

Singlet-Exciton Energy Transfer in Naphthalene Doped with Anthracene Following Two-Photon Picosecond Excitation: Dependence on Dopant Concentration

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The time dependence of the sensitized fluorescence of anthracene-doped naphthalene crystals following two-photon picosecond excitation was studied for various dopant concentrations. The experimental results indicate that the characteristic of the energy transfer rate is significantly different for different anthracene concentrations. This behaviour is discussed in terms of different transfer mechanisms taking place at low and high dopant concentrations.

1. Introduction

The transfer of excited-state energy is a general phenomenon which has been observed in organic solids [1], in inorganics, for example rare-earth doped crystals [2], as well as in biological systems [3]. In spite of the intense research, which has been performed concerning this phenomenon, a complete understanding of the energy transfer processes has not yet been achieved. The organic crystals render themselves as a particularly useful model substance which has been studied extensively both by stationary [1] and time-resolved measurements [4].

Various phenomenological models have been discussed to account for the observed energy transfer from the donor system to the acceptor species theoretically. In organic crystals the most frequently used concept is based on a diffusion or random walk model [5–7]. Another approach [8–10] was suggested by Förster, taking into account the long-range dipolar interaction between the donor and the acceptor and there also exist combined theories of the two approaches [11]. A quantum mechanical explanation of the energy transfer has been proposed by Haken and Strobl [12]. The different theories have been summarized in a recent review [13].

However, even though there exists a vast variety of information on energy transfer via singlet excitons in doped organic molecular crystals, it is still not decided which specific mechanism is responsible for the exciton migration and the trapping of the exciton at the acceptor. The primary experimentally available quantity is the

rate constant for the energy transfer, which can be determined most directly by studying the time dependence of the fluorescence following a short excitation pulse. The results presented in this work have been obtained using a two-photon excitation with a picosecond light pulse. This technique guarantees a truly homogeneous exciton density at time $t = 0$ and makes, in our view, the obtained rate constants more reliable than those obtained in previous work.

All the experiments reported in this paper were performed using anthracene-doped naphthalene single crystals. The large trap depth of the acceptors in this particular system ensures that thermal reactivation of the excited state energy into the host-exciton band can be neglected once the exciton has reached the acceptor.

2. Experimental

2.1. Crystals

The crystals used in this work were grown by the Stuttgarter Kristalllabor. The starting material was commercially available naphthalene, which was carefully purified using the procedure described previously [14]. In the neat crystals, which were grown from this material using the Bridgman method, no impurities were detectable spectroscopically. This implies for instance a residual concentration of less than 10^{-8} mole 2-methylnaphthalene per mole naphthalene. For the doped crystals highly purified anthracene was added to the melt. The resulting dopant concentrations varied between 4.1×10^{-7} and 3.8×10^{-5} mole anthracene/mole naphthalene which corresponds to an acceptor concentration between $2.3 \times 10^{15} \text{ cm}^{-3}$ and $2.1 \times 10^{17} \text{ cm}^{-3}$, respectively. The actual

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concentration in each sample was determined carefully via the quantum flux ratio with an absolute accuracy of $\pm 50\%$. The relative accuracy was better than $\pm 15\%$.

The crystals were cleaved in the crystallographic *ab*-plane and had a size of about $(5 \times 5 \times 1)$ mm³. The crystallographic quality of each sample was checked and they were oriented by means of a polarizing microscope. The samples were attached to the sample holder without strain, the *E* vector of the incident light pulse being parallel either to the *a* or the *b* crystal axis.

2.2. Instrumental Setup

The basic setup consisted of a mode-locked dye laser (Model SUA-33, Electro Photonics) followed by a single pulse selector (Model 16, Electro Photonics) which was composed of two crossed Glan-Taylor prisms and a Pockels cell. The Pockels cell was switched using a pulse shaping Blumlein network in connection with a modified predated krytron circuit.

The active medium in the laser was rhodamine 6G dissolved in methanol and a solution of DODCI in methanol was used as mode-locking dye. This arrangement yielded single pulses with a duration of 9 psec as measured with the two-photon fluorescence technique. The energy of a single pulse was about 1 μ J at a wavelength of 605 nm and by focussing the pulse a maximum photon flux in the order of $I \cong 10^{27}$ cm⁻² sec⁻¹ was achieved.

The samples were mounted in a continuous flow cryostat which allowed to vary the temperature from 4 K to room temperature. The donor and acceptor fluorescence were spectrally resolved using a 0.6 m spectrometer (Model HRP, Jobin Yvon) and then recorded with a fast photomultiplier (C 31024, RCA) and a transient digitizer (R 7912, Tektronix). The overall risetime of the system was 1.0 nsec.

2.3. Two-Photon Excitation

Most of the experiments on time-resolved spectroscopy, which have been published so far, employed a conventional one-photon excitation using uv-pulses. However, because of the high absorption coefficient of the host crystal the initial exciton density following a picosecond uv-pulse excitation is so high that exciton-exciton annihilation [15] becomes an important decay mechanism. By studying this process in pure naphthalene crystals

we have determined the annihilation rate constant γ_{ss} to be only slightly dependent on temperature having the approximate values of

$$\gamma_{ss} \cong 3 \times 10^{-10} \text{ cm}^3/\text{s} \quad \text{and}$$

$$\gamma_{ss} \cong 2 \times 10^{-10} \text{ cm}^3/\text{s}$$

at 5 K and 300 K, respectively [16]. This annihilation process makes the analysis of the energy transfer data quite difficult and therefore we have chosen to apply a two-photon excitation.

The two-photon absorption spectrum of neat naphthalene crystals is well known [17–19]. Although the first electronically excited singlet state *S*₁ in naphthalene has odd parity a two-photon transition can be induced from the *S*₀ ground state to a vibronic state of *S*₁. The two-photon absorption cross section is of the order of 10^{-50} cm⁴ sec \times *I*, where *I* is the incident photonflux [18]. For the photonflux used in this work this yields an absorption coefficient in the order of 5×10^{-2} cm⁻¹. Thus two-photon excitation with a picosecond pulse in the visible region assures bulk excitation and provides a homogeneous initial distribution of the excitons and avoids the disturbing influence of exciton-exciton annihilation.

3. Experimental Results

3.1. Pure Naphthalene Crystals

The fluorescence lifetimes of neat naphthalene crystals following two-photon excitation did not depend on the polarization of the incident light pulse with respect to the crystallographic axes. Figure 1 compares the observed lifetimes following two-photon excitation to those obtained following the usual uv-excitation [20]. For most samples the

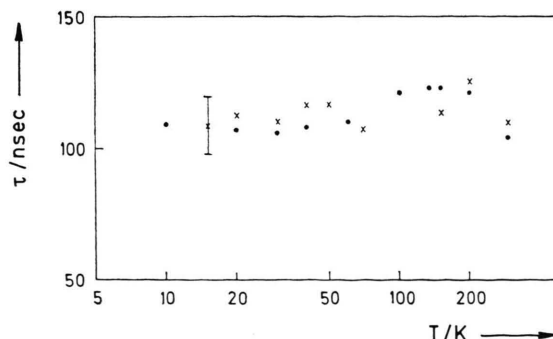


Fig. 1. Fluorescence lifetime of pure naphthalene crystals after low density uv-excitation (●) and following two-photon excitation (×).

deviation between the lifetimes obtained with the two different methods was within experimental error. In some cases however, the two-photon excitation yielded lifetimes, which were 15 to 20% shorter than the usual values. We believe that this occasional deviation was due to some unknown bulk defects which shortened the lifetime following two-photon excitation.

The decay of the naphthalene fluorescence after two-photon excitation was purely exponential in the range from 300 K to 15 K. Below 15 K we always observed an initially faster than exponential decay. This is most probably due to energy transfer to shallow traps caused by crystallographic defects or spectroscopically not detectable impurities.

3.2. Anthracene-Doped Naphthalene Crystals

For the investigation of the time dependence of the doped-crystal fluorescence the naphthalene fluorescence was monitored at 3381 Å (29578 cm⁻¹

= 0,0 – (512 + 1386) cm⁻¹), the anthracene fluorescence at 3868 Å (25856 cm⁻¹ = 0,0). The results obtained were significantly different in three different ranges of the anthracene concentration, N_A , which shall be designated as “high” ($N_A > 5 \times 10^{16}$ cm⁻³), “medium” (6×10^{15} cm⁻³ < N_A < 5×10^{16} cm⁻³), and “low” ($N_A < 6 \times 10^{15}$ cm⁻³), respectively.

The naphthalene-fluorescence decay in the high-concentration limit was purely exponential at all temperatures (Figure 2b). In the medium doping range its decay characteristic varied with temperature: at 300 K the decay was exponential again, whereas at low temperatures deviations from the exponential decay were observed at short times after the excitation. In the low concentration range the naphthalene fluorescence decay was strongly non-exponential in the whole range of temperature. This temperature dependence will be discussed in a later publication [21].

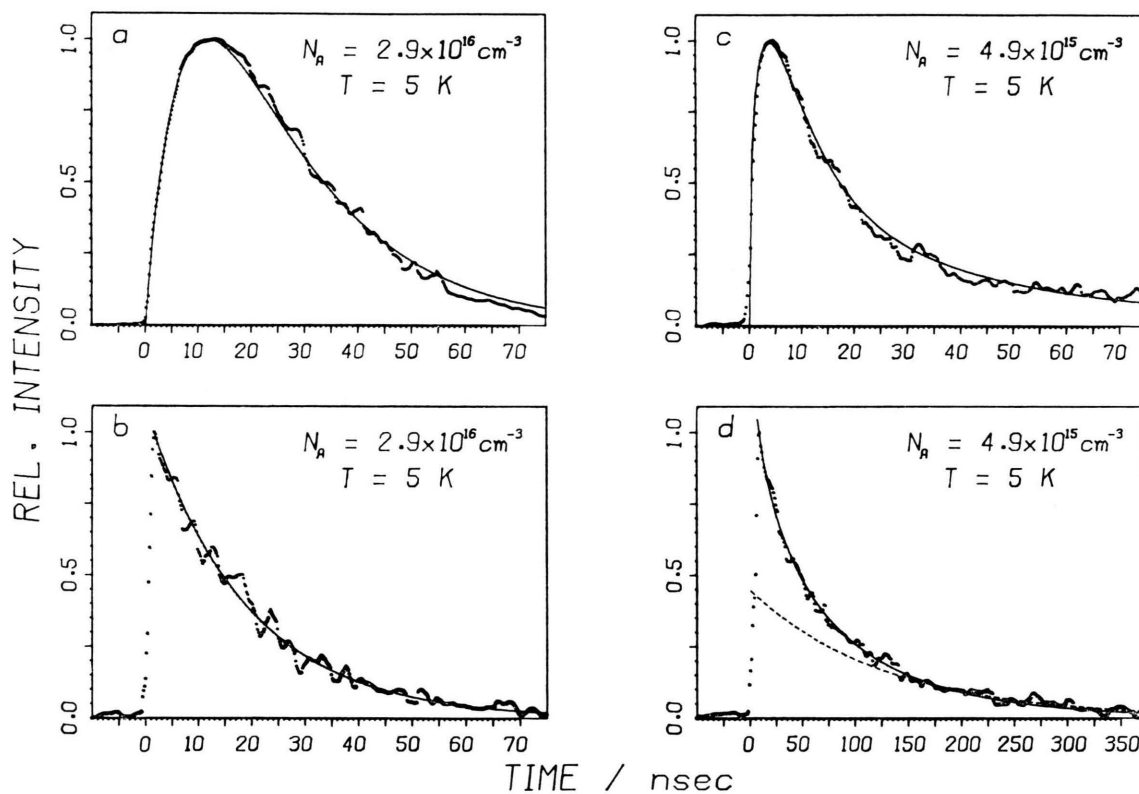


Fig. 2. Time-resolved fluorescence of a highly doped sample (curves a and b) and a sample with low acceptor concentration (curves c and d) at 5 K:

a) acceptor fluorescence, $N_A = 2.9 \times 10^{16}$ cm⁻³,

b) donor fluorescence, $N_A = 2.9 \times 10^{16}$ cm⁻³,

c) acceptor fluorescence, $N_A = 4.9 \times 10^{15}$ cm⁻³,

d) donor fluorescence, $N_A = 4.9 \times 10^{15}$ cm⁻³.

The full lines are calculated using Eqs. (5) and (6). Note the different time scale for figure d. Also in Fig. d, an exponential curve (dashed curve) is plotted in order to show the nonexponential decay for the sample with low acceptor concentration.

The *anthracene-fluorescence* in the high-concentration range showed an exponential rise and a superimposed exponential decay, as predicted by the strongly simplified rate equations assuming a time-independent energy transfer rate. At 300 K the maximum of the anthracene fluorescence was reached within about 20 ns after the excitation (Figure 3). For the samples in the medium and low concentration range the rise of the anthracene fluorescence was increasingly faster as the acceptor concentration decreased, with a minimum delay of about 4 ns between the exciting pulse and the maximum of the acceptor fluorescence, observed at the lowest concentration ($N_A \cong 4.9 \times 10^{15} \text{ cm}^{-3}$).

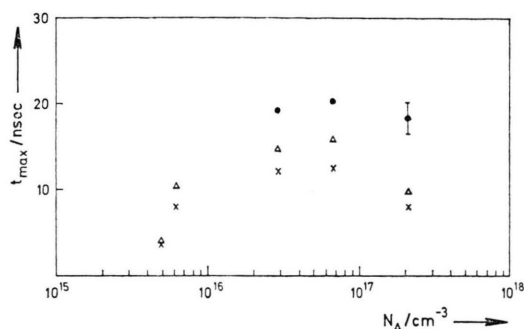


Fig. 3. Time t_{\max} after which the acceptor fluorescence reaches its maximum value, following δ -pulse excitation at $t=0$, as a function of acceptor concentration N_A at 300 K (\bullet), at 30 K (\triangle) and at 5 K (\times).

It is evident from these experimental results that the energy transfer rate k changes its characteristics, if the acceptor concentration is varied: In the *high-concentration* limit it is *time independent*. On the other hand the non-exponential decay of the donor fluorescence and the initial fast rise of the acceptor fluorescence, as it was observed in the *medium- and small-concentration* range, can only be understood in terms of a *time dependent* transfer rate $k=k(t)$. From these observations one must conclude that the excitons reach the acceptor sites the faster, the larger the average distance d between two acceptor molecules is. This puzzling conclusion will be discussed in the next section.

4. Discussion

4.1. The Diffusion Model

It is generally assumed that the energy transfer from a host crystal (donor) to guest molecules

(acceptor) can be adequately described as a diffusion process [4–6]. However, one has to be aware of the limits of the applicability of this model. A diffusion bottleneck arises, if the diffusion within the host lattice is not efficient enough to maintain a homogenous exciton distribution and a constant average distance between exciton and acceptor molecule. In this case the acceptor acts as a drain and causes a decrease of the exciton density around the acceptor thereby decreasing the effective rate of energy transfer. If the diffusion is very fast no such bottleneck occurs and the problem can be described in terms of the “hopping model” using a master equation [7]. On the other hand, if the step-width of the random walk problem is too large, the random walk picture is no longer adequate and should be replaced by a long range interaction model [8–10]. In this section we will attempt to discuss the experimental results in terms of the diffusion model, following the work of Heber [5]. The time behaviour of the donor fluorescence can be described in terms of the diffusion model by the following differential equation

$$\dot{n}_D(\mathbf{r}, t) = -k_D^0 n_D(\mathbf{r}, t) + D \Delta n_D(\mathbf{r}, t), \quad (1)$$

where n_D is the number of excited donor states per unit volume, k_D^0 is the reciprocal lifetime of the donor as determined from the pure naphthalene samples (Fig. 1) and D is the diffusion constant. By introducing the acceptors as absorbing sinks, which are characterized by a sphere with capture radius R_0 , one can eliminate the \mathbf{r} -dependence of n_D and together with the commonly accepted boundary conditions [22] this yields the well-known energy transfer rate

$$k(t) = 4\pi D R_0 N_A [1 + R_0(\pi D t)^{-1/2}] \\ = a + b t^{-1/2}, \quad (2)$$

where N_A is the concentration of acceptors per unit volume. The second part of Eq. (2) defines the abbreviations $a = 4\pi D R_0 N_A$ and $b = 4R_0^2 N_A \sqrt{\pi D}$. Thus the donor and the acceptor fluorescence obey the following rate equations:

$$\dot{n}_D(t) = -k_D^0 n_D(t) - k(t) n_D(t), \quad (3)$$

$$\dot{n}_A(t) = -k_A n_A(t) + k(t) n_D(t), \quad (4)$$

where n_A is the number of excited acceptors per unit volume and k_A is the reciprocal lifetime, which has been determined experimentally using selective

acceptor excitation to $k_A^{-1} = (8 \pm 2)$ ns. Eqs. (3) and (4) can be integrated. The solutions are:

$$n_D(t) = n_D(0) \exp \{-(k_D^0 + a)t - 2b\sqrt{t}\} \quad (5)$$

and

$$\begin{aligned} n_A(t) = n_D(0) \{ & 2b\gamma^{-1/2}(1 + a/\gamma) \\ & \times [w(b\gamma^{-1/2})e^{-k_A t} + w(\sqrt{\gamma t} - b\gamma^{-1/2}) \\ & \times \exp \{-(k_D^0 + a)t - 2b\sqrt{t}\}] \\ & + \frac{a}{\gamma} (\exp \{-(k_D^0 + a)t - 2b\sqrt{t}\} \\ & - \exp \{-k_A t\}) \}, \end{aligned} \quad (6)$$

where the function $w(z) = e^{-z^2} \int_0^z e^{x^2} dx$ is tabulated by Karpov [23] and $\gamma = k_A - (k_D^0 + a)$.

In order to obtain the experimental value of the energy transfer rate $k(t)$ a least square fit procedure was used for fitting the donor fluorescence according to Equation (5). Independently from this the acceptor fluorescence was calculated using Eq. (6) and by varying the parameters a and b one obtains a least square fit to the measured acceptor fluorescence. In this way $k(t)$ could be determined independently either from the donor or the acceptor fluorescence. Both results were identical within the limits of error. Figure 4 shows the resulting parameters a and b as a function of the acceptor concentration N_A . For high concentrations b vanishes, i.e. the energy transfer is described solely by the parameter a . At low concentrations a approaches zero, which means that the energy transfer is mainly determined by the parameter b .

4.2. The Limits of the Diffusion Model

All the experimental curves obtained for the whole range of concentration and temperature can be fitted using Eqs. (5) and (6). Thus the diffusion model at least formally reflects the physical situation correctly. As an example the fitting parameters obtained at 30 K for the high, the medium and the low concentration range are compiled in Table 1. The numbers quoted in Table 1 are estimated to be accurate at least within a factor of 2.

Table 1 shows that the observed parameters are strongly dependent on the concentration. For instance at medium concentrations both, a and b , are relevant indicating the existence of a diffusion bottleneck. This is reasonable since the diffusion length $L = \sqrt{2D\tau}$ (τ = exciton lifetime) is less or in the order of the average distance $d = N_A^{-1/3}$

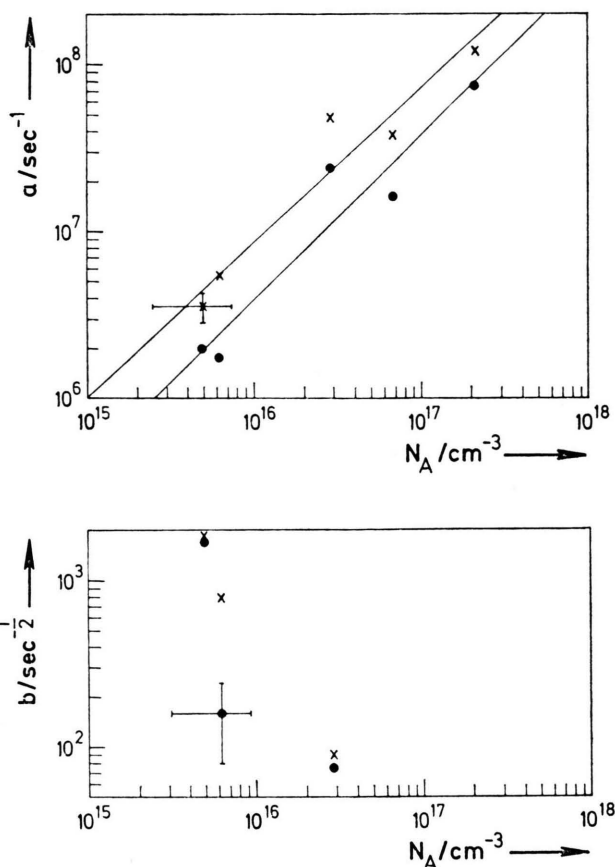


Fig. 4. Coefficients of the energy transfer rate $k(t) = a + bt^{-1/2}$ as a function of dopant concentration N_A at 30 K (●) and 5 K (×). The slopes of the least square fits of the coefficient a are equal to 0.99 at 30 K and equal to 0.92 at 5 K.

between the acceptor molecules. In the high concentration range, on the contrary, b is below the limits of detectability. Thus no diffusion bottleneck can be detected in this case, in agreement with the fact that $L > d$. On the other hand, in the low concentration range, the optimum fitting is obtained by assuming $k(t) = bt^{-1/2}$. The estimated diffusion length is significantly smaller than the observed trapping radius R_0 . Thus it seems that the energy transfer in this case is controlled by a long range capture mechanism.

We can conclude that the energy transfer is diffusion controlled only in a limited range of acceptor concentrations, thus a diffusion bottleneck is detectable only, if $d \gtrsim L > R_0$. At high concentrations ($d < L$) the energy transfer is described by a master equation, the solution of which is included

Table 1. Fitting parameters obtained for the high, medium and low concentration range.

N_A [cm ⁻³]	a [s ⁻¹]	b [s ^{-1/2}]	D [cm ² s ⁻¹]	$L = \sqrt{2D\tau}$ [Å]	R_0 [Å]	$d = N_A^{-1/3}$ [Å]	Comments
2.1×10^{17}	7.5×10^7	1.8×10^1	$> 1.7 \times 10^{-3}$	> 627	< 2	169	hopping motion
2.9×10^{16}	2.4×10^7	7.4×10^1	5.3×10^{-4}	565	13	327	} diffusion } bottleneck long range transfer
6.2×10^{15}	1.8×10^6	1.6×10^2	2.7×10^{-5}	214	83	544	
4.9×10^{15}	2.0×10^6	1.8×10^3	7.3×10^{-6}	127	439	588	

in Eqs. (5) and (6) for $b \rightarrow 0$. At low acceptor concentrations the energy transfer shows a time dependence which is formally the same as developed by Förster [8, 9]. For $a \rightarrow 0$ Eqs. (5) and (6) reduce to the well-known Förster equations.

4.3. The Energy Transfer Mechanism

The motion of excitons in the singlet system of organic molecular crystals and thus the energy transfer is due to the dipole-dipole interaction between the molecules. This interaction has a relatively long range. At higher acceptor concentrations the distance d between acceptors is small and the periodicity of the crystal potential is interrupted quite often. As a consequence the band structure will be strongly disturbed, which means that the excitons will be localized increasingly. Thus the only possible mechanism for exciton motion will be a statistical, incoherent hopping process as described by Eqs. (5) and (6) for $b = 0$.

At low acceptor concentrations, the periodicity of the crystal potential is more perfect. This means that the excitons, especially at low temperatures, are more delocalized than in the above case and therefore they tend to be more coherent.

Thus the trapping of such an exciton at the acceptor site is not only determined by the geometrical size and the trap depth of the trapping molecule, but is determined by the range of the exciton due to its delocalization. This means that the "capture radius" R_0 is not a property of the acceptor molecule but rather reflects the mechanism responsible for energy transfer.

5. Conclusions

The essential result of this work is the observation that the energy transfer rate $k(t)$ depends strongly

on the acceptor concentration. Whereas at high concentrations it is time independent, it has a time dependence of the form $k(t) = a + bt^{-1/2}$ in the range of medium concentration indicating that the exciton motion is diffusive. At low acceptor concentrations it is given by $k(t) = bt^{-1/2}$, which may be interpreted by assuming that the energy transfer in this case is determined by the wave-like nature of the exciton.

There has been some argument about whether the rate of energy transfer is time dependent or not. Powell and coworkers reported time dependent transfer rates [4, 24, 25], whereas the recent experiments with extreme time resolution by Campillo et al. [26] yielded time-independent transfer rates. In view of the present results it seems possible to settle this controversy: Whereas the acceptor concentrations in Powell's samples were in the low and medium range of concentration, the samples of Campillo et al. were doped very highly. Our results are in good agreement with those of Powell and coworkers. But because of the strong concentration dependence they also do not contradict the results of Campillo. Thus we believe that the different results of the two groups are simply due to the different concentrations used.

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