INTERMOLECULAR ENERGY TRANSFER
STUDIES WITH PICOSECOND LIGHT PULSES

D. REHM [‡] and K. B. EISENTHAL

IBM Research Laboratory, San José, California 95114, USA

Singlet–singlet energy transfer between rhodamine 6G (donor) and malachite green (acceptor) has been observed directly using picosecond light pulses. The results are in accordance with the Förster theory up to the earliest time studied, i.e. 20 psec.

The time development for the intermolecular transfer of electronic energy has, until recently, been studied by measurements of the molecular light emission. The observation of the transfer process has been limited to times of the order of the fluorescent lifetime, and naturally to systems which emit light [♯]. With the application of the picosecond method [2], which utilizes absorption, rather than fluorescence for detection, the dynamics of energy transfer nave been studied in a heretofore inaccessible time domain, the subnanosecond region and furthermore, this method can be applied to non-radiating molecular systems.

The method consists of exciting some fraction of the donor molecules with a linearly polarized picosecond light pulse. Molecules whose transition moments have a large component along the direction of the light field are preferentially excited and, therefore, the formerly isotropic system becomes anisotropic, i.e. more excited molecules are oriented parallel to the field direction and hence more unexcited molecules are oriented with their transition moments perpendicular to the field direction. In a rigid environment the induced anisotropy can only relax by unimolecular decay of the excited molecules and by energy transfer. In a system where the donor and acceptor molecules are of the same species, the randomization results from transfer between molecules of different orientations. On the other hand, in a mixed system the anisotropy in donor orientations can also relax by transfer between donor and acceptor molecules regardless of their

‡ Permanent address: Max–Planck Institute for Spectroscopy, Göttingen, Germany.
♯ For a review see ref. [1].

mutual orientation. The decay of the anisotropy is monitored by measuring the change in dichroism in the donor absorption with time of an attenuated picosecond probe pulse. The absorption is greater for probe light polarized perpendicular rather than parallel to the polarization of the exciting light because of the relative depletion of ground state molecules in what we call the 'parallel configuration'. By probing at successively later times after excitation the decay of the dichroism due to energy transfer and the unimolecular excited state decay can be determined. Measurement of the latter quantity in the absence of transfer is then used to obtain the time dependence of the energy transfer from the measured decay of the dichroism.

The system studied was rhodamine (5×10^{-4} M) as the donor and malachite green (5×10^{-3} M) as the acceptor in a glycerol environment in a cell of 0.01 cm path length at room temperature. The advantage of this two-component system over the one-component system rhodamine 6G previously studied is due to the fact that the acceptor molecules are randomly distributed with respect to the excited state donor molecules and furthermore, there is only one transfer step from the donor to the acceptor molecules. In the one-component rhodamine 6G experiments [2] the excitation with linearly polarized light results in a non-random distribution of unexcited molecules (acceptors) with respect to the excited molecules (donors). Furthermore, several transfer steps are possible before randomization has occurred and would, therefore, have to be included in any theoretical treatment. The clear advantage of the two-component system is in being able to calculate the donor decay function $\bar{w}(t)$ for the case of randomly distributed acceptor molecules.

Although the excited donor molecules are not randomly distributed the acceptor distribution is random with respect to the excited donor molecules independent of the donor position and orientation in the system.

The decay of the anisotropy induced by the excitation pulse is obtained by measurements of the transmitted parallel and perpendicular components of the probe beam. The absorption coefficient for the parallel component is given by

$$\alpha_{\parallel}(t) \sim \epsilon \int n(t,\Omega) l^2_{\mu_{\parallel}} \, d\Omega + \epsilon^* \int n^*(t,\Omega) l^2_{\mu^*_{\parallel}} \, d\Omega \, , \quad (1)$$

where $n(t,\Omega)$ is the number of unexcited donor molecules at time t having their transition moment μ oriented in the direction $\Omega \pm d\Omega$, and $l^2_{\mu_{\parallel}}$ is the square of the projection of the transition moment on the parallel direction of the probe field, and ϵ indicates the strength of the transition. The second term on the right-hand side of eq. (1) gives the absorption, if any, by excited state donor molecules. Since the donor molecules were uniformly distributed prior to the excitation pulse we find that

$$n(t,\Omega) = \frac{N}{4\pi} - n^*(0,\Omega)\overline{w}(t) \, , \quad (2)$$

where N is the total density of donor molecules, $n^*(0,\Omega)$ is the number of excited donors oriented in the direction Ω immediately after the excitation pulse, and $\overline{w}(t)$ is the donor decay function. Similarly,

$$n^*(t,\Omega) = n^*(0,\Omega)\overline{w}(t) \, . \quad (3)$$

The absorption coefficients for the parallel and perpendicular components are then given by

$$\alpha_{\parallel}(t) \sim c_1 - c_2 \, \overline{w}(t) \quad (4)$$

and

$$\alpha_{\perp}(t) \sim c_1 - c_4 \, \overline{w}(t) \, . \quad (5)$$

The ratio of the components of the transmitted probe beam at a time t after the excitation pulse is then found to be for a sample of path length d

$$\frac{I_{\parallel}(t)}{I_{\perp}(t)} = \frac{I^0_{\parallel}}{I^0_{\perp}} \exp[(c_2 - c_4)\overline{w}(t)d] \, . \quad (6)$$

Stimulated emission of the excited molecules by the probe beam is assumed to be unimportant because of vibrational relaxation [3] and equilibration by the time of the first measurement (20 psec). Stimulated emission arising from the spontaneous decay of the excited molecules was

found to be absent for the exciting pulse power and optical densities used in these experiments. Significantly higher light powers and concentrations were required before we observed stimulated emission. For a random distribution of acceptor molecules with respect to the excited donor molecules we may use expressions for $\overline{w}(t)$ which are independent of the anisotropic distribution of excited donor molecules. In Förster's [4] formulation of dipole-dipole transfer for molecules in a rigid environment [5-6] we have

$$\overline{w}(t) = \exp\left[-\frac{t}{\tau_0} - 0.845 \, \pi^{1/2} \, N_A \left(\frac{R_0}{R_g}\right)^3 \left(\frac{t}{\tau_0}\right)^{1/2} \right] \, , \quad (7)$$

where τ_0 is the excited donor lifetime in the absence of transfer,

$$c_A = \frac{N_A}{(4\pi/3) \, R_g^3}$$

is the concentration of acceptor molecules, and R_0, called the critical transfer distance, is a measure of the strength of the dipole-dipole coupling.

Vavilov [7] used a phenomenological approach to energy transfer to obtain an expression of the form

$$\overline{w}(t) = \exp\left[-\omega_0 c_A - \frac{t}{\tau_0} - kc_A t \right] \, , \quad (8)$$

where k is the transfer rate constant and the term $\omega_0 c_A$ corresponds to the instantaneous quenching of donor excitation within a sphere of action ω_0.

The decay of the anisotropy due to energy migration between the donor molecules or due to direct excitation of the acceptor molecules was negligible. This was shown by measurements made on blank samples containing only the donor molecules and only the acceptor molecules.

In fig. 1 we have plotted the experimental determined ratio $I_{\parallel}(t)/I_{\perp}(t)$ versus t/τ_0. τ_0 is the lifetime of the donor in absence of transfer and was measured to be 4.2×10^{-9} sec. The solid line corresponds to a best fit of the observed data according to eq. (7). We obtain a critical distance of $R_0 = (53 \pm 1)$Å which is in good agreement with the value calculated from spectra (48Å). The broken line corresponds to a best fit according to eq. (8) yielding a transfer rate constant $k = (3.1 \pm 0.1) \times 10^{11} \, M^{-1} \, sec^{-1}$ and a sphere of action $\omega_0 = (50 \pm 5) \, M^{-1}$. A comparison of the solid and broken curves shows that our data are in better agreement with the Förster theory. Furthermore, our data show that at
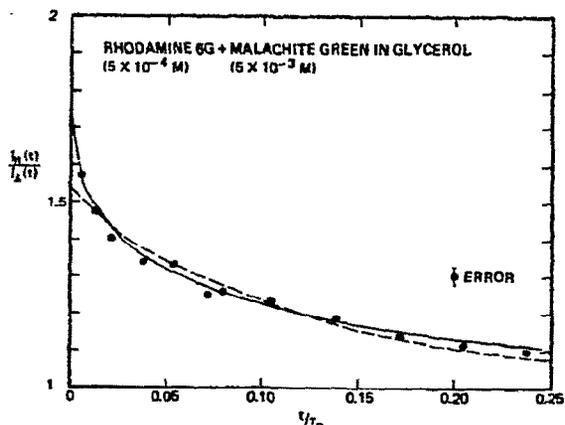
Fig. 1. Transmission ratios as a function of time after the excitation pulse.

least for a certain time domain the Förster and Vavilov curves overlap. This agreement for the two treatments for a portion of the time axis was first shown to be theoretically possible by Galanin [8].

The energy transfer studies of Bennett [9], using a fluorescence technique on systems different from the one studied here showed that the Förster theory gave a good fit to their experimental data in the nanosecond time domain. The results of this work indicate that the Förster theory is a good description of singlet-singlet energy transfer even up to the earliest times so far studied, viz. 20 psec.

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