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Theory of the kinetics of luminescence and its temperature dependence for Ag nanoclusters dispersed in glass host.

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Contents

Introduction

In this supporting information file we find a solution of the system of the first order linear homogeneous differential equations:

$$\begin{cases} \dot{n_1}(t) = -(\Gamma_{12} + k_1)n_1(t) + \Gamma_{21}n_2(t) \\ \dot{n_2}(t) = \Gamma_{12}n_1(t) - (\Gamma_{21} + k_2)n_2(t) \end{cases} \quad \text{(S1)}$$

where n_1(t) and n_2(t) are time-dependent functions of concentrations of electrons at S_1 and T_2 excited energy levels in agreement with energy level diagram of *Ag nanocluster* shown in Fig. 2 in the main body of paper, $\dot{n_1}(t)$ and $\dot{n_2}(t)$ are the first time derivatives of time-dependent functions of concentrations of electrons at S_1 and T_2 excited energy levels, k_1 and k_2 are the rates of spontaneous emission from S_1 and T_2 the excited states to S_0 the ground state levels which are functions of emission wavelength, Γ_{12} and Γ_{21} are temperature-dependent rate functions of the intersystem crossing process from S_1 to T_2 excited levels and from T_2 to S_1 excited levels, t is independent variable which stands for time.

According to Ref.[1] a general solution of the system of linear homogeneous differential equations (S1) can be written using the time-dependent function:

$$n(t) = \begin{cases} n_1(t) = c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t} \\ n_2(t) = c_3 e^{-\lambda_1 t} + c_4 e^{-\lambda_2 t} \end{cases} \quad \text{(S2)}$$

where c_1, c_2, c_3 and c_4 are arbitrary coefficients, λ_1 and λ_2 are reciprocals of lifetimes τ_1 and τ_2, t is independent variable which stands for time. Putting $t = 0$ in the general solution (S2) leads to the system of initial values equations for the system of differential Eqs. (S1):

$$\begin{cases} n_1(0) = c_1 + c_2 \\ n_2(0) = c_3 + c_4 \end{cases} \quad \text{(S3)}$$

Part 1

In Part 1 we find the unknown arbitrary coefficients c_1, c_2, c_3 and c_4 for the general solution (S2). Let us find these coefficients according to a procedure described in Ref.[1] We start with substituting $n_1 = c_1 e^{-\lambda_1 t}$ and $n_2 = c_3 e^{-\lambda_1 t}$ from the general solution (S2) into the system of Eqs. (S1):

$$\begin{cases} -\lambda_1 c_1 e^{-\lambda_1 t} = -(\Gamma_{12} + k_1)c_1 e^{-\lambda_1 t} + \Gamma_{21}c_3 e^{-\lambda_1 t} \\ -\lambda_1 c_3 e^{-\lambda_1 t} = \Gamma_{12}c_1 e^{-\lambda_1 t} - (\Gamma_{21} + k_2)c_3 e^{-\lambda_1 t} \end{cases} \quad \text{(S4)}$$

We divide both sides of the system of Eqs. (S4) by $e^{-\lambda_1 t}$:

$$\begin{cases} -\lambda_1 c_1 = -(\Gamma_{12} + k_1)c_1 + \Gamma_{21}c_3 \\ -\lambda_1 c_3 = \Gamma_{12}c_1 - (\Gamma_{21} + k_2)c_3 \end{cases} \quad \text{(S5)}$$

Adding the first and the second rows of the system of Eqs. (S5), we find:

$$-\lambda_1 c_1 - \lambda_1 c_3 = -(\Gamma_{12} + k_1)c_1 + \Gamma_{21} c_3 + \Gamma_{12} c_1 - (\Gamma_{21} + k_2)c_3 \quad \text{(S6)}$$

Eq. (S6) gives:

$$\lambda_1 c_1 + \lambda_1 c_3 = k_1 c_1 + k_2 c_3 \quad \text{(S7)}$$

Using the Eq. (S6) we find the expressions for the coefficients c_1 and c_3:

$$c_1 = \frac{(\lambda_1 - k_2)}{(k_1 - \lambda_1)} c_3 \quad \text{(S8)}$$

$$c_3 = \frac{(k_1 - \lambda_1)}{(\lambda_1 - k_2)} c_1 \quad \text{(S9)}$$

By the analogy, we substitute $n_1 = c_2 e^{-\lambda_2 t}$ and $n_2 = c_4 e^{-\lambda_2 t}$ from the general solution (S2) into the system of Eqs. (S1) and apply the same procedure for finding of relations between the coefficients, we have:

$$c_2 = \frac{(\lambda_2 - k_2)}{(k_1 - \lambda_2)} c_4 \quad \text{(S10)}$$

$$c_4 = \frac{(k_1 - \lambda_2)}{(\lambda_2 - k_2)} c_2 \quad \text{(S11)}$$

Substituting (S9) and (S11) into the second row of the system of initial values Eqs. (S3), we find:

$$\begin{cases} c_1 = n_1(0) - c_2 \\ n_2(0) = \frac{(k_1 - \lambda_1)}{(\lambda_1 - k_2)} c_1 + \frac{(k_1 - \lambda_2)}{(\lambda_2 - k_2)} c_2 \end{cases} \quad \text{(S12)}$$

Replacing the coefficient c_1 in the second row of the system of Eqs. (S12) by the first row of the system of Eqs. (S12), we get:

$$\begin{cases} c_1 = n_1(0) - c_2 \\ n_2(0) = \frac{(k_1 - \lambda_1)}{(\lambda_1 - k_2)} (n_1(0) - c_2) + \frac{(k_1 - \lambda_2)}{(\lambda_2 - k_2)} c_2 \end{cases} \quad \text{(S13)}$$

From the second row of the system of Eqs. (S13), we have:

$$\frac{(\lambda_2 - k_2)(\lambda_1 - k_2)}{(\lambda_1 - k_2)(\lambda_2 - k_2)} n_2(0) = \frac{(k_1 - \lambda_1)(\lambda_2 - k_2)}{(\lambda_1 - k_2)(\lambda_2 - k_2)} (n_1(0) - c_2) + \frac{(\lambda_1 - k_2)(k_1 - \lambda_2)}{(\lambda_1 - k_2)(\lambda_2 - k_2)} c_2 \quad \text{(S14)}$$

$$\frac{(\lambda_2 - k_2)(\lambda_1 - k_2)}{(\lambda_1 - k_2)(\lambda_2 - k_2)} n_2(0) - \frac{(k_1 - \lambda_1)(\lambda_2 - k_2)}{(\lambda_1 - k_2)(\lambda_2 - k_2)} n_1(0) = -\frac{(k_1 - \lambda_1)(\lambda_2 - k_2)}{(\lambda_1 - k_2)(\lambda_2 - k_2)} c_2 + \frac{(\lambda_1 - k_2)(k_1 - \lambda_2)}{(\lambda_1 - k_2)(\lambda_2 - k_2)} c_2 \quad \text{(S15)}$$

$$(\lambda_2 - k_2)(\lambda_1 - k_2) n_2(0) + (\lambda_1 - k_1)(\lambda_2 - k_2) n_1(0) = (\lambda_1 k_1 + \lambda_2 k_2 - \lambda_2 k_1 - \lambda_1 k_2) c_2 \quad \text{(S16)}$$

Let us define c_2 as equal to the left side of (S16):

$$c_2 = \frac{(\lambda_2 - k_2)(\lambda_1 - k_2) n_2(0) + (\lambda_1 - k_1)(\lambda_2 - k_2) n_1(0)}{(\lambda_1 - \lambda_2)(k_1 - k_2)} = \frac{(\lambda_1 - k_1)(\lambda_2 - k_2)}{(\lambda_1 - \lambda_2)(k_1 - k_2)} n_1(0) + \frac{(\lambda_2 - k_2)(\lambda_1 - k_2)}{(\lambda_1 - \lambda_2)(k_1 - k_2)} n_2(0) =$$
$$\frac{(\lambda_1 - k_1)(\lambda_2 - k_2)}{(\lambda_1 - \lambda_2)(k_1 - k_2)} n_1(0) - \frac{(k_2 - \lambda_2)(\lambda_1 - k_2)}{(\lambda_1 - \lambda_2)(k_1 - k_2)} n_2(0) \quad \text{(S17)}$$

Now we find the coefficient c_1. Substitution Eq. (S17) into the first row of the system of Eqs. (S13) gives:

$$c_1 = \frac{(\lambda_1-\lambda_2)(k_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0) =$$
$$\frac{(\lambda_1 k_1-\lambda_1 k_2-\lambda_2 k_1+\lambda_2 k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_1\lambda_2-\lambda_1 k_2-\lambda_2 k_1+k_1 k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0) =$$
$$\frac{(\lambda_1 k_1-k_1 k_2-\lambda_1\lambda_2+\lambda_2 k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0) = \frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0) \quad \text{(S18)}$$

Now we find the coefficients c_3 and c_4. Replacing the coefficient c_1 in the Eq. (S9) by the Eq. (S18), we find:

$$c_3 = \frac{(k_1-\lambda_1)}{(\lambda_1-k_2)} c_1 = \frac{(k_1-\lambda_1)}{(\lambda_1-k_2)}\left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) = \frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0) \quad \text{(S19)}$$

Replacing the coefficient c_2 in the Eq. (S11) by the Eq. (S17), we find:

$$c_4 = \frac{(k_1-\lambda_2)}{(\lambda_2-k_2)} c_2 = \frac{(k_1-\lambda_2)}{(\lambda_2-k_2)}\left(\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) + \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) = \frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0) \quad \text{(S20)}$$

Substitution the Eqs. (S17), (S18), (S19) and (S20) into the general solution (S2) gives the final solution of the system of differential Eqs. (S1) is:

$$n_1 = \left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_1 t} + \left(\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_2 t} \quad \text{(S21)}$$

$$n_2 = \left(\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_1 t} + \left(\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_2 t} \quad \text{(S22)}$$

Part 2

In Part 2 we check out the solution (S21) and (S22) for the system of differential Eqs. (S1). Addition the first and the second rows of the system of differential Eqs. (S1) gives:

$$\dot{n}_1(t) + \dot{n}_2(t) = -k_1 n_1(t) - k_2 n_2(t) \quad \text{(S23)}$$

We replace n_1(t) and n_2(t) in the differential Eq. (S23) by the Eqs. (S21) and (S22):

$$-\lambda_1\left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_1 t} - \lambda_2\left(\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_2 t} -$$
$$-\lambda_1\left(\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_1 t} - \lambda_2\left(\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_2 t} =$$
$$-k_1\left(\left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_1 t} + \left(\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_2 t}\right) -$$
$$-k_2\left(\left(\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_1 t} + \left(\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_1(0) - \frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)} n_2(0)\right) e^{-\lambda_2 t}\right) \quad \text{(S24)}$$

The Eq. (S24) is to be true for all values of t, then the coefficients of $e^{-\lambda_1 t}$ and $e^{-\lambda_2 t}$ must vanish. Now we consider the equation for the coefficients of $e^{-\lambda_1 t}$ which follows from the Eq. (S24):

$$-\lambda_1\left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)e^{-\lambda_1 t}-\lambda_1\left(\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)e^{-\lambda_1 t}=$$
$$-k_1\left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)e^{-\lambda_1 t}-k_2\left(\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)e^{-\lambda_1 t} \qquad \text{(S25)}$$

Division of the Eq. (S25) by $e^{-\lambda_1 t}$ gives:

$$-\lambda_1\left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)-\lambda_1\left(\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)=$$
$$-k_1\left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)-k_2\left(\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right) \qquad \text{(S26)}$$

Eq. (S26) gives:

$$\left(-\lambda_1\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}-\lambda_1\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}+k_1\frac{(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}+k_2\frac{(k_1-\lambda_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}\right)n_1(0)=\left(-\lambda_1\frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}-\lambda_1\frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}+\right.$$
$$\left.k_1\frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}+k_2\frac{(\lambda_2-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}\right)n_2(0) \qquad \text{(S27)}$$

Eq. (S27) becomes:

$$\left(\frac{(\lambda_1-k_2)(k_1-\lambda_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}-\frac{(\lambda_1-k_2)(k_1-\lambda_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}\right)n_1(0)=\left(\frac{(\lambda_2-k_2)(\lambda_1-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}-\frac{(\lambda_2-k_2)(\lambda_1-k_2)(k_1-\lambda_1)}{(\lambda_1-\lambda_2)(k_1-k_2)}\right)n_2(0) \qquad \text{(S28)}$$

Now we consider the equation for the coefficients of $e^{-\lambda_2 t}$ which follows from the Eq. (S28):

$$-\lambda_2\left(\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)e^{-\lambda_2 t}-\lambda_2\left(\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)e^{-\lambda_2 t}=$$
$$-k_1\left(\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)e^{-\lambda_2 t}-k_2\left(\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)e^{-\lambda_2 t} \qquad \text{(S29)}$$

Division of the Eq. (S29) by $e^{-\lambda_2 t}$ gives:

$$-\lambda_2\left(\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)-\lambda_2\left(\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)=$$
$$-k_1\left(\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right)-k_2\left(\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_1(0)-\frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}n_2(0)\right) \qquad \text{(S30)}$$

Eq. (S30) becomes:

$$\left(-\lambda_2\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}-\lambda_2\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}+k_1\frac{(\lambda_1-k_1)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}+k_2\frac{(\lambda_1-k_1)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}\right)n_1(0)=\left(-\lambda_2\frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}-\lambda_2\frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}+\right.$$
$$\left.k_1\frac{(k_2-\lambda_2)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}+k_2\frac{(\lambda_2-k_1)(\lambda_1-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}\right)n_2(0) \qquad \text{(S31)}$$

Eq. (S31) gives:

$$\left(\frac{(\lambda_1-k_1)(k_1-\lambda_2)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}-\frac{(\lambda_1-k_1)(k_1-\lambda_2)(\lambda_2-k_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}\right)n_1(0)=\left(\frac{(k_2-\lambda_2)(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}-\frac{(k_2-\lambda_2)(\lambda_1-k_2)(k_1-\lambda_2)}{(\lambda_1-\lambda_2)(k_1-k_2)}\right)n_2(0) \qquad \text{(S32)}$$

Part 3

In Part 3 we find the expressions for Γ_{12} and Γ_{21}. We replace c_3 in the first row and c_1 in the second row of the system of Eqs. (S5) by (S9) and (S8):

$$\begin{cases} -\lambda_1 c_1 = -(\Gamma_{12} + k_1)c_1 + \Gamma_{21}\frac{(k_1-\lambda_1)}{(\lambda_1-k_2)}c_1 \\ -\lambda_1 c_3 = \Gamma_{12}\frac{(\lambda_1-k_2)}{(k_1-\lambda_1)}c_3 - (\Gamma_{21} + k_2)c_3 \end{cases} \quad \text{(S33)}$$

We define λ_1 as the left side of the first and second rows of the system of Eqs. (S33)

$$\begin{cases} -\lambda_1 = -(\Gamma_{12} + k_1) + \Gamma_{21}\frac{(k_1-\lambda_1)}{(\lambda_1-k_2)} \\ -\lambda_1 = \Gamma_{12}\frac{(\lambda_1-k_2)}{(k_1-\lambda_1)} - (\Gamma_{21} + k_2) \end{cases} \quad \text{(S34)}$$

The first and the second rows of the system of Eqs. (S34) are equivalent to each other. Subsequently, we have:

$$-(\Gamma_{12} + k_1) + \Gamma_{21}\frac{(k_1-\lambda_1)}{(\lambda_1-k_2)} = \Gamma_{12}\frac{(\lambda_1-k_2)}{(k_1-\lambda_1)} - (\Gamma_{21} + k_2) \quad \text{(S35)}$$

Eq. (S35) gives:

$$\Gamma_{12}\frac{(k_1-k_2)}{(k_1-\lambda_1)} = \Gamma_{21}\frac{(k_1-k_2)}{(\lambda_1-k_2)} - (k_1 - k_2) \quad \text{(S36)}$$

Dividing the Eq. (S36) by (k_1-k_2), we find:

$$\Gamma_{12} = (k_1 - \lambda_1)\left(\Gamma_{21}\frac{1}{(\lambda_1-k_2)} - 1\right) \quad \text{(S37)}$$

We substitute the $n_1 = c_2 e^{-\lambda_2 t}$ and $n_2 = c_4 e^{-\lambda_2 t}$ from the general solution (S2) into the system of Eqs. (S1):

$$\begin{cases} -\lambda_2 c_2 = -(\Gamma_{12} + k_1)c_2 + \Gamma_{21}c_4 \\ -\lambda_2 c_4 = \Gamma_{12}c_2 - (\Gamma_{21} + k_2)c_4 \end{cases} \quad \text{(S38)}$$

By the analogy, we replace c_4 in the first row and c_2 in the second row of the system of Eqs. (S38) by (S10) and (S11):

$$\begin{cases} -\lambda_2 c_2 = -(\Gamma_{12} + k_1)c_2 + \Gamma_{21}\frac{(k_1-\lambda_2)}{(\lambda_2-k_2)}c_2 \\ -\lambda_2 c_4 = \Gamma_{12}\frac{(\lambda_2-k_2)}{(k_1-\lambda_2)}c_4 - (\Gamma_{21} + k_2)c_4 \end{cases} \quad \text{(S39)}$$

We define λ_2 as the left side of the first and second rows of the system of Eqs. (S39):

$$\begin{cases} -\lambda_2 = -(\Gamma_{12} + k_1) + \Gamma_{21}\frac{(k_1-\lambda_2)}{(\lambda_2-k_2)} \\ -\lambda_2 = \Gamma_{12}\frac{(\lambda_2-k_2)}{(k_1-\lambda_2)} - (\Gamma_{21} + k_2) \end{cases} \quad \text{(S40)}$$

The first and the second rows of the system of Eqs. (S40) are equivalent to each other. Subsequently, we have:

$$-(\Gamma_{12}+k_1)+\Gamma_{21}\frac{(k_1-\lambda_2)}{(\lambda_2-k_2)}=\Gamma_{12}\frac{(\lambda_2-k_2)}{(k_1-\lambda_2)}-(\Gamma_{21}+k_2) \quad \text{(S41)}$$

Eq. (S41) gives:

$$\Gamma_{12}\left(\frac{(k_1-k_2)}{(k_1-\lambda_2)}\right)=\Gamma_{21}\frac{(k_1-k_2)}{(\lambda_2-k_2)}-(k_1-k_2) \quad \text{(S42)}$$

Dividing the Eq. (S42) by (k_1-k_2), we get:

$$\Gamma_{12}=(k_1-\lambda_2)\left(\Gamma_{21}\frac{1}{(\lambda_2-k_2)}-1\right) \quad \text{(S43)}$$

The Eqs. (S37) and (S43) are equivalent. Subsequently, we have:

$$(k_1-\lambda_1)\left(\Gamma_{21}\frac{1}{(\lambda_1-k_2)}-1\right)=(k_1-\lambda_2)\left(\Gamma_{21}\frac{1}{(\lambda_2-k_2)}-1\right) \quad \text{(S44)}$$

Eq. (S44) gives:

$$\left(\Gamma_{21}\frac{1}{(\lambda_1-k_2)}-1\right)=\frac{(k_1-\lambda_2)}{(k_1-\lambda_1)}\left(\Gamma_{21}\frac{1}{(\lambda_2-k_2)}-1\right) \quad \text{(S45)}$$

$$\Gamma_{21}\left(\frac{(k_1-\lambda_1)(\lambda_2-k_2)-(k_1-\lambda_2)(\lambda_1-k_2)}{(k_1-\lambda_1)(\lambda_2-k_2)(\lambda_1-k_2)}\right)=\frac{(k_1-\lambda_1)-(k_1-\lambda_2)}{(k_1-\lambda_1)} \quad \text{(S46)}$$

$$\Gamma_{21}\left(\frac{(k_1\lambda_2-k_1k_2-\lambda_1\lambda_2+\lambda_1k_2)-(k_1\lambda_1-k_1k_2-\lambda_1\lambda_2+\lambda_2k_2)}{(k_1-\lambda_1)(\lambda_2-k_2)(\lambda_1-k_2)}\right)=\frac{(\lambda_2-\lambda_1)}{(k_1-\lambda_1)} \quad \text{(S47)}$$

$$\Gamma_{21}\left(\frac{(k_1-k_2)(\lambda_2-\lambda_1)}{(k_1-\lambda_1)(\lambda_2-k_2)(\lambda_1-k_2)}\right)=\frac{(\lambda_2-\lambda_1)}{(k_1-\lambda_1)} \quad \text{(S48)}$$

We define Γ_{21} as the left side of Eq. (S48):

$$\Gamma_{21}=\frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(k_1-k_2)} \quad \text{(S49)}$$

Substituting Eq. (S49) into Eq. (S37), we find Γ_{12}:

$$\Gamma_{12}=(k_1-\lambda_1)\left(\Gamma_{21}\frac{1}{(\lambda_1-k_2)}-1\right)=(k_1-\lambda_1)\left(\frac{(\lambda_2-k_2)(\lambda_1-k_2)}{(k_1-k_2)}\frac{1}{(\lambda_1-k_2)}-1\right)=(k_1-\lambda_1)\left(\frac{(\lambda_2-k_2)}{(k_1-k_2)}-1\right)=$$
$$(k_1-\lambda_1)\left(\frac{(\lambda_2-k_2)-(k_1-k_2)}{(k_1-k_2)}\right)=\frac{(\lambda_2-k_1)(k_1-\lambda_1)}{(k_1-k_2)} \quad \text{(S50)}$$

Part 4

In part 4 we find expressions for λ_1 and λ_2. We define λ_2 as the left side of Eq. (S49):

$$\lambda_2=\Gamma_{21}\frac{(k_1-k_2)}{(\lambda_1-k_2)}+k_2 \quad \text{(S51)}$$

Replacing λ_2 in Eq. (S50) by Eq. (S51) gives:

$$\Gamma_{12}=\left(\frac{(\lambda_2-k_1)(k_1-\lambda_1)}{(k_1-k_2)}\right)=\left(\frac{\left(\Gamma_{21}\frac{(k_1-k_2)}{(\lambda_1-k_2)}+k_2-k_1\right)(k_1-\lambda_1)}{(k_1-k_2)}\right)=\left(\Gamma_{21}\frac{1}{(\lambda_1-k_2)}-1\right)(k_1-\lambda_1) \quad \text{(S52)}$$

Eq. (S52) gives:

$$\Gamma_{12}(\lambda_1 - k_2) = \Gamma_{21}(k_1 - \lambda_1) - (k_1 - \lambda_1)(\lambda_1 - k_2) \quad \text{(S53)}$$

Eq. (S53) becomes:

$$\lambda_1{}^2 - (k_1 + k_2 + \Gamma_{12} + \Gamma_{21})\lambda_1 + k_1 k_2 + \Gamma_{21} k_1 + \Gamma_{12} k_2 = 0 \quad \text{(S54)}$$

Now we define λ_1 as the left part of Eq. (S49):

$$\lambda_1 = \Gamma_{21}\frac{(k_1 - k_2)}{(\lambda_2 - k_2)} + k_2 \quad \text{(S55)}$$

Substitution Eq. (S55) into Eq. (S50) gives:

$$\Gamma_{12} = \left(\frac{(\lambda_2 - k_1)\left(k_1 - \Gamma_{21}\frac{(k_1 - k_2)}{(\lambda_2 - k_2)} - k_2\right)}{(k_1 - k_2)}\right) = \left((\lambda_2 - k_1) - \Gamma_{21}\frac{(\lambda_2 - k_1)}{(\lambda_2 - k_2)}\right) = \frac{(\lambda_2 - k_1)(\lambda_2 - k_2) - \Gamma_{21}(\lambda_2 - k_1)}{(\lambda_2 - k_2)} =$$
$$\frac{\lambda_2^2 - k_1\lambda_2 - k_1\lambda_2 + k_1 k_2 - \Gamma_{21}(\lambda_2 - k_1)}{(\lambda_2 - k_2)} \quad \text{(S56)}$$

Eq. (S56) becomes:

$$\lambda_2^2 - (k_1 + k_2 + \Gamma_{21} + \Gamma_{12})\lambda_2 + k_1 k_2 + \Gamma_{21} k_1 + \Gamma_{12} k_2 = 0 \quad \text{(S57)}$$

Eqs. (S54) and (S57) are equivalent. Subsequently, solutions for these equations are the same. A general form of these equations can be written as:

$$ax^2 + bx + c = 0 \quad \text{(S58)}$$

A solution of Eq. (S58) can be found using a well-known formula:

$$x = \frac{-b \pm \sqrt{D}}{2a} \quad \text{(S59)}$$

where $D = \sqrt{b^2 - 4ac}$

Now we find solutions of Eqs. (S54) and (S57) using the Eq. (S59):

$$D = (\Gamma_{12} + \Gamma_{21} + k_1 + k_2)^2 - 4(\Gamma_{12}k_2 + \Gamma_{21}k_1 + k_1 k_2) = (\Gamma_{12} + \Gamma_{21})^2 + (k_1 + k_2)^2 + 2(k_1 + k_2)(\Gamma_{12} + \Gamma_{21}) - 4(\Gamma_{12}k_2 + \Gamma_{21}k_1 + k_1 k_2) = (\Gamma_{12} + \Gamma_{21})^2 + (k_1 + k_2)^2 + 2(k_1\Gamma_{12} + k_1\Gamma_{21} + k_2\Gamma_{12} + k_2\Gamma_{21}) - 4(\Gamma_{12}k_2 + \Gamma_{21}k_1 + k_1 k_2) = (\Gamma_{12} + \Gamma_{21})^2 + (k_1 - k_2)^2 + 2(k_1\Gamma_{12} - k_1\Gamma_{21} - k_2\Gamma_{12} + k_2\Gamma_{21}) = (\Gamma_{12} + \Gamma_{21})^2 + (k_1 - k_2)^2 + 2(k_1 - k_2)(\Gamma_{12} - \Gamma_{21}) \quad \text{(S59)}$$

$$\lambda_{1,2} = \frac{(\Gamma_{12} + \Gamma_{21} + k_1 + k_2) \pm \sqrt{(\Gamma_{12} + \Gamma_{21})^2 + (k_1 - k_2)^2 + 2(k_1 - k_2)(\Gamma_{12} - \Gamma_{21})}}{2} \quad \text{(S60)}$$

Taking into account that λ_1 and λ_2 are reciprocals of lifetimes τ_1 and τ_2, we find:

$$\tau_{1,2} = \frac{1}{\lambda_{1,2}} = \frac{2}{(\Gamma_{12} + \Gamma_{21} + k_1 + k_2) \pm \sqrt{(\Gamma_{12} + \Gamma_{21})^2 + (k_1 - k_2)^2 + 2(k_1 - k_2)(\Gamma_{12} - \Gamma_{21})}} \quad \text{(S61)}$$

References

(1) Adkins, W. A.; Davidson, M. G. *Ordinary differential equations*; Springer: New York, 2012.