explicit coupling between $\rho_i(t)$ and $\rho_j(t)$, an appropriate analytic solution will be attempted. For that purpose, the second exponential is expanded in a series and the fundamental theorem of integral calculus is used, permitting an easier algebraic handling:

$$-pk_o^{up}\int\limits_0^t \rho_j(t')dt' = \left(-pk_o^{up}t + pk_o^{up}\left\{qk_o^{up} + \gamma_2\right\}\frac{t^2}{2!} - pk_o^{up}\left\{qk_o^{up2}\left[p+q\right] + qk_o^{up}(\gamma_1 + 2\gamma_2) + \gamma_2^2\right\}\frac{t^3}{3!} + ..\right) \tag{6}$$

$$-qk_o^{up}\int\limits_0^t \rho_i(t')dt' = \left(-qk_o^{up}t + qk_o^{up}\left\{pk_o^{up} + \gamma_1\right\}\frac{t^2}{2!} - qk_o^{up}\left\{pk_o^{up2}\left[p+q\right] + pk_o^{up}(2\gamma_1 + \gamma_2) + \gamma_1^2\right\}\frac{t^3}{3!} + ..\right). \tag{7}$$

TABLE I. $\rho_i(t)$ and $\rho_j(t)$ factors:

A.1) Four first $\rho_i(t)$ factors:
$\alpha_i = pk_o^{up}$
$\beta_i = pk_o^{up}\left(\gamma_2 + qk_o^{up}\right)$
$\delta_i = pk_o^{up}\left(\gamma_2^2 + (2\gamma_2+\gamma_1)qk_o^{up} + (p+q)qk_o^{up2}\right)$
$\varepsilon_i = pk_o^{up}\left(\gamma_2^3 + 3qk_o^{up}\gamma_2^2 + q(k_o^{up})^3(p^2+4pq+q^2) + q(k_o^{up})^2\left[(2p+3q)\gamma_1 + (4p+3q)\gamma_2\right] +qk_o^{up}(\gamma_1^2 + 3\gamma_1\gamma_2)\right)$
A.2) Four first $\rho_j(t)$ factors:
$\alpha_j = qk_o^{up}$
$\beta_j = qk_o^{up}\left(\gamma_1 + pk_o^{up}\right)$
$\delta_j = qk_o^{up}\left(\gamma_1^2 + (2\gamma_1+\gamma_2)pk_o^{up} + (p+q)pk_o^{up2}\right)$
$\varepsilon_j = qk_o^{up}\left(\gamma_1^3 + 3pk_o^{up}\gamma_1^2 + p(k_o^{up})^3(p^2+4pq+q^2) + p(k_o^{up})^2\left[(3p+4q)\gamma_1 + (3p+2q)\gamma_2\right] +pk_o^{up}(\gamma_2^2 + 3\gamma_1\gamma_2)\right)$

The series expansion has been made around $t = 0$, since at that instant there is complete information on both ρ_i and ρ_j and their derivatives: $\rho_i(0)=\rho_j(0)=1$, $\rho_i'(0)= -(\gamma_1 + pk_o^{up})$, $\rho_j'(0)= -(\gamma_2 + qk_0^{up})$, $\rho_i''(0)=pk_o^{up2}(p+q) + pk_o^{up}(2\gamma_1+\gamma_2) + \gamma_1^2$, $\rho_j''(0) = qk_{o^{up}}^2(p+q) + qk_o^{up}(\gamma_1+2\gamma_2) + \gamma_2^2$, etc. For both ρ_i and ρ_j we get:

$$\rho_i(t) = e^{\left(-\{\gamma_1+\alpha_i\}\ t\ +\beta_i\frac{t^2}{2!} - \delta_i\frac{t^3}{3!} + \varepsilon_i\frac{t^4}{4!} - \ldots\right)} \tag{8}$$

$$\rho_j(t) = e^{\left(-\{\gamma_2+\alpha_j\}t+\beta_j\frac{t^2}{2!} - \delta_j\frac{t^3}{3!} + \varepsilon_j\frac{t^4}{4!} - \ldots\right)} \tag{9}$$

A restricted listing of α_i, β_i, δ_i... and α_j, β_j, δ_j... is presented in Table I.

Microscopic solutions (8) and (9) are exact: they satisfy differential Eqs. (3) for each of the t^n terms of the polynomial expansion as well as for the complete series, and they resemble a simple exponential decay, having specific rates γ_1 and γ_2, respectively, modified by smaller perturbations of order n in t, which depend on combinations of the numbers of coupled pairs p, q and rates γ_1, γ_2 and k_o^{up}.

Approximate analytic solutions for $\rho_f(t)$ can be obtained by truncating the polynomials up to the nth order in time t and introducing (8) and (9) into (3). This leads to an uncoupled differential equation for $\rho_f(t)$. For a first order correction in t, the equation and the solution are remarkably simple:

$$\begin{aligned}\rho_f'(t) &= -\gamma_3\rho_f(t) + qk_o^{up}\\ &\quad\times \exp\left\{-(\gamma_1+\gamma_2+(p+q)k_o^{up})t\right\}\\ \rho_f(t) &= \frac{qk_o^{up}}{\gamma_1+\gamma_2-\gamma_3+(p+q)k_o^{up}}\\ &\quad\times\left\{e^{-\gamma_3 t} - e^{-(\gamma_1+\gamma_2+k_o^{up}(p+q))t}\right\}.\end{aligned} \tag{10}$$

Solution (10) shows a behavior similar to the isolated pair model, but properly corrected for the actual number of interacting pairs at a microscopic level (*i.e.*, explicitly dependent on the doping of the macroscopic sample, as shown in the next section). The derivation of analytic solutions with higher order corrections in t is only possible by including terms up to t^2 in the differential equation (3):

$$\begin{aligned}\rho_f(t) &= \sqrt{\frac{\pi k_o^{up}}{2(q\gamma_1+p(\gamma_2+2qk_o^{up}))}} \times q\\ &\times\left[Erfi\left(\frac{\gamma_1+\gamma_2-\gamma_3+(p+q)k_o^{up}}{\sqrt{2k_o^{up}(q\gamma_1+p(\gamma_2+2qk_o^{up}))}}\right) + Erfi\left(\frac{-\gamma_1-\gamma_2+\gamma_3-(p+q)k_o^{up}+(q\gamma_1+p\gamma_2+2pqk_o^{up})k_o^{up}t}{\sqrt{2k_o^{up}(q\gamma_1+p(\gamma_2+2qk_o^{up}))}}\right)\right]\\ &\times e^{\left\{-\frac{(\gamma_1+\gamma_2-\gamma_3)^2+(p+q)^2k_o^{up2}+2(\gamma_1+\gamma_2-\gamma_3)(p+q)k_o^{up}+2\gamma_3k_o^{up}(2pqk_o^{up}+p\gamma_2+q\gamma_1)t}{2k_o^{up}(q\gamma 1+p(\gamma_2+2qk_o^{up}))}\right\}}.\end{aligned} \tag{11}$$

Even though better agreement is seen with the numerical results early in the system's evolution, Eq. (11) shows strong divergence at longer times due to the properties inherent to the imaginary error function *Erfi*[28]. This problem is properly shown and analyzed in Sec. 3.

So, for the sake of simplicity and better accuracy of solutions, we choose Eq. (10) as the analytic expression for $\rho_f(t)$.

The situation depicted in the previous paragraphs corresponds to donor and acceptor species of different nature and to upconversion processes that occur only from the donor to neighboring acceptors. For systems with one kind of optical center, upconversion processes can occur if the energy of the up-converted state is equal (resonant process) or close to (quasi-resonant, phonon assisted process) twice the energy of the intermediate excited state. In this case there is no distinction between donor and acceptor; upconversion processes do not have a preferential direction, and the results are formally similar, although considering $p = q$ and $\gamma_1 = \gamma_2$.

Macroscopic solutions

In a macroscopic sample, the concentration of luminescent centers is an average figure that goes from the dilution limit (few luminescent centers without neighbors) to the full occupation allowed by stoichiometry. Moreover, for a given average concentration, the microscopic situation shown in the previous section is obviously variable within the sample, since both numbers, p and q, change from one site to another in the crystal lattice.

Then it is useful to define two macroscopic indices, X and Y, which account for the average concentration of donor and acceptor centers, respectively. If an average number $\bar{p}$ of nearest neighbors surrounding the donors ($\bar{p}(X) = n^{\max}X$) and an average number $\bar{q}$ of donors around the acceptors are considered ($\bar{q}(Y) = n^{\max}Y$)[19,20,24], where $n^{\max}$ is the maximum number of next neighbors surrounding each donor in the crystal matrix (for example, $n^{\max} = 6$ in the cubic case that will be studied in Sec. 3, up to only $n^{\max} = 2$ in the case of a one-dimensional system such as some nanostructured organic systems [29]), the evolution of the donors in time is established by (see Ref. 20),

$$\begin{aligned}\bar{\rho}_i(t) &= \Delta_i^{stat}(X,Y,t) \times e^{\left(-(\gamma_1+\bar{p}k_o^{up})t+\bar{p}k_o^{up}(\gamma_2+\bar{q}k_o^{up})\frac{t^2}{2!}-\bar{p}k_o^{up}(\gamma_2^2+(\gamma_1+2\gamma_2)\bar{q}k_o^{up}+(\bar{p}+\bar{q})\bar{q}k_o^{up\,2})\frac{t^3}{3!}+\ldots\right)} \\ &= \Delta_i^{stat}(X,Y,t) \\ &\quad\times e^{\left(-(\gamma_1+n^{\max}Xk_o^{up})t+n^{\max}X\left\{k_o^{up}(\gamma_2+n^{\max}Yk_o^{up})\frac{t^2}{2!}-k_o^{up}(\gamma_2^2+(\gamma_1+2\gamma_2)n^{\max}Yk_o^{up}+(n^{\max})^2(X+Y)Yk_o^{up\,2})\frac{t^3}{3!}+\ldots\right\}\right)} \qquad (12)\end{aligned}$$

Equation (12) is analogous to Eq. (2) and in formal correspondence to previous results, where the $\Delta_i^{stat}(X,Y,t)$ includes all the information on the statistical fluctuations Δp and Δq (obtained from $p = \bar{p} + \Delta p$ and $q = \bar{q} + \Delta q$, respectively) over the complete optical center's population within the sample, and has been calculated using the same procedure developed in earlier work (see Appendix A.). The large second contribution is an average quantity that shows the effect of the coupled acceptor centers in the temporal evolution of the donors.

To summarize, Eq. (12) corresponds to a non-single exponential decay in which the first order contribution $-(\gamma_1 + n^{\max}Xk_o^{up})t$ is modulated explicitly over time by the processes in the donor centers (Y) and acceptor centers (X), both for upconversion (k_o^{up}) as for intra-center decay (γ_1 and γ_2), as well as by the statistical fluctuations of the optical center's population.

Similarly, for $\rho_{j(t)}$ the macroscopic average would be:

$$\begin{aligned}\bar{\rho}_j(t) &= \Delta_j^{stat}(X,Y,t) \times e^{\left(-(\gamma_2+\bar{q}k_o^{up})t+\bar{q}k_o^{up}(\gamma_1+\bar{p}k_o^{up})\frac{t^2}{2!}-\bar{q}k_o^{up}(\gamma_1^2+(2\gamma_1+\gamma_2)\bar{p}k_o^{up}+(\bar{p}+\bar{q})\bar{p}k_o^{up\,2})\frac{t^3}{3!}+\ldots\right)} \\ &= \Delta_j^{stat}(X,Y,t) \\ &\quad\times e^{\left(-(\gamma_2+n^{\max}Yk_o^{up})t+n^{\max}Yk_o^{up}(\gamma_1+n^{\max}Xk_o^{up})\frac{t^2}{2!}-n^{\max}Yk_o^{up}\left\{\gamma_1^2+(2\gamma_1+\gamma_2)n^{\max}Xk_o^{up}+(n^{\max})^2(X+Y)Xk_o^{up\,2}\right\}\frac{t^3}{3!}+\ldots\right)} \qquad (13)\end{aligned}$$

With respect to $\rho_{f(t)}$, in Eq. (10) the denominator includes the $(p+q)k_o^{up}$ term. Since both Δp and Δq are small variations in $p = \bar{p} + \Delta p$ and $q = \bar{q} + \Delta q$, respectively, then a single and trivial simplification has been made:

$$\gamma_1 + \gamma_2 - \gamma_3 + (\bar{p} + \Delta p + \bar{q} + \Delta q)k_o^{up} \longrightarrow \gamma_1 + \gamma_2 - \gamma_3 + (\bar{p} + \bar{q})k_o^{up}.$$

This choice has the advantage of preserving the formalism in Eq.(14) and does not affect calculations in the low and moderate doping concentration regime. Finally, for $\rho_{f(t)}$ we have:

$$\begin{aligned}\bar{\rho}_f(X,Y,t) &= \frac{\bar{q}k_o^{up}}{\gamma_1+\gamma_2-\gamma_3+(\bar{p}+\bar{q})k_o^{up}}\left\{e^{-\gamma_3 t} - e^{-(\gamma_1+\gamma_2+(\bar{p}+\bar{q})k_o^{up})t} \times \frac{1}{N_A}\sum_1^{N_A}\frac{1}{N_D}\sum_1^{N_D} e^{-(\Delta p+\Delta q)k_o^{up}t}\right\} \\ &+ \frac{1}{N_A}\sum_1^{N_A}\frac{1}{N_D}\sum_1^{N_D}\frac{\Delta q k_o^{up}}{\gamma_1+\gamma_2-\gamma_3+(\bar{p}+\bar{q})k_o^{up}}\left\{e^{-\gamma_3 t} - e^{-(\gamma_1+\gamma_2+(\bar{p}+\bar{q})k_o^{up})t} \times e^{-(\Delta p+\Delta q)k_o^{up}t}\right\} \\ &= \frac{n^{\max}Yk_o^{up}}{\gamma_1+\gamma_2-\gamma_3+n^{\max}(X+Y)k_o^{up}}\left\{e^{-\gamma_3 t} - \left[\Delta_f^{stat(1)}(X,Y,t) - \frac{\Delta_f^{stat(2)}(X,Y,t)}{n^{\max}Y}\right]e^{-(\gamma_1+\gamma_2+n^{\max}(X+Y)k_o^{up})t}\right\}. \qquad (14)\end{aligned}$$

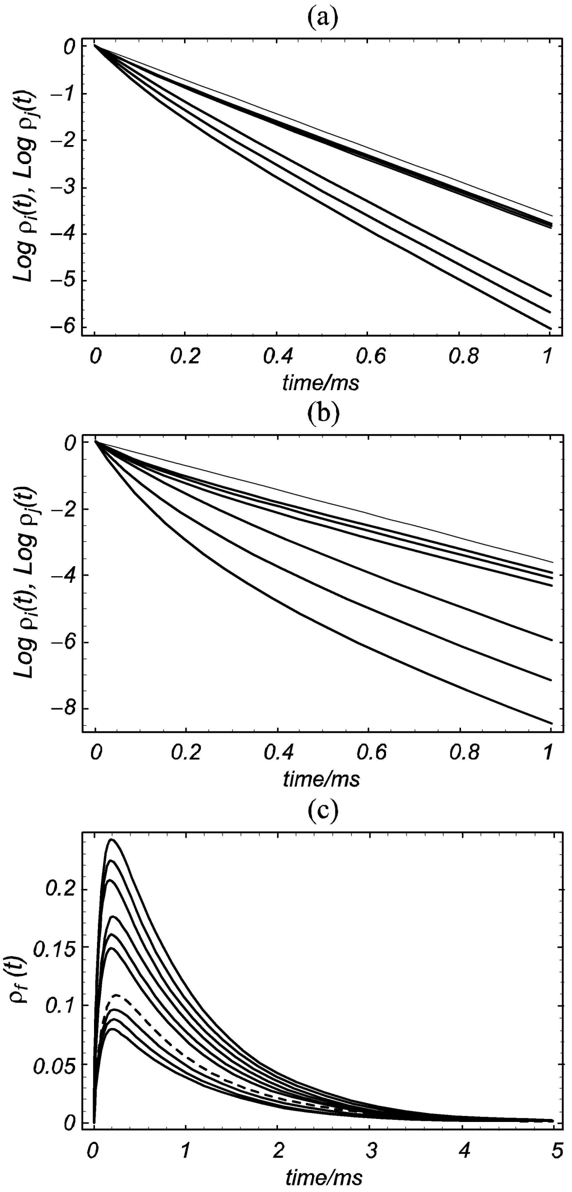

FIGURE 2. Microscopic temporary evolution of the probabilities $\rho_i(t), \rho_j(t)$ and $\rho_f(t)$. a)The upper straight line is the $-\gamma_1$ slope of isolated intra-ion donor decay. Donor center (upper triplet of lines) decaying from $|d*\rangle$ intermediate state show almost indistinguishable decay rates for *(p,q) = (1,3); (1,2); (1,1)* local environments and $k_o^{up} = 1400(s^{-1})$, whereas acceptor center (lower triplet of lines) decaying from $|a*\rangle$ intermediate state show faster decays as q increases (*(p,q) = (1,1); (1,2); (1,3)*) local environments and $k_o^{up} = 1400(s^{-1})$). b)same case for a higher upconversion rate $k_o^{up} = 5600(s^{-1})$ allow to identify that the donor decay rate lower as q increases (*(p,q) = (1,3); (1,2); (1,1)*) local environments) and c) acceptor center in an $|a^{up}\rangle$ up-converted state. The solid lines represents temporal evolution of the up-converted state at different local environments: upper triplet of lines (*(p,q) = (1,3); (2,3); (3,3),* in descendent order), intermediate triplet of lines (*(p,q) = (1,2); (2,2); (3,2),* in descendent order) and lower triplet of lines (*(p,q) = (1,1); (2,1); (3,1),* in descendent order) the dotted line corresponds to kinetic type equations [for all cases: $\gamma_1 = 3600(s^{-1}), \gamma_2 = 5000(s^{-1}), \gamma_3 = 1000(s^{-1})$ and $k_o^{up} = 1400(s^{-1})$].

The statistical factors $\Delta^{stat(1)}(X,Y,t)$ and $\Delta^{stat(2)}(X,Y,t)$ have been listed in the Appendix A. The problem of find the magnitude of k_o^{up} from the experimental data, may be solved either from the initial slopes of Eqs. (12) and (13) or from the maximum of the macroscopic probability $\bar{\rho}_f(X,Y,t)$. In this last case for instance, the maximum $(\bar{\rho}'_f(X,Y,t*) = 0)$ leads to an approximate quadratic equation in k_o^{up} with a non-negative solution (see Appendix B):

$$k_o^{up*} = \frac{e^{\gamma_3 t*}(\gamma_1 + \gamma_2)\,\bar{\rho}_f(t*)}{(Y - e^{\gamma_3 t*}(X+Y)\,\bar{\rho}_f(t*))\,n^{\max}}, \qquad (15)$$

a magnitude easy to calculate once the γ_1, γ_2 and γ_3 intrinsic decay rates have been determined experimentally from independent experiments carried out at the isolation limit for the luminescent system, and as the remaining parameters $X, Y, n^{\max}$ depend on the preparation of the sample and $t*$ and $\bar{\rho}_f(t*)$ established from the experimental decay curve. The k_o^{up*}figure can be used as an initial guess for the subsequent fit of the experimental data to the model Eqs. (12), (13), and (14).

3. Results

Using cubic elpasolites doped with optical centers as the model system, microscopic solutions (8), (9) and (10) have been plotted in Fig. 2 for an adequate set of rate values[19,20,22]. Figures 2a and 2b show relaxations from intermediate states$|d*\rangle$ and $|a*\rangle$ that follow the expected temporary behavior of optical centers decaying under the effect of energy transfer processes. For local environments with low donor and acceptor population (*i.e.* $p = q$ =1), decay curves are single exponential with expected initial slopes $(-\gamma_1 - k_o^{up})$ and $(-\gamma_2 - k_o^{up})$, respectively, but slightly modified by the higher order t^n terms in the expansion. The solutions also recover the γ_1 and γ_2 rates (intra-center decay rates at the limit of dilution) at long times after the initial excitation, which is in agreement with the experimental evidence. Figures 2a and 2b also include the effect produced by the increase of q and p, which leads to more marked deviations of the single exponential behavior from the excited states, because the upconversion processes become competitive and eventually more important than the intrinsic decays γ_1 and γ_2 at higher donor and acceptor concentrations.

Differences between full numerical solutions of the set of differential equations (3) and series expansion for $\rho_i(t)$ [Eq. (6)] and $\rho_j(t)$ [Eq. (7)] were negligible for a low concentration of luminescent centers except for very long times after excitation: in most of the cases a third or fourth order correction in t for the series expansion is enough to describe extremely well the initial temporary evolution of the system, but for extended temporal ranges or if the number of interacting optical centers is increased, higher order corrections in time are required.

A simple criterion may be stated to find the time interval in which the series is appropriate for an $n-$th order in the expansion. Convergence is achieved if the $(n+1)$*th* term in the polynomial series is smaller than the preceding nth term. Both have a binomial form that can be approximated by excess from the higher rate contribution ($r_{\max} = \max imum\,\{\gamma_1, \gamma_2, pk_o, qk_o\}$):

$$2^n (r_{\max})^n \frac{t^n}{n!} > 2^{n+1} (r_{\max})^{n+1} \frac{t^{n+1}}{(n+1)!}$$

$$\Rightarrow 0 \le t < \frac{n+1}{2r_{\max}}.$$

As a consequence and for $n \le 5$, a good agreement between the numerical and analytic results can be found in a time interval

$$0 \le t < \tfrac{3}{2}(r_{\max})^{-1},$$

while validity for longer time ranges can only be achieved for series with larger n. Computation of such expansions can easily be done in a recursive way using *Mathematica*[28].

However, we stress that most of the physically relevant information of the process (intra-center decay and energy transfer rates) is contained in the initial slope of the decay curves and, in order to obtain these rate values from experimental decay curves, we need only the early temporary evolution of the system.

Figure (2.c) includes information on the temporary evolution of $\rho_f(t)$or, in other words, relaxation from the up-converted state $|a^{up}\rangle$ at the microscopic scale, for different numbers p and q of interacting donors and acceptors. Variation in the local environment of optical centers shows clear effects on both the shape and the absolute value of the maximum of the curve decay, a result that is in agreement with what is suggested by the general trends of experimental data. Limitations of the kinetic-type solution are evident as it is a unique curve, not dependent on the concentration of donor and acceptor centers (drawn as a dotted line in Fig. 2c).

Figure 3 shows the differences between first-order [Eq. (10)] and second-order [Eq. (11)] microscopic analytic solutions for $\rho_f(t)$in the case of low concentration of luminescent centers ($p = q = 1$). Both solutions are in agreement for early temporal evolution, accurately reproducing the rising slope of the up converted state. However, the term including the imaginary error function, *Erfi(x)*, (which in spite of its name is actually a real number) increases strongly some time after the maximum $\rho_f(t*)$ of the up converted probability, and darkens the behavior of the remaining two other terms of Eq. (11)[28]. Solving Eq. (3) including higher order terms t^3, t^4 should compensate for this problem, but there is no simple way of integrating the differential equation and obtaining simple analytic solutions such as (10) or (11). Figure 3 also includes a full solution for $\rho_f(t)$ obtained from direct numerical integration of the set of differential equations (3), which is located between first and second order analytic equations (10) and (11). The differences between full numerical solutions and the analytic expression (10) are small, an outstanding result that shows how robust the method is in particular for the study of relaxation from the up converted state $|a^{up}\rangle$ even if, for the sake of simplicity, a first order approximation like (10) is chosen as the representative formalism of a further inclusion of statistical effects.

Finally, in Fig. 4, macroscopic decays have been plotted as *Log*(*Intensity*) vs. time in the case of centers relaxing from intermediate $|d*\rangle$ and $|a*\rangle$ states, or directly as *Intensity* vs. time curves for acceptors relaxing from the $|a^{up}\rangle$ up-converted state, due to the direct proportionality between $\bar{\rho}(X, Y, t)$ and the intensity of the luminescence. Macroscopic decay curves from $|d*\rangle$ and $|a*\rangle$ states show that consideration of the statistical fluctuations of the optical center's population enhances the non-single exponential behavior, although the effect is small, in agreement with previous works[20,22]. A similar effect occurs for relaxations from the up-converted $|a^{up}\rangle$ state, slightly flattening the shape of the macroscopic curve and changing the time t* for the maximum of the luminescent intensity, compared to the microscopic one.

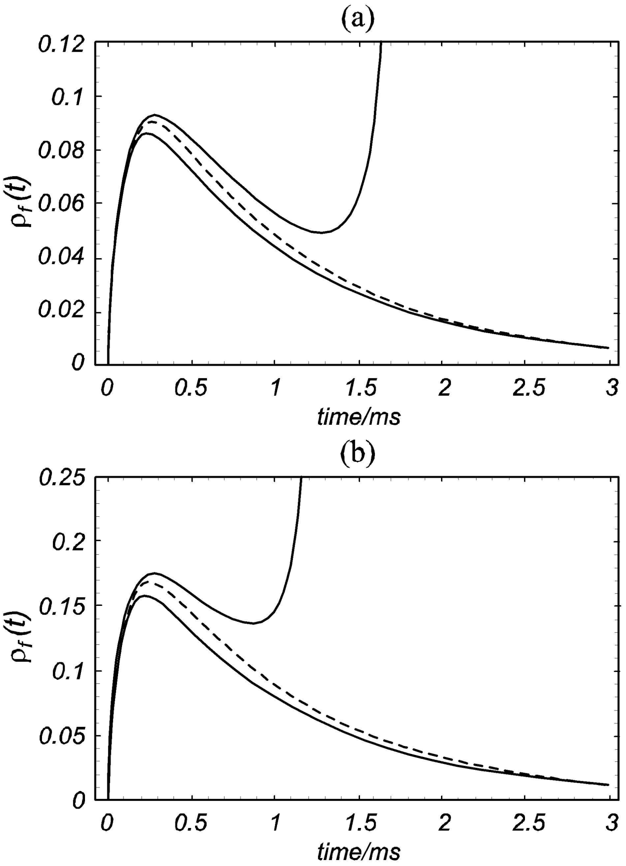

FIGURE 3. Microscopic temporary evolution of the probability $\rho_f(t)$. First and second order analytic solution compared to numerical solutions. a) diluted local environments ((*p, q*) = *(1,1)*) and $k_o^{up} = 1200(s^{-1})$, b) increment on q ((*p, q*) = *(1,2)*) and $k_o^{up} = 1200(s^{-1})$. Upper solid line corresponds to second order analytic solution (note divergence at $t > 1$ (ms)); dashed line is the full numerical solution and lower solid line the first order analytic solution. [For all cases: $\gamma_1 = 3600(s^{-1}), \gamma_2 = 5000(s^{-1})$, $\gamma_3 = 1000(s^{-1})$].

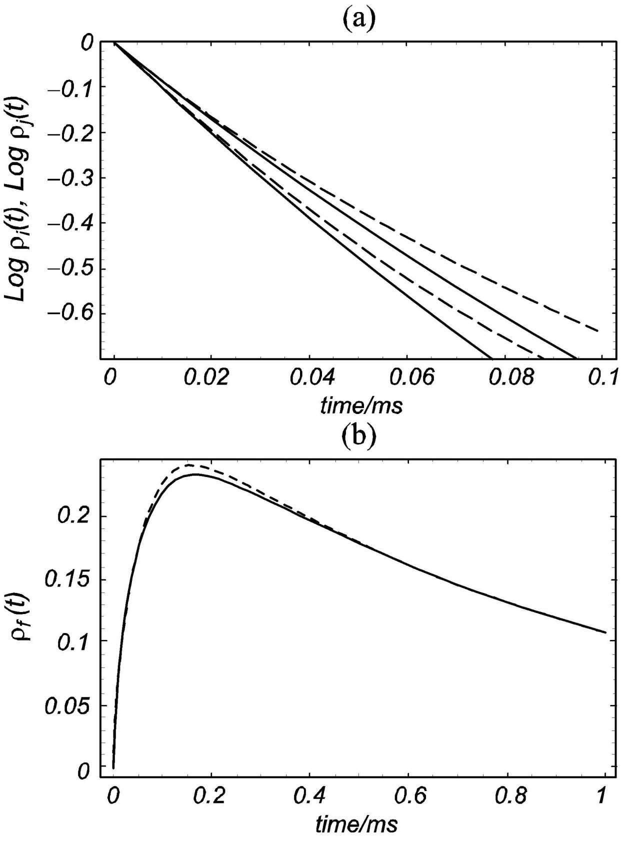

FIGURE 4. Decay curves for a cubic system. a) $|d*\rangle \rightarrow |d^o\rangle$ early temporary decay for the donor centers and $|a*\rangle \rightarrow |a^o\rangle$ acceptor centers (in both cases upper dashed line is the microscopic type solution *((p,q) = (1,1))* and lower full line corresponds to macroscopic averaged solution for an analogous doping concentration of *X = Y = 0.167*) and b) $|a^{up}\rangle \rightarrow |a^o\rangle$ decay for the acceptor centers from the up-converted state near the maximum: the curve is flattened. For all cases $\gamma_1 = 3600(s^{-1}), \gamma_2 = 5000(s^{-1})$, $\gamma_3 = 1000(s^{-1}), k_o^{up} = 5600(s^{-1})$, the dashed line is the microscopic type solution *((p,q) = (1,1))* and the full line corresponds to macroscopic averaged solution for an analogous doping concentration of *X = Y = 0.167* .

The macroscopic formalisms (12), (13) and (14) make it possible to study the whole concentration range of optical centers in the host crystal, since the equations are expressed in terms of unrestricted doping values (*i.e.* $0 \leq X + Y \leq 1$). However, we are limiting the model's validity range to low doping, less than 20%, to avoid the use of very large polynomials in the microscopic solutions $\rho_i(t)$ and $\rho_j(t)$, and considering that most of the experimental evidence is obtained within this concentration range. There is also another fact that supports this upper limit: doping higher than 20% increases substantially the possibility of finding clusters of pairs, which would make possible the appearance of three or more centers microscopic mechanisms for the upconversion processes.

At the microscopic level, we have shown that the proposed formalism produces more general equations with explicit information on the microscopic rates, composition and crystallographic details of a given donor center and its environment, and proving the limitations of the widely used kinetic-type equations. On the other hand, at the macroscopic level, and as shown in Fig. 4, consideration of the statistical fluctuations of the optical center's population improves the understanding of the shapes of the decay curves and make it possible to fit better values for transfer rates from experimental data.

4. Discussion and conclusions

The microscopic polynomial solutions found for $\rho_i(t)$ and $\rho_j(t)$ are mathematically exact for each order of correction in the time variable and of course for the complete series. Plotting their results for a set of values representative of decay and transfer rates show non-single exponential curves that are dependent on the particular environment of a donor center, mostly due to the effect of considering that the probabilities of all the states involved in the process are time-dependent. The observed behavior of the initial slopes is dependent on microscopic donors' and acceptors' local environment; $-(\gamma_1 + pk_o^{up})$ and $-(\gamma_2 + qk_o^{up})$ for $\rho_i(t)$ and $\rho_j(t)$, respectively, followed by long term $-(\gamma_1)$ and $-(\gamma_2)$ slopes, are in perfect agreement with the experimental evidence[20,21].

Analytic solutions to microscopic $\rho_f(t)$ are possible truncating polinomials $\rho_i(t)$ and $\rho_j(t)$ up to the nth order in time and solve the differential equation (3.c) for $\rho_f(t)$. Although the solution chosen for the temporal evolution of the up converted state $\rho_f(t)$ is the simplest one (first order in t for $\rho_i(t)$ and $\rho_j(t)$), there is still a considerable improvement over early solutions provided by models of the kinetic type, because it explicitly includes the actual local environment of luminescent centers in the sample and has a behavior that closely approaches that of the numerical solutions. Improved analytical solutions for $\rho_f(t)$ are limited to second order in t for $\rho_i(t)$ and $\rho_j(t)$), but results are more complex and less stable from the mathematical point of view than the simplest case.

At a higher stage, the macroscopic solutions include the effect of the statistical distribution of optical centers in the crystal lattice. This consideration has the effect of increasing the slope of the early temporary decay for the case of both $\bar{\rho}_i(t)$ and $\bar{\rho}_j(t)$, as well as a slight increasing of the non-single exponential behavior, and of flattening the shape of the decay curve of the up converted state $\bar{\rho}_f(t)$.

To summarize, the inclusion of non-isolated pairs permits a more elaborate study of the experimental decay curves of UPET-type upconversion processes than those approximations based on kinetic models that are commonly found in the literature. In contrast with the latter, the master equations (12), (13) and (14) developed in this paper are nonparametric and contain explicit information on the microscopic intra-center decay and energy transfer rates (which can be calculated from first principles) of the crystallographic characteristics of the particular crystal matrix that contains the optical centers (through $n^{\max}$), and of their actual concentration (through X and Y). This allows a much more detailed analysis of experimental data and, if the objective of the study is to calculate the rates from them, a more precise estimate.

This approach is useful for samples with low to moderate dopings, since if $X$and or$Y$ are high, eventually three-center upconversion processes can be achieved. The study of UPET processes in systems of different symmetry and/or lower dimensionality can be easily extended from this work and will be made elsewhere.

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Appendix A. Expressions for the statistical terms $\Delta^{stat}(X,Y,t)$

The $\Delta^{stat}(X,Y,t)$ terms are the result of averaging the deviations Δp and Δq from the mean values, $\bar{p}$and $\bar{q}$, of the number of acceptor centers surrounding the donor, and of the number of donor centers surrounding a generic acceptor, respectively. In order to obtain an appropriate formalism (though with a somewhat slower convergence), the exponential terms which include fluctuations Δp and Δq have been expanded in a series and have been averaged directly over the populations, N_D and N_A, of donors and acceptors, respectively. The distribution of optical centers in the appropriate sites of the crystal lattice is of the binomial type, and in the equations below,

$$\mu_p^{(k)} = \frac{1}{N}\sum (\Delta p)^k \qquad \text{and} \qquad \mu_q^{(k)} = \frac{1}{N}\sum (\Delta q)^k$$

correspond to the kth central moments of the binomial distribution of the pairs.[19,20] The final results consider that $\mu^{(1)}$ is always nil.

$$\bar{\rho}_i(t) = \frac{1}{N_D}\sum_1^{N_D}\frac{1}{N_A}\sum_1^{N_A} e^{\left(-(\gamma_1+(\bar{p}+\Delta p)k_o^{up})t+(\bar{p}+\Delta p)k_o^{up}(\gamma_2+(\bar{q}+\Delta q)k_o^{up})\frac{t^2}{2!}-\ldots\right)} = \Delta_i^{stat}(X,Y,t)$$
$$\times\, e^{\left(-(\gamma_1+\, n^{\max}Xk_o^{up})+\, n^{\max}X\left\{k_o^{up}(\gamma_2+n^{\max}Yk_o^{up})\frac{t^2}{2!}-k_o^{up}(\gamma_2^2+(\gamma_1+2\gamma_2)n^{\max}Yk_o^{up}+(n^{\max})^2(X+Y)Yk_o^{up2})\frac{t^3}{3!}+\ldots\right\}\right)}, \qquad \text{(A.1)}$$

where:

$$\Delta_i^{stat}(X,Y,t) = \frac{1}{N_D}\sum_1^{N_D}\frac{1}{N_A}\sum_1^{N_A}\left\{1-\left[-\Delta p k_o^{up}t + k_o^{up}\left[\bar{p}\Delta q k_o^{up}+\Delta p\bar{q}k_o^{up}+\Delta p k_o^{up}(\gamma_2+\Delta q k_o^{up})\right]\frac{t^2}{2!}-\ldots\right]\right.$$
$$\left.+\left[-\Delta p k_o^{up}t + k_o^{up}\left[\bar{p}\Delta q k_o^{up}+\Delta p\bar{q}k_o^{up}+\Delta p k_o^{up}(\gamma_2+\Delta q k_o^{up})\right]\frac{t^2}{2!}-\ldots\right]^2-\ldots\right\}$$

or, in terms of the central moments $\mu_p^{(k)}$ and $\mu_q^{(k)}$,

$$\Delta_i^{stat}(X,Y,t) = \left\{1+(k_o^{up})^2\,\mu_p^{(2)}\frac{t^2}{2}-(k_o^{up})^3\left[\mu_p^{(3)}+\bar{p}\mu_q^{(2)}\right]\frac{t^3}{3!}\right.$$
$$\left.+(k_o^{up})^2\left[(\bar{p})^2\mu_q^{(2)}+\mu_p^{(2)}\{(\gamma_2)^2+2\bar{q}\gamma_2+\mu_q^{(2)}\}\right]\frac{t^4}{8}-\ldots.\right\}$$
$$=\left\{1+(k_o^{up})^2\,n^{\max}X(1-X)\frac{t^2}{2}-(k_o^{up})^3 n^{\max}\left[X(1-X)(1-2X)+n^{\max}XY(1-Y)\right]\frac{t^3}{3!}\right.$$
$$\left.+(k_o^{up})^2\left[(n^{\max})^3X^2Y(1-Y)+n^{\max}X(1-X)\,\{\,(\gamma_2)^2+2n^{\max}Y\gamma_2+n^{\max}Y(1-Y)\}\right]\frac{t^4}{8}-\ldots\right\}.$$

$$\bar{\rho}_j(t) = \frac{1}{N_D}\sum_1^{N_D}\frac{1}{N_A}\sum_1^{N_A} e^{\left(-(\gamma_2+(\bar{q}+\Delta q)k_o^{up})t+(\bar{q}+\Delta q)k_o^{up}(\gamma_1+(\bar{p}+\Delta p)k_o^{up})\frac{t^2}{2!}-\ldots\right)} = \Delta_j^{stat}(X,Y,t)$$
$$\times\, e^{\left(-(\gamma_2+\, n^{\max}Yk_o^{up})t\,+\,n^{\max}Y\left\{k_o^{up}(\gamma_1+n^{\max}Xk_o^{up})\frac{t^2}{2!}-k_o^{up}(\gamma_1^2+(2\gamma_1+\gamma_2)n^{\max}Xk_o^{up}+(n^{\max})^2(X+Y)Xk_o^{up2})\frac{t^3}{3!}+\ldots\right\}\right)} \qquad \text{(A.2)}$$

where:

$$\Delta_j^{stat}(X,Y,t) = \Big\{1 + (k_o^{up})^2\, n^{\max} Y(1-Y)\frac{t^2}{2} - (k_o^{up})^3 n^{\max}\left[Y(1-Y)(1-2Y) + n^{\max} Y X(1-X)\right]\frac{t^3}{3!}$$
$$+ (k_o^{up})^2\left[(n^{\max} Y k_o^{up})^2 n^{\max} X(1-X) + (n^{\max} X k_o^{up})^2 n^{\max} Y(1-Y)\right.$$
$$\left. +(\gamma_1 k_o^{up})^2 n^{\max} Y(1-Y) + 2n^{\max} X (k_o^{up})^2 \gamma_1 n^{\max} X(1-X)\right]\frac{t^4}{4} - ...\Big\}.$$

$$\bar{\rho}_f(X,Y,t) = \tfrac{1}{N_A}\sum_1^{N_A}\tfrac{1}{N_D}\sum_1^{N_D}\tfrac{(\bar{q}+\Delta q)k_o^{up}}{\gamma_1+\gamma_2-\gamma_3+(\bar{p}+\bar{q})k_o^{up}}\left\{e^{-\gamma_3 t} - e^{-(\gamma_1+\gamma_2+(\bar{p}+\bar{q})k_o^{up})t}\times e^{-(\Delta p+\Delta q)k_o^{up}t}\right\}$$
$$= \frac{\bar{q}k_o^{up}}{\gamma_1+\gamma_2-\gamma_3+(\bar{p}+\bar{q})k_o^{up}}\left\{e^{-\gamma_3 t} - e^{-(\gamma_1+\gamma_2+(\bar{p}+\bar{q})k_o^{up})t}\times \tfrac{1}{N_A}\sum_1^{N_A}\tfrac{1}{N_D}\sum_1^{N_D} e^{-(\Delta p+\Delta q)k_o^{up}t}\right\}$$
$$+ \tfrac{1}{N_A}\sum_1^{N_A}\tfrac{1}{N_D}\sum_1^{N_D}\tfrac{\Delta q k_o^{up}}{\gamma_1+\gamma_2-\gamma_3+(\bar{p}+\bar{q})k_o^{up}}\left\{e^{-\gamma_3 t} - e^{-(\gamma_1+\gamma_2+(\bar{p}+\bar{q})k_o^{up})t}\times e^{-(\Delta p+\Delta q)k_o^{up}t}\right\}$$
$$= \frac{n^{\max} Y k_o^{up}}{\gamma_1+\gamma_2-\gamma_3+n^{\max}(X+Y)k_o^{up}}\left\{e^{-\gamma_3 t} - \left[\Delta_f^{stat(1)}(X,Y,t) - \frac{\Delta_f^{stat(2)}(X,Y,t)}{n^{\max} Y}\right] e^{-(\gamma_1+\gamma_2+n^{\max}(X+Y)k_o^{up})t}\right\}; \qquad \text{(A.3)}$$

then,

$$\Delta_f^{stat(1)}(X,Y,t) = \frac{1}{N_A}\sum_1^{N_A}\frac{1}{N_D}\sum_1^{N_D} e^{-(\Delta p+\Delta q)k_o^{up}t} = \frac{1}{N_A}\sum_1^{N_A}\frac{1}{N_D}\sum_1^{N_D}\left[1 - (\Delta p+\Delta q)k_o^{up}t + \{(\Delta p+\Delta q)k_o^{up}\}^2\frac{t^2}{2} - ...\right]$$
$$= \left[1 + (k_o^{up})^2\left\{\mu_p^{(2)} + \mu_q^{(2)}\right\}\frac{t^2}{2!} - (k_o^{up})^3\left\{\mu_p^{(3)} + \mu_q^{(3)}\right\}\frac{t^3}{3!} + ...\right]$$
$$= \left[1 + (k_o^{up})^2\left\{n^{\max} X(1-X) + n^{\max} Y(1-Y)\right\}\frac{t^2}{2!}\right.$$
$$\left. -(k_o^{up})^3\left\{n^{\max} X(1-X)(1-2X) + n^{\max} Y(1-Y)(1-2Y)\right\}\frac{t^3}{3!} + ...\right]$$

and

$$\Delta_f^{stat(2)}(X,Y,t) = \tfrac{1}{N_A}\sum_1^{N_A}\tfrac{1}{N_D}\sum_1^{N_D}\Delta q\cdot e^{-(\Delta p+\Delta q)k_o^{up}t}$$
$$= \left[\tfrac{1}{N_A}\sum_1^{N_A}\tfrac{1}{N_D}\sum_1^{N_D}\left\{\Delta q - \Delta q(\Delta p+\Delta q)k_o^{up}t + \Delta q(\Delta p+\Delta q)^2(k_o^{up})^2\tfrac{t^2}{2!} - ...\right\}\right]$$
$$= \left[\left\{-\mu_q^{(2)}k_o^{up}t + \mu_q^{(3)}(k_o^{up})^2\frac{t^2}{2!} - \left(3\mu_p^{(2)}\mu_q^{(2)} + \mu_q^{(4)}\right)(k_o^{up})^3\frac{t^3}{3!} + ...\right\}\right]$$
$$= \left[\left\{-n^{\max} Y(1-Y)k_o^{up}t + n^{\max} Y(1-Y)(1-2Y)(k_o^{up})^2\frac{t^2}{2!} - ...\right\}\right].$$

Appendix B

The shape of the luminescent intensity from the macroscopic average of upconverted luminescent states shows a maximum at t* (*i.e.* $\bar{\rho}'_f(X,Y,t*) = 0$) and considering Eq. (14):

$$\bar{\rho}'_f(X,Y,t*) \equiv 0 = \Big\{-\gamma_3 e^{-\gamma_3 t*} + \left[\gamma_1+\gamma_2+n^{\max}(X+Y)k_o^{up}\right]\left[\Delta_f^{stat(1)}(t*) - \frac{\Delta_f^{stat(2)}(t*)}{n^{\max} Y}\right] e^{-[\gamma_1+\gamma_2+n^{\max}(X+Y)k_o^{up}]t*}$$
$$- \left[\left\{\Delta_f^{stat(1)}\right\}'(t*) - \frac{\left\{\Delta_f^{stat(2)}\right\}'(t*)}{n^{\max} Y}\right] e^{-[\gamma_1+\gamma_2+n^{\max}(X+Y)k_o^{up}]t*}\Big\}, \qquad \text{(B.1)}$$

where:

$$\left\{\Delta_f^{stat(1)}\right\}'(t*) \cong \frac{2\left(\Delta_f^{stat(1)}(t*)-1\right)}{t*} \text{ and } \left\{\Delta_f^{stat(2)}\right\}'(t*) \cong \frac{\Delta_f^{stat(2)}(t*)}{t*}. \tag{B.2}$$

Replacing and reordering in terms of $\gamma_1, \gamma_2, \gamma_3, k_o^{up}, X, Y, n^{\max}, t*$ and $\bar{\rho}_f(t*)$:

$$-\gamma_3 e^{-\gamma_3 t*} + \left[e^{-\gamma_3 t*} - \frac{\gamma_1+\gamma_2-\gamma_3+n^{\max}(X+Y)k_o^{up}}{n^{\max}Y k_o^{up}}\bar{\rho}_f(t*)\right] \times \left[\gamma_1+\gamma_2+n^{\max}(X+Y)k_o^{up} - \frac{1}{t*} - \frac{\left\{\Delta_f^{stat(1)}(t*)-2\right\}}{\left\{\Delta_f^{stat(1)}(t*) - \frac{\Delta_f^{stat(2)}(t*)}{n^{\max}Y}\right\}t*}\right] = 0 \tag{B.3}$$

and, as $t*$ is not far from $t = 0$,

$$\frac{\left\{\Delta_f^{stat(1)}(t*)-2\right\}}{\left\{\Delta_f^{stat(1)}(t*) - \frac{\Delta_f^{stat(2)}(t*)}{n^{\max}Y}\right\}t*} \cong \frac{-1}{\left(1-(1-Y)n^{\max}k_o^{up}t*\right)t*} \longrightarrow -\frac{1}{t*} \tag{B.4}$$

and finally, Eq. (B.3) becomes quadratic in k_o^{up}

$$-\gamma_3 e^{-\gamma_3 t*} + \left[e^{-\gamma_3 t*} - \frac{\gamma_1+\gamma_2-\gamma_3+n^{\max}(X+Y)k_o^{up}}{n^{\max}Y k_o^{up}}\bar{\rho}_f(t*)\right]\left[\gamma_1+\gamma_2+n^{\max}(X+Y)k_o^{up}\right] = 0 \tag{B.5}$$

with solutions:

$$k_o^{up*} = \frac{e^{\gamma_3 t*}(\gamma_1+\gamma_2)\,\bar{\rho}_f(t*)}{\left(Y - e^{\gamma_3 t*}(X+Y)\,\bar{\rho}_f(t*)\right)n^{\max}} \text{ and } k_o^{up*} = -\frac{(\gamma_1+\gamma_2-\gamma_3)}{\{1-Y\,n^{\max}\}} \tag{B.6}$$

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