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\textsuperscript{35} as eq A1 (HH method).

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

(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. \( \langle \ldots \rangle_{AV} \) 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.

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

(A2)

Figure A1 illustrates the method of numerical calculation for \( F_{\text{calc}}(t) \). 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 \( \langle \ldots \rangle_{AV} \) is also calculated by a summation as follows:

\[ F_{\text{calc}}(t) = \frac{1}{m-n} \sum_{j=0}^{m-n} \exp \left\{ -(t/m) \sum_{i=0}^{n} k_{ET}(j+i) \right\} \]  

(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 $\Delta t$. $\tau$ represents MD time.

Fluorescence decay is to be calculated from $t = t_j$ to $t = t_{j+n} - 1$ 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 $l \leq n - 1$. $k_{ET}(l)$ is used $n + 1$ times when $n \leq l \leq m - n$. $k_{ET}(l)$ is used $m - l + 1$ times when $l \geq m - n + 1$. This implies that $k_{ET}(l)$ with $n \leq l \leq m - n$ 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 $k_{ET}(l)$ ($0 \leq l \leq m$) are not equivalent for the calculation of fluorescence decay.

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

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

(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 $k_{ET}(l)$ ($n \leq l \leq m - n$) 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,
$F_{\text{calc}}(t)$ obtained by the both method should be same. Only the differences in $F_{\text{calc}}(t)$ between the both method are time domain of MD average at $l \leq n-1$ and at $l \geq m-n+1$. 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

$$2\Delta t_c(1+2+3+\ldots+n) + \Delta t_c(n+1)(m-2n+1)$$

$$= \Delta t_c(n+1)(m-n+1),$$

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