FÖRSTER TRANSFER RATES FOR CHLOROPHYLL a*

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Abstract—A convenient formula has been derived for the calculation of Förster transfer rates between chlorophyll a molecules. The formula is applicable over limited ranges of absorption maxima positions, Stokes' shifts, solvents, relative orientations and intermolecular distances. The limitations on the applicability of the Förster transfer model are discussed. Finally, some implications for *in vivo* energy transfer are considered.

INTRODUCTION

The vast majority of chlorophyll (Chl) molecules *in vivo* function as antenna or light-gathering pigments which absorb photons and then transfer the resultant singlet excitation energy among each other until it is trapped by a few special Chl molecules in the photosynthetic reaction center. The excitation energy is then converted into useful chemical oxidizing and reducing capacity via a series of electron transfers. The mechanism of singlet excitation migration has long been the subject of study. For Chl whose excited singlet states are weakly coupled, the excitation is transferred via the Förster mechanism (Förster, 1948 and 1965). The subject of excitation transfer and some of its implications for photosynthesis have been covered in recent reviews by Knox (1975 and 1977).

We have noted that there is a significant need for a convenient formula for the calculation of Förster transfer rates between Chl a molecules, especially a formula that covers ranges of absorption maxima positions, Stokes' shifts, solvents, relative orientations and intermolecular distances. The derivation of such a formula is the subject of this paper.

FÖRSTER TRANSFER MECHANISM

The four state model of Förster transfer is described in Fig. 1 and Table 1. The system consists of molecules A and B and the surrounding solvent medium. The first symbol in parentheses following the letter designating the molecule (i.e. A or B) denotes the populated electronic state of the molecule and the second symbol denotes the electronic state for which the intramolecular geometry and solvent arrangement are appropriate. Thus, $A(S_1, S_0)$ means
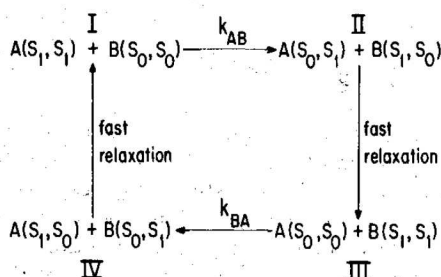
FÖRSTER TRANSFER CYCLE

Figure 1. A four state diagram representing Förster transfer between molecules A and B. See text and Table 1 for a description of the symbols.

that molecule A is in its first excited electronic state, S_1, with an intramolecular geometry and solvent arrangement appropriate for its ground electronic state, S_0. All four states of the system are specified in Table 1. The Förster transfer rate constants are k_{AB} and k_{BA} (Fig. 1). The other two rate constants, designated 'fast relaxation' in Fig. 1, are the rate constants for thermal equilibration to a Boltzmann population of vibrational levels; this relaxation should be of the order $10^{12}-10^{13}$ s^{-1} at 25°C.

In the range of applicability of the Förster transfer mechanism, the equilibration rate constant is much faster than both k_{AB} and k_{BA}, and therefore the equilibrium populations of II and IV are quite small, while the ratio of the populations of I and III is k_{BA}/k_{AB}. An explicit form of the Förster transfer rate constant is given in the next section.

DERIVATION OF THE RATE FORMULA

A quantum mechanical derivation of the Förster transfer rate expression has been given by Förster (1965). Since we agree with Förster's derivation up to the point of departure for our derivation of an explicit formula for excitation transfer between chlorophyll a(Chl a) molecules, the derivation of Förster need not be repeated here. Our derivation