Supplemental Material A

Mathematical basis for numerical calculation of fluorescence decay

Expression for a calculated fluorescence dynamics by MD was first given by Henry and Hochstrasser[35] as eq A1 (HH method).

$$F_{calc}(t) = \left\langle \exp\{-\int_{t'}^{t'+t} [k_0 + k_{ET}(\tau)] d\tau \right\rangle_{AV} \qquad \text{(A1)}$$

k_0 is deactivation rate without ET, and $k_{ET}(\tau)$ ET rate given by eq 1 or eq 4 in text. Here we assume that k_0 is much less than $k_{ET}(\tau)$, and so negligible compared to ET rate. $\langle ... \rangle_{AV}$ denotes an averaging procedure with respect to *t'*. Lower and upper limit of the integration in the original equation given by Henry and Hochstrasser, are 0 and *t*, but these should be *t'* and *t'* + *t* as in eq A1.

$$F_{calc}(t) = \left\langle \exp\{-\Delta t \sum_{i=0}^{n} k_{ET}(j+i) \right\rangle_{AV} \qquad \text{(A2)}$$

Figure A1 illustrates the method of numerical calculation for $F_{calc}(t)$. In eq A2 $\int_{t'}^{t'+t} k_{ET}(\tau) d\tau$ was approximated by a summation, $\Delta t \sum_{i=0}^{n} k_{ET}(j+i)$. More accurately, the integral may be numerically calculated by Simpson method. In eq A2 $\Delta t = t/m$ and $k_{ET}(j+i)$ denotes ET rate at $t = t_{j+i}$. Numerically $\langle ... \rangle_{AV}$ is also calculated by a summation as follows:

$$F_{calc}(t) = \frac{1}{m-n} \sum_{j=0}^{m-n} \exp\{-(t/m) \sum_{i=0}^{n} k_{ET}(j+i)\} \qquad \text{(A3)}$$

n is number of data points of fluorescence decay, which is assumed that *m* is much larger than *n*.

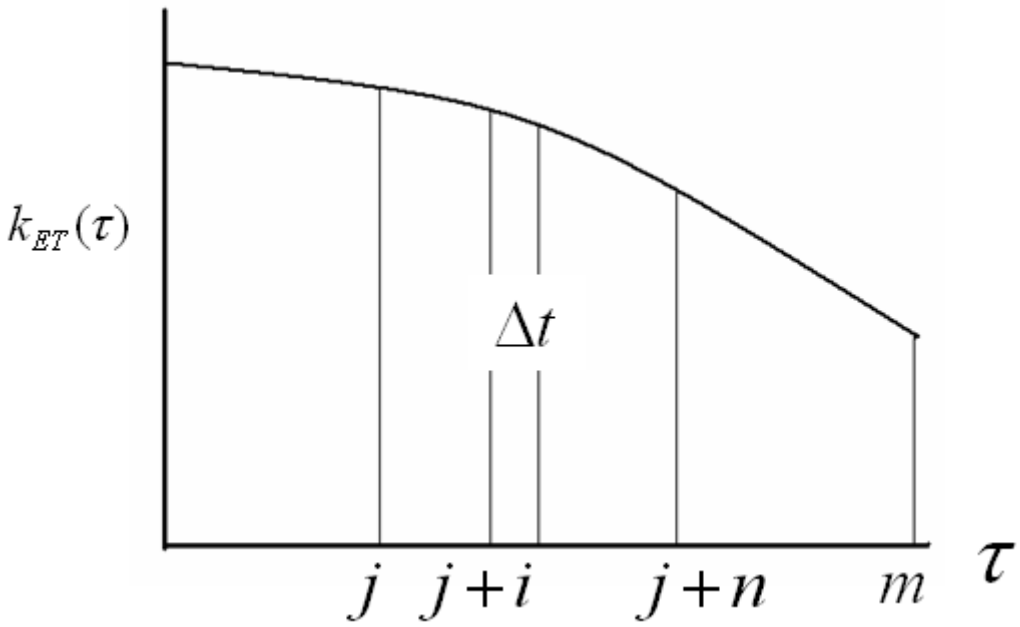

Figure A1 Numerical calculation of fluorescence decay with $k_{ET}(\tau)$.
Time range of MD was divided into m intervals of Δt. τ represents MD time. Fluorescence decay is to be calculated from $t = t_j$ to $t = t_{j+i}$. $\langle ... \rangle_{AV}$ may be taken from $t' = 0$ to $t' = t_n$ (m=$2n$)

From eq A3 we can see that $k_{ET}(0)$ is used for the numerical calculation of fluorescence decay once, $k_{ET}(1)$ twice, $k_{ET}(2)$ three times, and $k_{ET}(l)$ ($l = i + j$) l +1 times, when $l \le n-1$. $k_{ET}(l)$ is used n + 1 times when $n \le l \le m-n$. $k_{ET}(l)$ is used $m-l+1$ times when $l \ge m-n+1$. This implies that $k_{ET}(l)$ with $n \le l \le m-n$ are most important upon the fluorescence decay, but $k_{ET}(l)$ with l near 0 or m are not important. Namely, according to HH method, the values of $k_{ET}(l)$ ($0 \le l \le m$) are not equivalent for the calculation of fluorescence decay.

On the other hand our method is numerically calculated with eq A4.

$$F_{calc}(t) = \frac{1}{m-n} \sum_{j=0}^{m-n} \exp\{-k_{ET}(j)t\} \qquad \text{(A4)}$$

t extends from 0 to $n\Delta t$. In Eq A4 $k_{ET}(j)$ (j = 0 to m) is used only once. All values of $k_{ET}(l)$ ($n \le l \le m-n$) are used n+1 times in the HH method, and 1 time in our method, so that after dividing $F_{calc}(t)$ at every point of time by number of used frequency,

$F_{calc}(t)$ obtained by the both method should be same. Only the differences in $F_{calc}(t)$ between the both method are time domain of MD average at $l \le n-1$ and at $l \ge m-n+1$. Accordingly, the both method should be equivalent, if *m* is much larger than *n*.

Calculation time of averaging procedure by HH method at each *t* may be

$$2\Delta t_c(1+2+3+.....+n)+\Delta t_c(n+1)(m-2n+1)$$
$$=\Delta t_c(n+1)(m-n+1) \quad ,$$

while the calculation time of our method is $\Delta t_c m$ at each *t*. Δt_c denotes the calculation time of each step of the averaging procedure. Our method is much advantageous in the calculation time.