THE FIRST ORDER DISTRIBUTION FUNCTION OF D–A TRANSFER RATES IN ENERGY TRANSFER

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The differential equation governing the temporal variation of the distribution density, $\phi(X, t)$, of D–A transfer rates has been derived directly from the macroscopic differential equations of energy transfer for the cases where the covariance coefficient of D–A transfer rate, X, and D–D transfer rate, W, equals 0 or 1. $\phi(X, t)$ may be expressed as a function of $\phi_0(X)$, the static distribution density of D–A transfer rates, and $F(t)$, the decay dynamics of the donor fluorescence. $F(t)$ derived by normalizing $\phi(X, t)$ coincides with the results of Burshtein's hopping model.

1. Donor fluorescence dynamics

The dynamics of a system containing random distributed N_D donors and N_A acceptors can be described by a set of differential equations [1]

$$dP_i(t)/dt = -rP_i(t) - \sum_{i \neq i'} [W_{ii'} P_i(t) - W_{i'i} P_{i'}(t)]$$

$$- \sum_j X_{ij} P_i(t), \tag{1}$$

where $P_i(t)$ is the probability of the ith donor being excited at time t, X_{ij} is the transfer rate of the ith donor to the jth acceptor, $W_{ii'}$ is the transfer rate between the ith and the i'th donors, r is the intrinsic decay rate of the donor fluorescence, the first summation runs over all donors, while the second runs over all acceptors. Approximations in (1) include: (i) weak, uniform excitation; and (ii) no A–D back transfer.

The observed donor decay curve is proportional to

$$\sum_i P_i(t) = F(t) = \exp(-rt)f(t).$$

$f(t)$ is dependent only on the energy transfer process. Summing (1) over i we have

$$df(t)/dt = -\bar{X}(t)f(t), \tag{2}$$

with the initial condition

$$f(0) = 1, \tag{3}$$

where

$$\bar{X}(t) = \left[\sum_{i,j} X_{ij} P_i(t)\right] / \sum_i P_i(t) \tag{4}$$

is the average transient D–A transfer rate and is related to concrete processes. With these notations the solution of eq. (2) may be written in a normalized form as

$$f(t) = \exp\left[-\int_0^t \bar{X}(t)\,dt\right]. \tag{5}$$

2. The first order distribution density function of D–A transfer rates

Let (D^*) be the set of all the excited donors. The number of donors in this set, $N_{D^*}(t)$ is time dependent and equals $eF(t)N_D$, where e is the excitation ratio, i.e. $N_{D^*}(0)/N_D$. Dividing (D^*) into subsets according to X and W, the D–A and D–D transfer rates of a donor to all acceptors and all the other donors. At t, the number of excited donors with X in $[X, X + dX]$ and W in $[W, W + dW]$ equals $N_{D^*}(t)D(X, W, t)\,dX\,dW$, where $D(X, W, t)$ is the distribution density of the donor according to their X and W, which is normalized

$$\int_{(D^*)} dW\,dX\,D(X, W, t) = 1.$$

We may also define $\phi(X, t)$ and $\psi(W, t)$ as the first order distribution densities of the D–A transfer rates and D–D transfer rates of the excited donors

$$\phi(X, t) = \int_{(D^*)} dW\,D(X, W, t);$$

$$\psi(W, t) = \int_{(D^*)} dX\,D(X, W, t).$$

Obviously, both of them are normalized. Thus, $\bar{X}(t)$ in eq. (5) may be expressed as

$$\bar{X}(t) = \int_{(D^*)} X\phi(X, t)\,dX,$$

and (5) can be written as

$$f(t) = \exp\left[-\int_0^t dt \int_{(D^*)} X\phi(X, t)\,dX\right], \tag{6}$$

which shows that the decay curve may be determined by the first order distribution density of D–A transfer rates.

Let g_{XW} be the covariance coefficient of X and W. If $g_{XW} = 0$, i.e. X and W are independent, $D(X, W, t)$ will be $\phi(X, t)\psi(W, t)$, the distribution of D–D transfer rates in any subset $(D*X)$ will be $\psi(W, t)$. On the other hand, if $W = AX$, where A is a constant, then $g_{XW} = 1$, and $D(X, W, t) = \phi(X, t)$.

3. The static distribution density of D–A transfer rates

Let $F_0(t) = \exp(-rt)f_0(t)$ be the donor fluorescence decay for the static model [2,3] where D–D transfer may be neglected. With the distribution density of D–A transfer rates, $f_0(t)$ may also be written as

$$f_0(t) = \int_0^\infty \exp(-Xt)\phi_0(X)\,dX, \tag{7}$$

where $\phi_0(X)$ is the static distribution density of D–A transfer rates. Since the excitation is uniform at $t = 0$ for all kinds of transfer in our assumption,

$$\phi(X, 0) = \phi_0(X). \tag{8}$$

$\phi_0(X)$ may be obtained from $f_0(t)$. If we substitute t in eq. (7) with $-iq$, it then becomes

$$f_0(-iq) = \int_0^\infty \phi_0(X)\exp(iXq)\,dX$$

and $\phi_0(X)$ can be obtained by Fourier transformation

$$\phi_0(X) = \left(\tfrac{1}{2}\pi\right)\int_{-\infty}^\infty f_0(-iq)\exp(-iXq)\,dq. \tag{9}$$

For electric multipole interaction between donor and acceptor, eq. (9) will be [4]

$$\phi_0(X) = (1/\pi X)\int_0^\infty du$$
$$\times \exp\left[-Xu^{s/3}\left(c_A\Gamma(1 - 3/s)\right)^{-s/3}X_0^{-1} - u\cos(3\pi/s)\right]$$
$$\times \sin[(3\pi/s) - u\sin(3\pi/s)], \tag{10}$$

where s is the index of multipole interaction and c_A is the acceptor concentration. For $s = 6$, eq. (10) may be integrated analytically and results in the well known expression

$$\phi_0(X) = \left(c_A/2\right)\left(X_0/X^3\right)^{1/2}\exp\left(-\pi c_A^2 X_0/4X\right).$$

4. The equation of motion of $\phi(X, t)$ in an energy transfer process

Considering a system containing donors and acceptors, a delta excitation is applied at $t = 0$. The excitation is uniform, so the property of the excited donors at $t = 0$ reflects the entirety of the donor, and eq. (8) holds.

Under weak excitation the number of unexcited donors is close to N_D. Let (DX) be a subset of unex-

cited donors with D–A transfer rate in the interval $[X, X + dX]$. The number of donors in (DX) is $N_D\phi_0(X)\,dX$. As already mentioned in section 2, the number of donors in $(D*)$ is $eN_D F(t)$, and the number of donors in one of its subsets $(D*X)$ is $eN_D F(t)\phi(X, t)\,dX$.

Now considering the temporal variation of the population of the subset $(D*X)$, $eN_D\,\partial[F(t)\phi(X, t)]\,dX/\partial t$. Contributions to this variation are from: (1) the intrinsic decay of donors, $-reN_D F(t)\phi(X, t)\,dX$; (2) D–A transfer from $(D*X)$ to all accepters, $-XeN_D F(t)\phi(X, t)\,dX$ (3) D–D transfer from $(D*X)$ to (DX'), the unexcited donors with D–A transfer rate unequal to X; the above three terms make the population of $(D*X)$ decreased, and (4) D–D transfer from subset $(D*X')$, excited donors with D–A transfer rate unequal to X, to (DX) unexcited donor with D–A transfer rate X, which makes the population of $(D*X)$ increased. (3) and (4) are related to the details of the energy transfer process. In this paper we only deal with the simplest cases.

For $g_{XW} = 0$, X and W are independent, term (3) may be expressed as

$$-eN_D F(t)\,dX\int_{(D*X)} W\phi(X, t)\psi(W, t)\,dW$$
$$= -(W)eN_D F(t)\phi(X, t)\,dX.$$

Here

$$(W) = \int_{(D*X)} W\psi(W, t)\,dW = \int_{(D*)} W\psi(W, t)\,dW$$

is the ensemble average of D–D transfer rates and it may depend on time t. The independence of X and W ensures that the transfer rate of the donors in $(D*X)$ to the donors in (DX) equals its total D–D transfer rate W times the ratio of the population of (DX) to the donor number of the entirety, i.e. $W\phi_0(X)\,dX$. Therefore, term (4) may be written as

$$eN_D\phi_0(X)F(t)\,dX\int_{(D*)} W\phi(X't)\psi(W, t)\,dX'dW$$
$$= (W)eN_D F(t)\phi_0(X)\,dX.$$

Taking all the four terms into account, we have
$$\partial[F(t)\phi(X, t)]/\partial t = -[r + X + (W)]F(t)\phi(X, t) + (W)F(t)\phi_0(X).$$

It may be rearranged as
$$\partial\phi(X, t)/\partial t = -[X + (W) + df(t)/f(t)\,dt] \times \phi(X, t) + (W)\phi_0(X), \tag{11}$$

with eq. (8) as the initial condition. Eq. (11) may be integrated and leads to
$$\phi(X, t)$$
$$= [\phi_0(X)/f(t)]\exp\left[-Xt - \int_0^t (W)\,dt'\right]$$
$$\times \left[1 + \int_0^t dt'\, f(t')(W)\exp\left(Xt' + \int_0^{t'} (W)\,dt''\right)\right]. \tag{12}$$

Normalizing $\phi(X$

$$f(t) = f_0(t)\exp\left[$$
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Normalizing $\phi(X, t)$ and using (7) gives

$$f(t) = f_0(t)\exp\left[-\int_0^t (W)\,dt\right]$$
$$+\int_0^t dt'\ (W)f(t')f_0(t-t')$$
$$\times\exp\left[-\int_{t'}^t (W)\,dt''\right],$$ (13)

which may also be obtained by directly substituting (12) into (6).

5. $\phi(X, t)$ and $f(t)$ for $g_{XW} = 1$

In concentration quenching a center can act both as a donor or as an acceptor depending on whether D–D transfer or cross relaxation happens at the center. If both processes are caused by the same kind of interaction mechanism and hence their rates have the same dependence on the separation between two centers, then $W_i = A_{Xi}$, where A is a constant. By similar considerations as in sect. 4, the equation of motion of $\phi(X, t)$ in this case is

$$\partial\phi(X, t)/\partial t = -\left[X(1+A) + df(t)/f(t)\,dt\right]$$
$$\times\phi(X, t) + AX\phi_0(X).$$ (14)

The solution of eq. (14) with the initial condition (8) is

$$\phi(X, t) = [\phi_0(X)/f(t)]\exp[-(1+A)Xt]$$
$$\times\left[1 + A\int_0^t dt'\ f(t')\exp[X(1+A)t'].$$ (15)

Normalization gives

$$f(t) = f_0[(1+A)t] - [A/(1+A)]$$
$$\times\int_0^t dt'\ f(t')\,df_0[(1+A)(t-t')]/dt'.$$ (16)

Eqs. (13) and (16) coincide with the results of Burshtein's hopping model [5].

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