# On the Interpretation of Excited-state Decay Data for the Determination of the Equilibrium Constants in Compartmentalized Systems

**Jan van Stam, Steven De Feyter, Noël Boens and Frans C. De Schryver***

*Laboratorium Moleculaire Dynamica en Spectroscopie, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee (Leuven), Belgium*

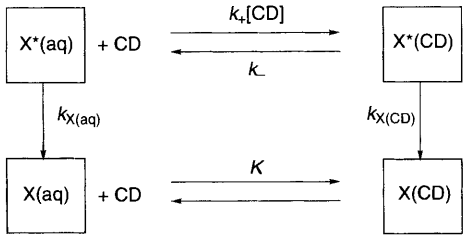
Excited-state decay data from host–guest systems can be used to determine the rate constants of the processes associated with these compartmentalized systems; the implementation of compartmental analysis (originally developed for fluorescence decay data) when applied to triplet-state decays is discussed.

Host–guest complexes play important roles in *e.g.* biology, biochemistry, medicine and technology. These supramolecular systems have gained increasing interest in science. Photophysical studies allow the investigation of ground-state reactions as well as reactions in the excited state. As an example, the $pK_a$ values for 2-naphthol in the ground- and excited-states in aqueous solution have been determined from fluorescence decay data by global compartmental analysis.[1] For 2-naphthol forming inclusion complexes with different cyclodextrins both the ground-state and excited-state $pK_a$ values have been determined.[2] The equilibrium constants for the ground-state and triplet-state inclusion complex of xanthone (X) and cyclodextrin (CD) in aqueous solution have been reported recently by Liao *et al.*[3] They measured the change in absorption as a function of time of the triplet of xanthone, dissolved in a large excess of water or within a cyclodextrin cavity. From local† fittings of a bi-exponential decay function to the data, Liao *et al.* claim to be able to calculate the necessary rate constants for the determination of the excited-state equilibrium constant. According to their treatment,[3] the relaxation process is described by a composite rate constant, $k_{obs} = k_- + k_+[CD]$, where $k_-$ denotes the xanthone triplet-state dissociation rate constant from a cyclodextrin into the aqueous bulk and $k_+$ denotes the second-order rate constant for the formation of an inclusion complex between a xanthone in the triplet state and a cyclodextrin (Scheme 1). Nevertheless, Liao *et al.* fit a bi-exponential function to the data, claiming that one of the exponential factors equals $-k_{obs}$ and the other gives the decay of the triplet in water.[3] These two approaches, however, are contradictory, as the assumption that the relaxation is described only by $k_{obs}$ requires the triplet states to last for an infinitely long time while the use of a bi-exponential function to fit the data can never give $k_{obs}$ as it is formulated in ref. 3. To determine the correct values related to the excited-state equilibrium constant from the excited-state decay data, it is recommended to perform a global[4–6] compartmental[7] analysis. Conform to this analysis, the system can be outlined as shown in Scheme 1, where $k_{X(aq)}$ describes the deactivation from aqueous xanthone triplet and $k_{X(CD)}$ is the corresponding deactivation rate constant from the xanthone triplet complexed with a cyclodextrin. X(aq) and X(CD) denote aqueous and cyclodextrin complexed xanthone, respectively, and * denotes the triplet state.

Defining

$$S_1 = k_{X(aq)} + k_+[CD] \quad (1)$$

$$S_2 = k_{X(CD)} + k_- \quad (2)$$




**Scheme 1**

$$\text{and } P = k_-k_+[CD] \quad (3)$$

and the exponential factors $\gamma_{1,2}$ as:

$$\gamma_{1,2} = -\frac{1}{2}\left\{(S_1 + S_2) \pm \sqrt{(S_1 - S_2)^2 + 4P}\right\} \quad (4)$$

the time evolution of the two excited-state concentrations are given by:[7]

$$[X(aq)^*]_t = \beta_{11}\exp(\gamma_1 t) + \beta_{12}\exp(\gamma_2 t) \quad (5)$$

$$[X(CD)^*]_t = \beta_{21}\exp(\gamma_1 t) + \beta_{22}\exp(\gamma_2 t) \quad (6)$$

The exponential factors, $\gamma_{1,2}$, are related to the decay times $\tau_{1,2}$ by

$$\gamma_{1,2} = -1/\tau_{1,2} \quad (7)$$

Assuming, as Liao *et al.* did,[3] that the deactivation of the triplet states is slow compared to the interchange between the two triplet-state compartments, *i.e.* $k_{X(aq)}$ and $k_{X(CD)}$ are very small compared to $k_+[CD]$ and $k_-$, leads to simplified expressions for the exponential factors; $\gamma_1 = -(k_+[CD] + k_-)$ and $\gamma_2 = 0$. Denoting the concentrations of the aqueous and the complexed xanthone triplet at time $t = 0$ as $[X(aq)^*]_0$ and $[X(CD)^*]_0$, respectively, and setting $[X^*]_0 = [X(aq)^*]_0 + [X(CD)^*]_0$ yields the pre-exponential factors:[7]

$$\beta_{11} = \frac{[X(aq)^*]_0k_+[CD] - [X(CD)^*]_0k_-}{k_+[CD] - k_-} \quad (8a)$$

$$\beta_{12} = \frac{k_-}{k_+[CD] - k_-}[X^*]_0 \quad (8b)$$

$$\beta_{21} = \frac{[X(CD)^*]_0k_- - [X(aq)^*]_0k_+[CD]}{k_+[CD] - k_-} = -\beta_{11} \quad (8c)$$

$$\beta_{22} = \frac{k_+[CD]}{k_+[CD] - k_-}[X^*]_0 \quad (8d)$$

Evidently, the decay of a two-state excited-state system, where no deactivation from the excited states occurs, is described by a sum of a mono-exponential decay function and a constant term, and not by a bi-exponential decay function:

$$[X(aq)^*]_t = \beta_{11}\exp\{-(k_+[CD] + k_-)t\} + \beta_{12} \quad (9a)$$

$$[X(CD)^*]_t = -\beta_{11}\exp\{-(k_+[CD] + k_-)t\} + \beta_{22} \quad (9b)$$

If, however, assuming a bi-exponential model to be the correct one to fit to the data and neglecting the decay from cyclodextrin-complexed triplet-state xanthone, *i.e.* the way Liao *et al.* treated their data,[3] one finds, after the use of eqns. (1)–(4) the following exponential factors:

$$\gamma_{1,2} = -\frac{1}{2}\left\{\begin{array}{c}(k_+[CD] + k_{x(aq)} + k_-) \pm \\ \sqrt{(k_+[CD] + k_{x(aq)} - k_-)^2 + 4k_-k_+[CD]}\end{array}\right\} \quad (10)$$

From eqn. (10) it can be concluded that the use of a bi-exponential model can never yield an exponential factor equal to $-k_{obs}$ and consequently it follows that the analysis performed by Liao *et al.*[3] cannot give the proper values of the rate constants. Furthermore, for complex systems, undergoing excited-state reactions, it is recommended to follow a global[4–6]

analysis approach, as all data will contain information on all rate constants of the system.

The qualitative conclusions given by Liao *et al.*[3] are consistent with the data reported: the xanthone ground-state distribution between the aqueous bulk and the β-cyclodextrins changes towards more aqueous xanthone in the triplet state, as was found by others.[8] The quantitative results, however, are in error. The only way to determine these rate constants in a consistent way is by means of global compartmental analysis.[7] This analysis also has the advantage that no assumption of an infinite lifetime of the excited state has to be made.

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## Footnotes

* E-mail: Frans.DeSchryver@Chem.KULeuven.ac.be

† The term local (single-curve is a synonym) means that the data obtained in every experiment are evaluated separately, *i.e.* the data from different experiments are not combined and evaluated simultaneously. Following a local analysis, no use is made of underlying relations between the parameters of interest when data are collected under different experimental circumstances. In global analysis, however, all the data are evaluated simultaneously and the relationships between different parameters are used to constrain the model. These relationships manifest in the linking scheme, where parameters can be globally linked, *i.e.* they are held common for all experimental data evaluated, or they can be regionally linked, *i.e.* they are held common for a part of the data evaluated. It is well known that global analysis is superior to local analysis.

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