Biophysical Chemistry 9 (1979) 211–214

THE FREQUENCY DISTRIBUTION OF THE ORIENTATION FACTOR OF DIPOLE–DIPOLE INTERACTION

Hans TOMPA
CORE, University of Louvain, 1348 Louvain-la-Neuve, Belgium

and

Anne ENGLERT
Laboratoire de Chimie Générale I, Faculté des Sciences, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

Received 21 September 1978

An analytical expression is derived for the frequency distribution of the orientation factor in the non-radiative transfer of electronic excitation energy.

Long-range non-radiative transfer of electronic excitation energy between luminophores attached to distant sites of a molecule has recently aroused considerable interest since the efficiencies of transfer can be related to the separation R of the chromophoric groups [1]. This method is of special interest for values of R of the order of 15–50 Å and has been used in particular in studies of the dimensions of peptide hormones [2–4]. The energy transfer depends also on the orientation between the transition dipoles of the donor, D, and the acceptor, A, luminophores; this dependence is given by an orientation factor κ^2 defined by [5]

$$\kappa = \cos\theta_{DA} - 3\cos\theta_D \cos\theta_A . \tag{1}$$

In this expression θ_{DA} is the angle between D and A and θ_D and θ_A are the angles between D and A and the line joining them, respectively. Considering that κ^2 can be determined only approximately [5] it is usually assumed that the value $\langle\kappa^2\rangle_{ran} = 2/3$ corresponding to luminophores rotating rapidly and isotropically is a good representation for the orientation dependence of various transfer properties.

In the case of molecules which can take up a large ensemble of conformations which do not vary during the lifetime of the excited state of the donor (static averaging regime), the frequency distribution of κ^2 as the orientations of D and A take on randomly all possible values in space is required in the expressions of the transfer properties as functions of R [6]. Although this distribution has been obtained in numerical form [7], to the best of our knowledge no analytical expression has been given for it so far and it is the purpose of this paper to derive such an expression.

The orientation of a dipole is determined in spherical polar coordinates by the angles θ and ψ; we use the line joining D and A as the axis and since we are interested only in the relative orientations of D and A we can put arbitrarily $\psi_D = 0$ and can write ψ for ψ_A. Then

$$\cos\theta_{DA} = \cos\theta_D \cos\theta_A + \sin\theta_D \sin\theta_A \cos\psi \tag{2}$$

and

$$\kappa = \sin\theta_D \sin\theta_A \cos\psi - 2\cos\theta_D \cos\theta_A . \tag{3}$$

The "volume element" for the orientations of D and A is:

$$dV = \sin\theta_D \, d\theta_D \sin\theta_A \, d\theta_A \, d\psi . \tag{4}$$

We can regard this expression as defining the joint frequency distribution of the variables θ_D, θ_A, and ψ:

the frequency of finding D and A with orientations in the range θ_D and $\theta_D + d\theta_D$, θ_A and $\theta_A + d\theta_A$, ψ and $\psi + d\psi$, is proportional to $\sin\theta_D \sin\theta_A$. To find the frequency distribution of any variable, independent of the values of the other variables — known in statistics as the marginal frequency distribution of that variable — we have to integrate (4) over the other two variables. Since the joint frequency distribution is here a product of independent factors, integration will simply yield frequency distributions proportional to $\sin\theta_D$, $\sin\theta_A$, or 1 (uniform distribution), respectively. To obtain the frequency distributions we have to divide these values by the triple integral over (4); since we are only interested in the absolute value of ψ, all three angles vary from 0 to π and the integral is 4π.

To find the frequency distribution of any quantity depending on θ_D, θ_A, and ψ we can transform the variables so that the quantity of interest becomes one of the variables and integrate over the other two variables.

We first introduce $c_1 = \cos\theta_D$, $c_2 = \cos\theta_A$ so that

$$dV = dc_1\, dc_2\, d\psi. \tag{5}$$

We then transform c_1, c_2, ψ to c_1, c_2, κ as the new set, i.e. transform simply ψ to κ:

$$dV = dc_1\, dc_2 (\partial\psi/\partial\kappa)_{c_1,c_2}\, d\kappa. \tag{6}$$

From (3) we have, neglecting the sign and since c_1, c_2 constant implies θ_D, θ_A constant:

$$|(\partial\kappa/\partial\psi)_{c_1,c_2}| = \sin\theta_D \sin\theta_A \sin\psi \tag{7}$$

or

$$(\partial\psi/\partial\kappa)_{c_1,c_2} = [(1-c_1^2)(1-c_2^2) - (\kappa + 2c_1c_2)^2]^{-1/2} = W^{-1/2} \tag{8}$$

so that

$$dV = W^{-1/2} dc_1 dc_2 d\kappa. \tag{9}$$

The frequency distribution of κ is then

$$f(\kappa) = \frac{1}{4\pi} \int_{c_1 \min}^{c_1 \max} dc_1 \int_{c_2 \min}^{c_2 \max} W^{-1/2} dc_2. \tag{10}$$

The range of c_2 is determined by the requirement that W must not be negative and the limits $c_{2\max}$, $c_{2\min}$ are given by $W = 0$; since W is a quadratic function of c_2, as can be seen by writing it in the form

$$W = -(3c_1^2+1)c_2^2 - 4\kappa c_1 c_2 + (1 - c_1^2 - \kappa^2) \tag{11}$$

it vanishes for

$$c_2 = (-2\kappa c_1 \pm \sqrt{Q})/(3c_1^2+1), \tag{12}$$

where

$$Q = 4\kappa^2 c_1^2 + (3c_1^2+1)(1-c_1^2-\kappa^2) = (3c_1^2 + 1 - \kappa^2)(1-c_1^2). \tag{13}$$

If real values of c_2 are to exist, Q must not be negative and this will determine the limits of integration over c_1. It is easily confirmed that $c_{2\max}$ and $c_{2\min}$ as determined by (12) are both within the range [−1,1] so that all values of c_2 between them are physically significant. The integral over c_2 is evaluated easily via the inverse sine function and is

$$\int_{c_1 \min}^{c_2 \max} W^{-1/2} dc_2 = \frac{\pi}{(3c_1^2+1)^{1/2}} \tag{14}$$

so that

$$f(\kappa) = \frac{1}{4} \int_{c_1 \min}^{c_1 \max} \frac{dc_1}{(3c_1^2+1)^{1/2}}. \tag{15}$$

In most applications the quantity of interest is not κ but rather $\kappa^2 = k$ and this is a convenient point in the development to change over to the distribution of k. We have

$$d\kappa = dk/2\sqrt{k} \tag{16}$$

but on the other hand positive and negative values of κ contribute to any definite value of k so that the frequency distribution of k is

$$g(k) = \frac{f(\kappa)}{\sqrt{k}} = \frac{1}{4\sqrt{k}} \int_{c_1 \min}^{c_1 \max} \frac{dc_1}{(3c_1^2+1)^{1/2}}. \tag{17}$$

If Q is to be non-negative we have from (13)

$$c_1^2 \geqslant (k-1)/3 \tag{18}$$

since the second factor of Q is never negative for physically significant values of c_1.

For $k \leqslant 1$ (18) is always satisfied so that the limits of integration are ±1; the integral can be evaluated via the inverse hyperbolic sine function or the logarithm:

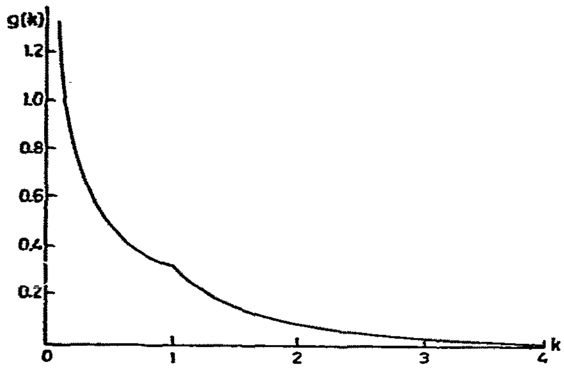

Fig. 1. Normalized frequency distribution as function of k.

$$g(k)=\frac{1}{4\sqrt{k}}\int_{-1}^{1}\frac{\mathrm{d}c_1}{(3c_1^2+1)^{1/2}}$$

$$=\frac{1}{2\sqrt{k}}\int_{0}^{1}\frac{\mathrm{d}c_1}{(3c_1^2+1)^{1/2}}=\frac{1}{2\sqrt{3k}}\operatorname{arsh}\sqrt{3}$$

$$=\frac{1}{2\sqrt{3k}}\ln(2+\sqrt{3});\qquad k\leqslant 1. \tag{19}$$

For $k > 1$ (18) determines the lower limit of integration so that

$$g(k)=\frac{1}{2\sqrt{k}}\int_{c_1\,\mathrm{min}}^{1}\frac{\mathrm{d}c_1}{(3c_1^2+1)^{1/2}}$$

$$=\frac{1}{2\sqrt{3k}}\ln(2+\sqrt{3})-\ln(\sqrt{k}-\sqrt{k-1});$$

$$1\leqslant k\leqslant 4. \tag{20}$$

There are no physically significant values of c_1 for $k > 4$, in agreement with the fact that from (3) κ is always within the range [−2,2]. Eqs. (19) and (20) are therefore the frequency distribution of k.

It is easily verified that $g(k)$ is properly normalized:

$$\int_0^4 g(k)\mathrm{d}k=\int_0^1\frac{\ln(2+\sqrt{3})}{2\sqrt{3k}}\,\mathrm{d}k$$

$$+\int_1^4\frac{\ln(2+\sqrt{3})-\ln(\sqrt{k}+\sqrt{k-1})}{2\sqrt{3k}}\,\mathrm{d}k=1. \tag{21}$$

Table 1
Normalized frequency distribution $g(k)$ as function of k

k	$g(k)$	k	$g(k)$
0	∞	1.1	0.277
0.1	1.202	1.2	0.233
0.2	0.856	1.4	0.176
0.4	0.601	1.6	0.138
0.6	0.491	1.8	0.110
0.8	0.425	2	0.089
1	0.380	2.5	0.052
1.01	0.351	3	0.028
1.02	0.336	3.5	0.012
1.05	0.309	4	0

The second term in the second integral is evaluated via the substitution $k = \mathrm{ch}^2 u$ involving the hyperbolic cosine function and integration by parts.

It is also easily verified, using the same substitution, that the first moment, i.e. the mean value of k, which is known to be 2/3, is given correctly by $g(k)$:

$$\int_0^4 g(k)k\mathrm{d}k=\int_0^1\frac{\ln(2+\sqrt{3})}{2\sqrt{3}}\,k\mathrm{d}k$$

$$+\int_1^4\frac{\ln(2+\sqrt{3})-\ln(\sqrt{k}+\sqrt{k-1})}{2\sqrt{3}}k\mathrm{d}k=\frac{2}{3}. \tag{22}$$

Table 1 gives the values of $g(k)$ as a function of k, fig. 1 shows a simple plot of these values. It is to be noted that the first derivative of $g(k)$ is discontinuous at $k = 1$ and the tangent to the right-hand branch is vertical at this point; no physically evident reason has occurred to so far for this behaviour, but mathematically it can be described by the following consideration: whereas there are acceptor orientations for any arbitrary donor orientation to yield a given value of k as long as k does not exceed unity the range of donor orientations for which there are such acceptor orientations decreases sharply as k becomes greater than one.

References

[1] L. Stryer and R.P. Haugland, Proc. Nat. Acad. Sci. U.S. 58 (1967) 719.

[2] J. Eisinger, Biochemistry 8 (1969) 3902.
[3] P.W. Schiller, Proc. Nat. Acad. Sci. U.S. 69 (1972) 975.
[4] M. Leclerc, S. Premilat, A. Englert, Proc. Fifth Am. Peptide Symposium, ed. M. Goodman and J. Meienhofer, (J. Wiley, New York, 1977) p. 364.
[5] R.E. Dale and J. Eisinger, Biopolymers 13 (1974) 1573.
[6] M. Leclerc and A. Englert, Proc. Nat. Acad. Sci. U.S. 75 (1978) 1050.
[7] R. Guillard and A. Englert, Biopolymers 15 (1976) 1301.