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USE OF PICOSECOND LASERS FOR STUDYING PHOTOSYNTHESIS*

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Abstract

We review the recent application of picosecond laser techniques to the study of photosynthesis. Two techniques are emphasized. In the first a streak camera is used in conjunction with a mode locked laser to determine the 'exciton' migration time to the photosynthetic reaction center. In the second a novel nonlinear optical technique is described which enables certain deductions to be made about the topology of the photosynthetic unit. Bacteria and higher plant data are presented.

Introduction

Photosynthesis is necessary for life on earth. The precise manner by which plants convert solar energy into useful chemical energy is still not fully understood. Clearly, an attempt to improve our understanding of this very important process could have many far-reaching practical implications in our present energy- and food-conscious world. For example, the development of novel solar-energy conversion systems as alternative energy sources and the increase of agricultural output are among the desirable spin-offs. Because the photosynthetic process relies intimately on the absorption of light, it is no surprise that the laser would be an invaluable tool in unravelling its mysteries. To understand how picosecond laser techniques in particular can be useful we review briefly some features of photosynthesis and the concept of the photosynthetic unit (PSU).

In green plants, there are special sub-cellular organelles called chloroplasts, usually ellipsoidal and about 2-10 μ m in length, where photosynthesis occurs. The deceptively simple equation summarizes the process:

That is, water, carbon dioxide, and light are utilized by the chloroplasts to manufacture oxygen and carbohydrates. The light quanta provide energy in excess of the necessary 112 kcal/mole CO_2 to drive the process. There has been considerable evidence accumulated over the past forty years that the photosynthetic apparatus consists of units within the chloroplasts. Emerson and Arnold⁽¹⁾ using repetitive pulses of exciting light of variable intensity and frequency established that such a 'unit' composed of 2500 Chlorophyll (Chl) molecules acting in cooperation, evolved one O_2 molecule. Since four hydrogen atoms are transferred from two H_2O to CO_2 to evolve one O_2 , it became convenient to consider a smaller sub-unit called the photosynthetic unit (PSU) accomplishing each hydrogen transfer using about 600 Chl molecules. In green plants there are two photosystems, PS I and PS II, which are in close proximity and which act in cooperation to transfer one hydrogen atom and each absorbing a quanta of light. In general, a minimum of eight quanta are necessary to generate O_2 and to reduce one CO_2 molecule. In green plants these reactions need the cooperation of 40 to 400 Chlorophyll *a* (Chl *a*) molecules and of additional accessory antenna pigments to harvest the light photons and to convey the electronic excitation to a trapping site, called a reaction center. The reaction center and its associated antenna pigments form a PSU, the smallest entities capable of photosynthesis. Photosystem I, the smaller of the two units, produces upon light absorption both a strong reductant and a weak oxidant, whereas System II, upon absorption of a photon produces a strong oxidant and a weak reductant. Electron flow from the weak reductant to the weak oxidant is coupled to the conversion of adenosine diphosphate and inorganic phosphate to adenosine triphosphate (ATP). ATP assists the strong reductant to reduce CO_2 to a carbohydrate (CH_2O), and the strong oxidant oxidizes H_2O to O_2 . Photosynthetic bacteria have only one photosystem, which closely resembles that of PS I.

The following equations summarize the process of photosynthesis in higher plants:

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Equation (2) describes the absorption of light by a pigment molecule R in the chloroplast and Equation (3) the nonradiative transfer from the pigment to a Chl *a* molecule. Actually a series of transfers occur between the same and different pigments first. The various pigments in the PSU acting in cooperation seemed geared to accept radiation in the range 300 to 1100 nm, where the sun emits 75% of its radiant energy. These pigments eventually funnel the energy to Chl *a* molecules. Equations (4) and (5) describe the process of energy migration whereby the absorbed excitation is transferred a distance to a reaction center in much the same manner as a bucket brigade passes water to a fire. This is often referred to as "exciton migration". Equation (6) describes the reduction of P, the primary electron donor, and the oxidation of X, the primary electron acceptor. These first few steps ending in Equation (6) are generally referred to as the realm of "physical" photosynthesis while the remaining chemical equations involving CO₂, O₂, H₂O, CH₂O and a secondary electron acceptor Y are considered the realm of "chemical" photosynthesis.

Realize that these equations merely represent a summary of what is occurring. In reality numerous additional intermediate steps occur. Indeed, there are also a number of exceptions to the above summary (e.g. photosynthetic bacteria).

In this paper, we will confine our discussion to the physical or primary aspects of photosynthesis. These "primary events" occur on a picosecond time scale. Here the picosecond light source can be invaluable as absorption of a laser photon by one of the antenna molecules sets off a complex sequence of events leading to the reduction of an acceptor in just a few hundred picoseconds^(2,3). How this is brought about can be deduced using techniques of picosecond chronoscopy. Fluorescent decay times from specific molecules give direct information as to how long the molecule remains a specific state before transferring its energy internally or to a neighbor^(4,5). Similarly photo-induced absorbance changes provide a tipoff to the photochemical fate of various oxidized species^(2,3). We will specifically limit discussion here to the manner by which light is absorbed by the photosynthetic apparatus and funneled to a reaction center to gain additional insight into this "exciton migration" problem and into the topology of the PSU.

The Photosynthetic Unit

Let us imagine the PSU to be an isolated structure represented by a simple two dimensional matrix of Chl *a* molecules as shown in Figure 1. Actually the PSU is far more complicated⁽⁶⁾, however, this model will allow us to understand a number of contributing phenomena. The black dots represent Chl *a* molecules and RC represents a reaction center. In this simple representation we show only Chl *a* molecules. As a first approximation this is justifiable because other pigment molecules eventually transfer their energy to Chl *a*. The nonradiative energy transfer between pigment molecules⁽⁷⁾ and between Chl *a* and Chl *a* are believed due to a dipole-dipole interaction (Förster⁽⁷⁾ transfer). We will see later in this paper that picosecond techniques clearly identify this as the appropriate mechanism. The Förster mechanism is very sensitive to the distance *r* between the molecules and the transfer rate is proportional to 1/*r*⁶. Because of the sensitivity of the dipole-dipole interaction with distance and since the concentration of Chl in the PSU is about 0.1 M, each step is about a picosecond. The excitation hops about the PSU between nearest neighbors until the excitation is trapped at the reaction center. The net migration time for this process may be determined by measuring the fluorescence lifetime of emission from the first excited singlet state of Chl *a* since its decay time measures the disappearance of these states due to trapping at the reaction center. The experimentally determined rates may then be used to justify various theoretical models of the PSU.

The very high intensities associated with picosecond optical techniques allow the PSU to be multiply excited, a situation not normally encountered. Then, in addition to the ordinary exciton migration to the reaction center, an additional process exists: the singlet excitons can collide with one another or with triplet states leading to exciton annihilation, and therefore to a further decrease in quantum efficiency and decay time. This process can be visualized with the aid of figure 2. In case I, two molecules in their first excited singlet states are near each other. A dipole-dipole interaction causes a nonradiative transition whereupon one molecule relaxes to the ground state while

Fig. 1. Simplified representation of the photosynthetic unit. Light is absorbed by Chlorophyll a molecules (black dots) which funnel the excitation to the reaction center (RC).

the other is excited to a higher energy state S_2 . In the case of Chl a, the molecule in the S_2 state quickly relaxes by internal conversion in approximately a picosecond to the first excited singlet, the excess energy is given off as heat. If one monitors the fluorescence from S_1 in such a situation one observes a decrease in the lifetime and quantum efficiency. Since the manner in which these "excitons" interact should strongly reflect the geometry of the PSU, a study of quantum efficiency/lifetime as a function of light intensity should provide additional insight into PSU topology. Another annihilative possibility is shown in case II of figure 2. Singlets, via intersystem crossing often form triplet states. In Chl a these states are also very efficient annihilators of singlets. Triplets usually require nanoseconds to build a significant population and so do not normally have the opportunity to interact with singlets during the lifetime of singlets formed by picosecond pulses. However, with multiple pulse excitation, triplets from earlier pulses may interact strongly with singlets formed during later pulses.

It is interesting that some researchers⁽⁸⁾ still deny the importance, indeed existence, of these annihilative processes in photosynthesis. These processes are well known^(9,10) in solid state physics and as we shall demonstrate in this paper, are very easily observed in both solid state analogues of the PSU and in vivo and provide an additional tool to probe PSU topology.

Experimental Setup

A single pulse is selected from a mode-locked Nd:YAG(Nd³⁺:yttrium aluminum garnet) laser by means of a longitudinal-mode potassium dihydrogen phosphate (KDP) Pockels cell⁽¹¹⁾. Two additional KDP harmonic generating crystals are used to generate 530 and 353 nm wavelength pulses. The 530 nm beam is used to excite photosynthetic samples while the 353 nm beam was used only on certain solid state analogue systems. The 530 nm pulses is approximately 20 ps (FWHM) in duration and is propagated over a long delay path to the sample, allowing diffraction to smooth spatial inhomogeneities. The beam expands to a diameter of 9 mm and is truncated to a known diameter with uniform intensity across its radial profile by means of a 3 mm aperture placed on axis. A lens images this desired profile onto the

Fig. 2. Schematic of the singlet-singlet (Case I) and singlet-triplet (Case II) annihilation processes. See text for explanation.

sample. A beam-splitting mirror after the aperture direct a portion of the beam to a Laser Precision energy meter. Since the radial profile on the sample is accurately known, the beam intensity for each shot can be calculated.

Two types of experiments were performed. In the first, the resulting fluorescence at 700 nm for Chl *a* or 920 nm for bacteriochlorophyll *a* was observed from the front of the sample cuvette using an Electro-Photonics streak camera with modified f/1 optics and either an S-20 or S-1 streak tube where appropriate. An SSR 500-channel silicon vidicon optical multichannel analyzer (OMA) was lens coupled to the streak camera so that the fluorescent streak could be conveniently displayed on an oscilloscope or chart recorder. Calibration is accomplished by passing a single pulse from the laser through an etalon with 92% reflective coatings on each surface. Emerging from the etalon are a series of pulses each spaced by the roundtrip time of the etalon and each decreased in intensity by the product of the reflectivities of the mirrors. From this calibration the linearity of the sweep rate and sensitivity was demonstrated (see figure 8 d).

Quantum efficiencies could be determined using a modification of the above experiment, with the streak camera replaced by a photomultiplier.

Concentration Quenching in Pigments

We have made fluorescence lifetime⁽³⁾ measurements on photosynthetic pigment molecules to demonstrate that a Förster⁽⁴⁾ dipole-dipole mechanism is appropriate to describe the nonradiative transfer occurring in the PSU. Figure 3 shows fluorescence from Chl *b* in a solution of chloroform. As the concentration is increased the lifetime decreases, an effect commonly called concentration quenching. The important point to note in this data is that the lifetimes ranging from a nanosecond at low concentrations to less than 15 ps at 0.1 M, follows closely at $1/r^6$ dependence, consistent with a Förster mechanism. Also, the decay curves are temporally nonexponential and in fact agree with the functional form predicted using a Förster mechanism. Similar concentration effects were observed in Chl *a* solutions.

Fig. 3. Densitometer traces of streak photographs of Chlorophyll b in chloroform showing strong dependence of fluorescent lifetime with concentration. Figures 3a, 3b and 3c show, respectively, concentrations of 0.0038, 0.023 and 0.1 M. (After Reference 4).

Application of Quantum Efficiency Technique to Photosynthetic Units

The appropriate bimolecular rate equation (Stern-Volmer) describing the decay of excited singlets within a crystal or PSU may be written as follows:

$$\frac{dn_s}{dt} = CI(t) - kn_s - \gamma n_s^2 \quad (11)$$

where n_s is the number of singlets in the excited state, $I(t)$ represents the laser intensity, k is the inverse of the fluorescence lifetime, and γ is the bimolecular rate constant. For picosecond excitation several simplifications have been made. Only the bimolecular interactions of singlets with other singlets are considered because of the assumed long buildup time for triplets. Also interaction of singlets with the charge transfer state in the reaction center is neglected. For the case of picosecond excitation $I(t)$ can be represented as a delta function and the solution to equation 11 for $t > 20$ ps

found to be (12)

$$n_s(t) = \frac{1}{\frac{\gamma}{k} + \left[\frac{1}{n(0)} + \frac{\gamma}{k} \right]} e^{-kt} \quad (12)$$

where $n(0)$ is the number of singlets excited at $t = 0$ by the picosecond pulse. Since the fluorescence intensity follows the decay of n_s , it is clear that the fluorescence decays nonexponentially with time in the multi-excitation regime. We can determine the ratio of the quantum efficiency at intensity I , $\phi(I)$, divided by the low intensity quantum efficiency ϕ_0 to be

$$\frac{\phi(I)}{\phi_0} = \frac{k}{\gamma I} \ln \left[1 + \frac{\gamma I}{k} \right] \quad (13)$$

here $\Gamma \equiv \gamma n(0)/I$. Measurements of $\phi(I)/\phi_0$ vs I yield, therefore, estimates of γ/k and with knowledge of the absorption cross-sections, the size of the PSU.

Streak camera data enable a direct estimate of γ and k to be made. It is often easier however to obtain information from the quantum efficiency curves since this method is very sensitive even at very low intensities, while in some cases, it is difficult to obtain streak camera lifetime measurement in a regime where the lifetime is constant with intensity.

Measurements in Solid State Analogues

As a test of the simple formalism expressed in the above equations, both quantum efficiency and lifetime measurements were made in a pure anthracene crystal. Singlets were generated in anthracene using a single 20 ps pulse at 354 nm. Because the quantum efficiency is so high in anthracene, interactions with triplets may be ignored. Note that in terms of photosynthetic models anthracene represents a "two dimensional" photosynthetic unit without reaction centers and without such complicating effects as caging and heterogeneity that are associated with mixtures of different pigments. The reason that anthracene can be regarded as two dimensional is that the exciton motion is much easier along the ab plane than in the orthogonal direction. It is clear then that the anthracene ab plane can be regarded as a lake and represents an idealized "lake" model⁽⁶⁾ of the PSU. Figure 5 shows quantum efficiency plotted as a function of photon density for anthracene at room temperature. We have chosen γ/k such that the theoretical fit to the experimental data is a good fit. The intensity at which this nonlinear optical effect sets in is only 10^{12} photons/cm². The fluorescent lifetime in anthracene decreases from several nanoseconds at low intensities, to 250 ps at 2×10^{14} photons/cm², to 50 ps at 4×10^{14} photons/cm², to less than 30 ps at 10^{15} photons/cm². The nonexponential decays are consistent with the simple equation (12) above. See figure 5.

In Vivo Measurements

The simplest photosynthetic systems are the bacteria, resembling a homogeneous PS I. Quantum efficiency measurements performed⁽¹³⁾ on ch-omatophores of several strains of the bacterium Rhodospseudomonas spheroides are shown in figure 6. These quantum efficiency curves bear a strong resemblance in shape to the curve obtained in anthracene.

Especially interesting are the results for the PM8 and the GA mutants of R. spheroides. PM8 is derived from the Ga mutant but lacks reaction centers. Thus one would expect the bimolecular rate constant γ to be the same for both species but expect the trapping to differ. The two curves are within experimental error identical in shape except the Ga curve is displaced in intensity by about a factor of eight. Thus we would conclude that the lifetime of PM8 to be eight times longer than that of Ga. The fluorescence lifetime as measured with a streak camera are 650 ± 150 ps for PM8 and 125 ± 50 ps for Ga, consistent within experimental error to the above hypothesis. Clearly, the presence of a reaction center tends to reduce the effective density of excitons within the PSU in the Ga mutant so that higher pumping intensities are required to maintain the same exciton density.

The quantum efficiency curve⁽¹⁴⁾ for a more complex photosynthetic system, S. pyrenoidosa, is shown in figure 7. This species shows a drop beginning at 10^{13} photons/cm². This curve is much broader than those of the bacteria and probably reflects the presence of PS II. We believe that there are three important factors in addition to the exciton equations (12) and (13) which determine the shape of this curve. First, the transfer rate to the reaction center, k , effectively changes as the reaction centers become filled leading to an intensity dependent rate. Secondly, at a given intensity, some PSU are receiving more excitations than others due to a Poisson distribution of multiple

Fig. 4. Normalized quantum efficiency versus incident intensity for anthracene. Excitation was at 354 nm and fluorescence at 420 nm was observed. The data provided an excellent fit to equation (13) in the text.

hits. Thus, this must be taken into account by averaging over all the distributions. Finally, pigment heterogeneity in the PSU may play an important role. According to a model introduced by Swenberg et al.⁽¹⁵⁾, heterogeneity introduced by the Chl *a* and Chl *b* molecules might lead to the broadening of the quantum efficiency curves. This occurs because the Chl *b* singlets are at a slightly higher energy than the Chl *a* singlets and consequently energy can be transferred easily from Chl *b* to Chl *a* but not vice versa. For this reason the Chl *b* forms barriers to the transport of excitation energy from Chl *a* to the reaction center. In fact, at the concentrations of Chl *b* known to be present in the PSU, subsystems of varying sizes are effectively formed. The onset of exciton annihilation in these subsystems will be quite different leading to a broadening of the curve. Much less broadening would be expected in the more homogeneous systems found in the bacteria. It is interesting also that the quantum efficiency decreases at much higher intensities in the bacteria than in *C. pyrenoidosa* because of the smaller sizes and different cross sections. Consequently, the bacteria are not as efficient light collectors and the onset of annihilative processes is at much higher intensities.

The role of heterogeneity also helps explain the observed lifetimes. The lifetime for *C. pyrenoidosa*, for example, was estimated⁽¹⁶⁾ from the data of figure 8 to be 650 ± 150 ps. A well known theoretical estimate by Lay and Pearlstein⁽¹⁷⁾ predicts a lifetime of only 30 ps for a homogeneous system of appropriate size and dimensions. The lifetimes that we consistently observe are more in agreement with those predicted by Swenberg et al.⁽¹⁵⁾ who take into account heterogeneity effects.

Importance of Single Pulse Operation in Quantum Efficiency and Lifetime Measurements

Early picosecond measurements in photosynthesis involved the use of the full mode-locked laser train rather than a single pulse as in this present work. In experiments with the optical gate^(18,19) the data was typically accumulated from all of the pulses in the train to improve the signal to noise ratio. In experiments with streak cameras^(7,8,20,21) fluorescence from a single pulse near the center of the train was typically examined. As these trains consist of about 100 high-intensity pulses, pulses exciting the sample before the pulse chosen for streak camera investigation may populate the reaction centers, leave a residual population of antenna chlorophyll molecules in the triplet state or otherwise change the system. Thereafter, singlets generated by the pulse to be examined interact

Fig. 5. OMA/oscilloscope displays of streak photos of the 420 nm fluorescence from anthracene under different conditions of 354 nm excitation intensity: (a) 2×10^{14} photons/cm², (b) 4×10^{14} photons/cm² and (c) 10^{15} photons/cm².

with the altered system. As previous picosecond studies involved excitation intensities exceeding 10^{14} photons/cm² their data must also reflect the exciton annihilative processes observed here. We believe the observations in references 4,8,18,19,20 and 21 can be explained by their use of full mode-locked pulse trains and by a singlet-triplet annihilation process (Figure 2, Case II). Triplets, which evolve from singlets by intersystem crossing live longer than the time interval between pulses in the train. Thus, the triplet population will increase from pulse to pulse until a steady state value, N_{Tss} , is established through a combination of singlet-singlet and singlet-triplet processes, eventually becoming independent of I. In this saturated regime, an appropriate Stern-Volmer equation for n_s is simply expressed as $dn_s/dt = -\gamma_{ST}N_{Tss}n_s$ and has a nearly exponential decay rate, $\gamma_{ST}N_{Tss}$, independent of I. This picture is similar to the previous experimental observations where the observed lifetimes were much shorter than observed here. The singlet state decay constant, $\gamma_{ST}N_{Tss}$, was observed to be in the range 10^{10} to 3×10^{10} sec.⁻¹.

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Fig. 6. Normalized 920 nm fluorescence quantum efficiency versus 530 nm excitation photon density for several mutants of the photosynthetic bacteria Rhodospseudomonas spheroides. The squares, darkened circles and triangles represent the PM8, 2.4.1, and Ga mutant data respectively. (After Reference 13.)

Fig. 7. Normalized 700 nm fluorescence quantum efficiency versus 530 nm excitation photon density for the green alga C. pyrenoidosa. (After Reference 14.)

Fig. 8. OMA/oscilloscope displays of 700 nm fluorescent streaks from *C. pyrenoidosa* excited with a single 20-ps, 530 nm pulse. Excitation intensities are (a) 10^{14} , (b) 3×10^{14} and (c) 3×10^{15} photons/cm². The measured 1/e points are (a) 375, (b) 175 and (c) < 50 psec. This variation in fluorescence lifetime with intensity is consistent with singlet-singlet exciton annihilation processes occurring within the photosynthetic unit. (d) Train of calibration pulses generated by passing a single 530 nm pulse through two parallel mirrors, each with 92% reflectivity. The resulting train has a known exponentially decaying envelope function and can be used to calibrate the apparatus. (After Reference 16.)

References

1. Emerson, R. and W. Arnold, J. Gen. Physiol. **16**, 191 (1932).
2. Kaufmann, K. J., P. L. Dutton, T. L. Netzel, J. S. Leigh and P. M. Atzeps, Science (Wash. D.C.) **188**, 1301 (1975).
3. Rockley, M. G., M. W. Windsor, R. J. Cogdell and W. W. Parson, Proc. Natl. Acad. Sci. U.S.A. **72**, 2251 (1975).
4. Shapiro, S. L., V. H. Kollman and A. J. Campillo, FEBS Lett. **54**, 358 (1975).
5. Campillo, A. J. and S. L. Shapiro, In "Picosecond Pulses" (S. L. Shapiro, ed.), Chapter 7, Springer-Verlag, (IN PRESS).
6. Sauer, K., In "Bioenergetics of Photosynthesis" (Govindjee, ed.), Chapter 3, Academic Press, New York (1975).

7. Förster, T., *Z. Naturforschg* 4a, 321 (1949).
8. Beddard, G. S., G. Porter, C. J. Tredwell, J. Barber, *Nature (London)*, 258, 166 (1975).
9. Fröhlich, D. and H. Mahr, *Phys. Rev.* 148, 868 (1966).
10. Tolstoi, N. A. and A. P. Abramov, *Opt. i Spektroskopiya* 19, 830 (1965).
11. Hyer, R. C., H. D. Sutphin and K. R. Winn, *Rev. Sci. Instrum.* 46, 1333 (1975).
12. Swenberg, C. E., N. E. Geacintov and M. Pope, *Biophysical J.* (IN PRESS).
13. Campillo, A. J., T. Monger, W. W. Parson and S. L. Shapiro, (TO BE PUBLISHED).
14. Campillo, A. J., S. L. Shapiro, V. H. Kollman, K. R. Winn and R. C. Hyer, *Biophysical J.*, 16, 93 (1976).
15. Swenberg, C. E., R. Dominijanni and N. E. Geacintov, *Photochem. Photobiol.* (IN PRESS).
16. Campillo, A. J., V. H. Kollman and S. L. Shapiro, *Science (Wash. D.C.)*, 193, 227 (1976).
17. Bay, Z. and R. M. Pearlstein, *Proc. Nat. Acad. Sci. U.S.A.* 50, 1071 (1963).
18. Seibert, M. and R. R. Alfano, *Biophys. J.* 14, 269 (1974).
19. Alfano, R. R., W. Yei, R. Govindjee, B. Becher and T. G. Ebrey, *Biophys. J.*, 16, 541 (1976).
20. Paschenko, V. Z., A. B. Rubin, L. B. Rubin, *Kvantovaya Elektron, (Moscow)* 2, 1336 (1976).
21. Paschenko, V. Z., S. P. Protasov, A. B. Rubin, K. N. Timofeev, L. M. Zamozava, L. B. Rubin, *Biochem. Biophys. Acta.* 408, 143 (1975).

From Förster

$$K_{nr} = \frac{1}{\tau_0} \left(\frac{R_0}{R} \right)^6$$

$$\sim 2 \times 10^{12} / \text{sec}$$

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \rho - \frac{\rho}{\tau}$$

Converts to heat conduction and diffusion equation.

From Bay - Pearlstein; Pearlstein
 $\langle n \rangle \sim N$
 $t_F \sim 30 \text{ psec}$

Case 1: $S_i + S_i \xrightarrow{\gamma_{ss}} S_o + S_n$; $S_n \rightarrow S_i + \text{heat}$

Case 2: $S_i + T_i \xrightarrow{\gamma_{st}} S_o + T_n$; $T_n \rightarrow T_i + \text{heat}$

(a)

(b)

(c)

130 PS

A

B

C

TIME

65 psec

A,B,C

TIME