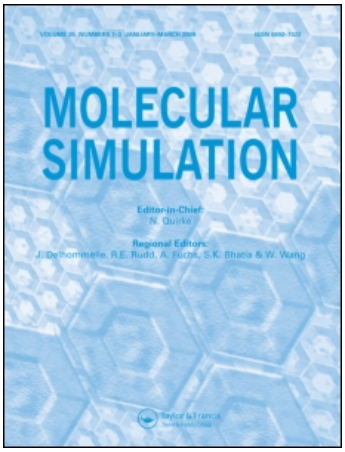

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A Monte-Carlo Method for Modelling the Photosystem II Operation and Intersystem Electron Transport in Higher Plants

I. Rojdestvenski[a]; L. Savitch[a]; N. Huner[a]; M. Cottam[b]
[a] Department of Plant Sciences, University of Western Ontario London, Ontario, Canada [b] Department of Physics, University of Western Ontario London, Ontario, Canada

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A MONTE-CARLO METHOD FOR MODELLING THE PHOTOSYSTEM II OPERATION AND INTERSYSTEM ELECTRON TRANSPORT IN HIGHER PLANTS

I. ROJDESTVENSKI*, L. SAVITCH*, N. HUNER* and M. COTTAM**

University of Western Ontario, London, Ontario N6A 3K7, Canada

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We suggest a method of numerical modelling of the kinetics of the PSII charge separation and concomitant electron transport between the photosystems PSI and PSII. We employ a dynamic Monte-Carlo procedure with adjustable variable time scale, that enables us to work with a model which has characteristic times ranging over 8–10 orders of magnitude. We present the test results for our procedure. We design a simple mathematical macroscopic model of the charge separation and the electron transfer, that is based on several characteristic times. We apply the suggested procedure to calculate the time-dependent kinetics of the model under various conditions, relevant to typical situations in the time-resolved fluoresence experiments.

KEY WORDS: Photosystems, dynamic Monte Carlo, electron transport.

1 INTRODUCTION

In higher plants, photosystems I and II are primary devices that absorb light quanta and transform their energy into the energy of charge separation, that is used at later stages of the CO_2 assimilation. The process of charge separation in PSII is a complex process , involving, the collection of light quanta by light harvesting complex (LHCII), the transfer of the quanta energy in the form of excitations to the reaction center chlorophyll (named P680 after the light wavelength in nanometers, at which its absorption spectrum has a maximum), donation of electrons by the excited P680's to the contiguous electron carriers, and the splitting of water molecules to restore the electronic structure of P680. These stages are discussed in detail in numerous papers (see, *e.g.* Reference [1, 2, 3]). The light absorption is accompanied by *chlorophyll a* fluorescence emission, which is a valuable tool to probe the rates and yields of photochemical performance.

The reactions of photosynthesis are divided into light dependent and light independent. The former occur in thylakoid membranes, in the immediate vicinity of LHCII antennae exposed to light, and are, in general, very fast, with the characteristic times ranging from 1 ps to 1 ms. These reactions accomplish charge separation and

*Department of Plant Sciences
**Department of Physics

electron transfer from PSII to PSI and further, to $NADP^+$ molecules, to produce NADPH, H^+ and ATP. The light independent reactions, that utilize the synthesized ATP and NADPH in carbon assimilation and other metabolic pathways, take place in the stroma, are enzyme-catalyzed and occur with the characteristic times in the order of magnitude of 1s to 1–10 min.

Room temperature fluorescence induction measurements are capable of providing information about the dependence of the steady-state yield of photosynthesis on the slower rates of carbon assimilation, but also about fast, photochemical processes induced after the dark-adapted plant is exposed to light. The latter can be quantified by the time-resolved fluorescence technique [2]. The curves of the fluorescence yield vs time reveal certain characteristic features, from which, in principle, many important parameters of the photosystems I and II can be revealed. The quantitative analysis of these curves, however, is difficult because the theoretical understanding of the processes of electron transfer between different elements comprising the photosystems is far from being completely understood.

The computer experiment by its nature is somewhat halfway between the real experiment and the theory. Compared to any analytical approach, it is much less in need of certain oversimplifications that make the theory analytically solvable. On the other hand, it is more flexible than a real experiment, as it gives a researcher much more command over the experimental conditions.

The Monte-Carlo method has been introduced in 1953 [4], and since then has proved itself to be a powerful tool in investigating thermodynamics of various models in theoretical physics and physical chemistry (see, *e.g.* [5]). The main advantage of the method is, that within a certain model, it allows a researcher to deal with a variety of model parameters, such as types of interactions and transitions, energy distributions, etc., by means of essentially the same algorithm, varying only the set of transition probabilities. The structure of the method makes it very plausible for applications in physical chemistry, namely in reaction kinetics, since the transition probabilities obey the same detailed balance equations as the rates of the chemical reactions do. A very good example of the application of the Monte-Carlo method to model microscopically the electron transport between the PSI and PSII photosystems is given in [6].

In its standard formulation the method is accurate in determining the steady state of a model, but fails, however, to provide accurate results for the dynamics of relaxation to a steady state. This is a general consequence of the fact that the way to construct the transition probabilities is not unique, and each set of the transition probabilities, although leading to the same steady state, provides for different convergence and, hence, different dynamics of the relaxation process.

In the present, paper we suggest a simple model of the charge separation in PSII reaction centers based on several characteristic times of electron transfer between subsequent carriers. In order to achieve physically proper kinetics of the transport processes, we introduce a modified Monte-Carlo procedure with a varying time scale, which allows us to study the temporal evolution of the system for the times ranging from 1 ns to several milliseconds. We present the computer modelling data and discuss the results obtained within the context of current experimental results in time-resolved fluorescence and modern theoretical concepts.

The structure of the paper is as follows. In the Section 2 we discuss a model of PSII charge separation, and the properties of the intermediate electron carriers. In Section 3, we introduce the Monte-Carlo procedure, as well as the appropriate set of transition probabilities, and present the results of a comparison of the numerical simulation data with the accurate analytical solutions for two different types of differential equations. In Section 4, we display the results of our PSII modelling and discuss these results in connection with the experimental data for higher plants. In Section 5 we give some concluding remarks, as well as discuss further development of the suggested method.

2 SCHEMATIC REPRESENTATION OF THE PSII CHARGE SEPARATION

The overall simplified scheme of the PSII photooxidation according to Ref. [2] is as follows. A quantum of energy is absorbed by the P680 reaction center, which, within the time of about 1 ps, is transferred into the excited state, P680*. This excited state decays back to the ground state along three possible pathways. One pathway is by fluorescence emission, which we assume here to have the characteristic time of about 100 ps. This estimate comes from the fact that, under the steady-state conditions, the fluorescence yield comprises only about 3 percent of the total quantum yield. The second pathway is via transfer of one electron to the pheophytin molecule, which, after having accepted the electron, becomes $Pheo^-$, and the reaction center is oxidized to become $P680^+$. The characteristic time of this process is about 3 picoseconds. After that, within the time of about 30 ns, the $P680^+$ oxidizes the so-called Z electron carrier to Z^+ state, and returns to P680 ground state. In turn, Z^+ splits the molecule of water to regain its missing electron. The third pathway corresponds to the non-radiative decay of the excited state through heat.

In its turn, the $Pheo^-$ donates its electron to a molecule of QA quinone (time about 300 ps), which further transfers it to QB quinone (time about 30 μs). Subsequently, QB donates electrons to the intersystem electron transfer chain which, concomitantly, generates a pH gradient across the thylakoid membrane.

We should note here that, although the process of the electron transfer are essentially quantum, they take place in the presence of a phonon bath, which comes to the thermodynamic equilibrium much faster than any of the above processes occur. That is why we can describe this system with a classical system of probabilities, rather than the quantum probability amplitudes [7]. It is worth mentioning that the presented scheme does not take into account some recently developed concepts of photochemical feedback limitations and cyclic electron transport (see, *e.g.* [3]). However, as we discuss below, it is relatively easy to incorporate these effects into the model by altering the system of transition probabilities.

3 METHOD OF MATHEMATICAL MODELLING

To design the method of stochastic simulation, we assume the system to contain the following components:

- P680g, the P680 reaction centers in the ground state;
- P680*, the P680 reaction centers in the excited state;
- P680g, the P680 reaction centers in the oxidized state
- Pheo, the Pheophytin molecules;
- $Pheo^-$, the Pheophytin molecules in the reduced state;
- QA, the QA molecules;
- QA^-, the QA molecules in the reduced state;
- QB, the QB molecules;
- QB^-, the QB molecules in the reduced state;
- Z, the Z carrier molecules;
- Z^+, the Z carrier molecules in the oxidized state;

The interaction between different components is accomplished via the following reactions:

1) $P680g + h\nu \rightarrow P680^*$ – the primary excitation of the reaction center, time $\tau_1 = 1$ ps;
2) $P680^* \rightarrow P680g + h\nu'$; – fluorescence, time $\tau_2 = 1$ ns;
3) $P680^* + Pheo \rightarrow P680^- + Pheo^-$; – pheophytin reduction, time $\tau_3 = 3$ ps;
4) $Pheo^- + QA \rightarrow Pheo + QA^-$ – reduction of QA, time $\tau_4 = 30$ μs;
5) $QA^- + QB \rightarrow QA + QB^-$ – reduction of QB, time $\tau_5 = 100$ μs;
6) $QB^- \rightarrow QB + e^-$ – oxidation of QB in further processes, time $\tau_6 = 1$ ms;
7) $P680^+ + Z \rightarrow P680g + Z^+$ – $P680^+$ reduction and oxidation of Z, time $\tau_7 = 3$ ms;
8) $Z^+ + e^- \rightarrow Z$; – reduction of Z carrier via water splitting reactions, time $\tau_8 = 30$ ns.

We also take into account that certain reaction centers, although being able to absorb a photon, are not capable of the electron transport. That is why we, in fact introduce two populations of P680 centers – P680 and P680i, the latter not participating in the charge separation (see Ref. [8]).

We will further denote [A] the concentration of the component A. Let us now introduce the transition probabilities for a certain reaction, i, involving two metabolites, A and B, in the form:

$$P_i = \min(1, \alpha[A]\,[B]/\tau_i), \tag{1}$$

α characterizing the time scale. The above is based on a simple consideration, that if a characteristic time of a single reaction in α units is τ_i/α, then the probability of one reaction act is proportional to the inverse time, as well as to concentrations of both metabolites. This simple scheme does not account for many subtle effects of PSII photochemistry, such as, for example, the down regulation of PSII through the build up of the pH gradient (photosynthetic control). However, these effects may be easily incorporated in the probabilities by replacing expressions (1) by more appropriate ones.

Our Monte-Carlo procedure is now set up as follows. We start off with a certain concentration distribution. Each Monte-Carlo step comprises an attempt to accomplish one of the above reactions, according to the corresponding transition

probability, which is calculated by means of (1). In the case of single metabolite reactions, as the reactions 2) 6) and 8), the second concentration is equal to 1. For the reaction 1) we take the "concentration" of photons proportional to the incoming light irradiance.

Directly the suggested scheme is not suitable for the calculations. The reason is that, due to enormous differences in the characteristic times,the probabilities for the slow processes become to low to be accounted for in reasonable computer times. As well, the nature of the most pseudo random number generators, gives no chance for a more or less consistent account for the events with the probability, say, of the order of magnitude of 10^{-9}. On the other hand, the fast processes too often have their probability equal to 1 (Eq. (1)), which distorts the proper resolution of the relaxation kinetics.

To overcome the stated problems, we introduce a scheme of a varying time scale. That is, at every step, we calculate the values

$$q_i = \frac{[A][B]}{\tau_i}, \tag{2}$$

Then we introduce the α value as:

$$\alpha = \frac{0.5}{\max(\{q_i\})} \tag{3}$$

After that we calculate the probabilities, employing (1). From the above, it is obvious that the largest of the transition probabilities is always equal to 0.5. Thus, we observe automatically the proper hierarchy of the time scales, as well as the proper kinetics.

At every step of the procedure, we attempt to accomplish all the reactions in turn. For that purpose we produce a real number from a random sequence and compare it to the corresponding transition probability (2). If our number is less than the transition probability, we "accomplish" the reaction by upgrading the concentrations of the reagents by one "molecule", according to the stoichiometry of the reaction. As our P680 concentration is normalized to 1, we take this increment, corresponding to one "molecule", equal to 10^{-4}.

After all the reactions are attempted, we recalculate the probabilities for the new concentrations, calculate the time scale parameter α, and upgrade time by adding α to it.

4 RESULTS OF MODELLING AND EXPERIMENTAL RESULTS

To test the suggested scheme we applied it to a simple and analytically solvable case of only one metabolite and one reaction, the differential equation and the initial conditions being, respectively:

$$dC/dt = -\gamma C^2, \quad C|_{t=0} = 1 \tag{4}$$

The analytical solution has the form of:

$$C(t) = \frac{1}{(\gamma t + 1)}$$

In Figure 1 we present our numerical solution (open circles) compared to the exact solution (solid line). The results show excellent correspondence. In addition, a useful feature of the suggested time-scaling algorithm is reflected, that is the experimental points are equidistant along the vertical axis. This feature provides for more experimental points within the areas of more rapid changes in the function value.

Next we applied the procedure to the system of the reactions 1)–8) above. We took the characteristic times as specified in the previous Section. The initial concentrations of the intermediates of the PSII photooxidation were taken approximately as in the dark-adapted leaves, *i.e.* 300 chlorophyll molecules and 30 quinone acceptors per 1 reaction center, 10 mg of chlorophyll per cm^2 of a leaf area. To evaluate the light intensity we took it to be approximately 10^{-10} photons per 1 reaction center per picosecond, which corresponds to the light of about 800 $\mu E/(m^2 s)$ with 80% of the light energy being lost by heat. Also we assumed that 10% of the P680 reaction centers do not participate in the electron transfer. To calculate the fluorescence yield we averaged the probability of fluorescence, which is proportional to the concentration of the excited P680 centers of both types, over a 1 ms time.

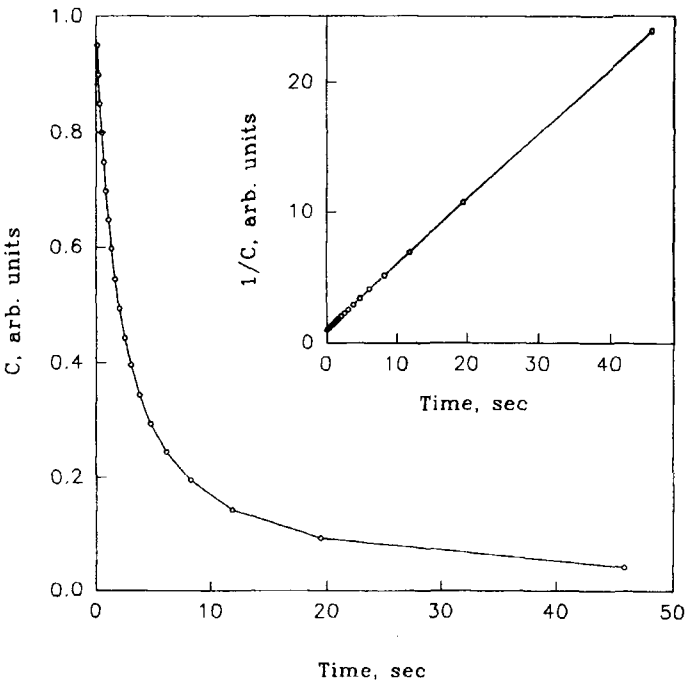

Figure 1 Numerical solution of equation (4) (circles) and the exact solution (solid line). The increment of changing C per each step is 10^{-4}.

In the Figure 2 we present the time dependences of the concentrations of different metabolites normalized to 1, as well as the time dependence of the fluorescence yield (see the legend). It can be seen that for the given set of parameters the fluorescence, as well as the other concentrations, rapidly reach steady state, and then remain unchanged. In the real experiment, however, this would be true only approximately at this time scale. This is because in our simple model we take into account neither the PSI oxidation of PSII nor the C_3 carbon assimilation cycle, with their characteristic times that would have a feedback effect on the PSII operation. The concentration of the oxidized Z-donors (letter F) rapidly reaches the value close to the concentration of the P680 centers (letter A), capable of transporting electrons, and then remains stable.

During the computer experiment we monitored the value of α, which was rapidly changing from step to step, ranging from ~ 1 to $\sim 10^6$. In our opinion, this fact brings the evidence that both the fast and the slow kinetics are well represented in our modelling procedure.

Next we tried to model the situation when electron transport is slowed down at the stage of interactions of QB with the PSI. For this purpose we increased the τ_7 characteristics time, putting it equal to 1 s. The results are presented in Figure 3. At the initial stage of time evolution the fluorescence yield, as well as the concentration the oxidized Z-donors, behave similarly to that in Figure 2. However, due to the slow reoxidation of the QB carriers, the QB accumulate in the reduced state (letter E). As the QB-reduced concentration almost linearly reaches the maximal value, a linear buildup of the QA-reduced concentration takes place at a time scale of 0.5 s

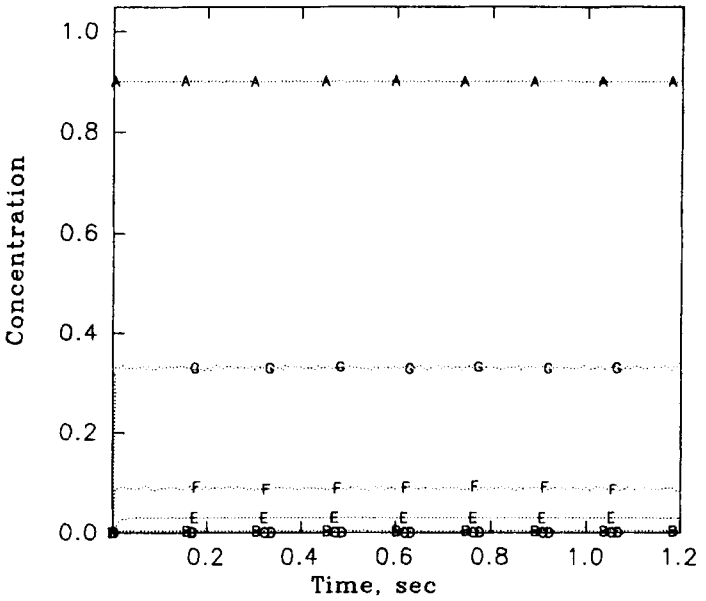

Figure 2 The results of modelling of the PSII photochemistry under "normal" conditions. Characteristic times as stated in Section 3. Legend: A-P680; B-$P680^+$; C-$Pheo^-$; D-QA^-; E-QB^-; F-Z^+; G-fluorescence.

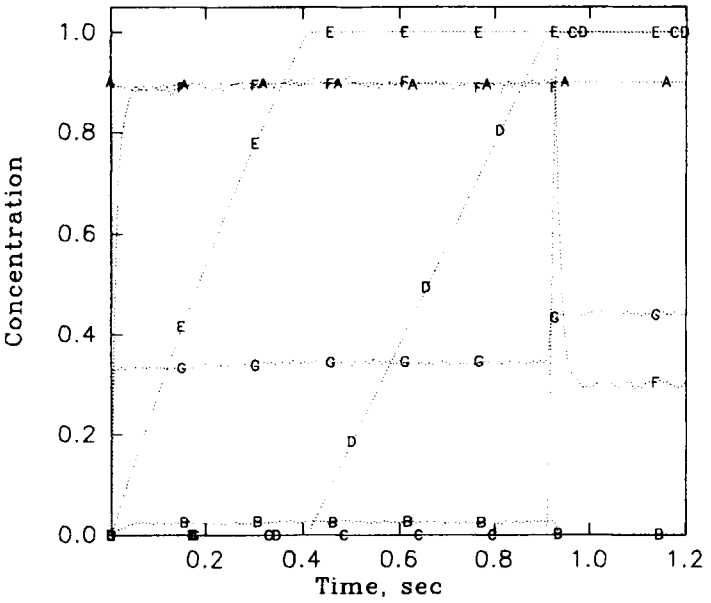

Figure 3 The results of modelling of the PSII photochemistry under the conditions of blocked QB-PSI electron transport. Characteristic times as stated in Section 3, except $\tau_7 = 1$ s. Curve labeling same as Figure 2.

(letter D). As the accumulation of the QA-reduced is complete, the oxidation of the Z-donors slows down, which results in the rapid fall of the concentration of Z-donors in the oxidized state (letter F), as well as rapid step-like growth of the fluorescence yield (letter G). Then a new steady state is reached in a time scale of approximately 1 s.

Certain herbicides, as, for example, DCMU, are capable of blocking the photosynthetic activity of the plants by blocking the electron transfer between QA and QB. This situation can be modelled within the framework of our model by putting the time τ_5 equal to infinity. In Figure 4 we present our results for this situation. The main features of this graph are similar to those in Figure 3. However, the step-like growth of the fluorescence yield occurs much faster, in 0.3–0.4 s, and the steady-state fluorescence value is noticeably higher. As well, as the electron transport is completely blocked at the QA→QB stage, the steady-state concentration of the oxidized Z-donors is zero.

5 CONCLUSIONS

The above results show that by varying the characteristic reaction times one can emulate the influence of different stress factors on photosynthetic electron transport, achieving physically meaningful results. In addition, the presented model and the method itself are extremely flexible and open to adjustments and upgrades, that

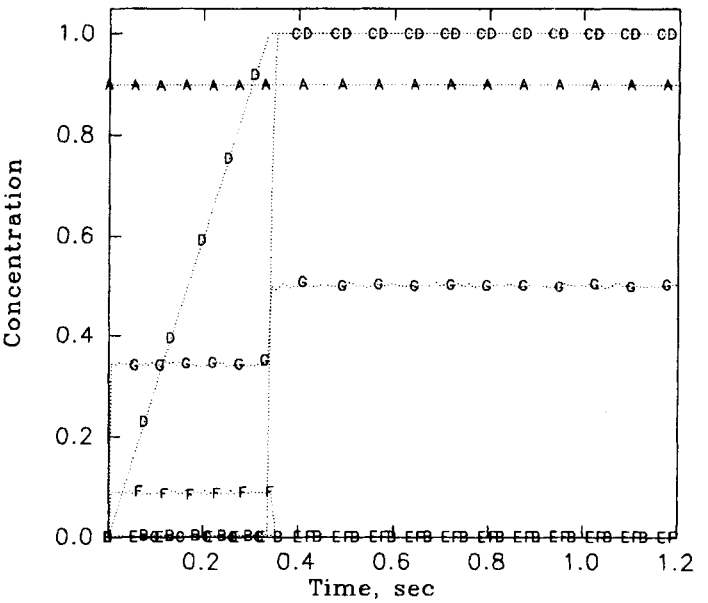

Figure 4 The results of modelling of the PSII photochemistry under the DCMU treatment. Characteristic times as stated in Section 3, except $\tau_5 = 10^8$ s. Curve labeling same as Figure 2.

allow for easy incorporation of mechanisms controlling the electron transport. In our opinion, the suggested modification of the Monte-Carlo method may be used to study kinetics in a number of physical situations involving substantially different time scales.

Among possible future generalizations of the model one can consider incorporating into it the PSI (see, *e.g.* Ref. [6]), coupled to the Calvin cycle, a more detailed description of the oxygen-splitting system, which provides electrons for the reduction of oxidized Z-donors, regulation of the PSII photochemistry through photosynthetic control as well as non-photochemical quenching through the xanthophyll cycle [8].

References

[1] L. Taiz and E. Zeiger, "*Plant physiology*", The Benjamin/Cummings Publishing Company, California (1991).

[2] G. H. Krause and E. Weis, "Chlorophyll fluorescence and photosynthesis: The Basics"., *Ann. Rev. Plant Physiol. Plant Mol. Biol.*, **42**, 313–49 (1991).

[3] M. K. Joshi and P. Mohanty, "Probing photosynthetic performance by chlorophyll a fluorescence: Analysis and interpretation of fluorescence parameters", *J. Sci. & Ind. Research*, **54**, 155–74 (1995).

[4] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, "Equation of state calculation by fast computing machines", *J. Chem. Phys.*, **21**, 1087–92 (1953).

[5] K. Binder, "Applications of the Monte-Carlo method in Statistical Physics", Springer-Verlag, Berlin (1987).

[6] F. Mitchell, A. Spillmann, W. Haehnel, "Plastoquinol diffusion in linear photosynthetic electron transport", *Biophys. J.*, **58**, 1011–24 (1990)

[7] V. Rupasov, private communication.

[8] N. P. A. Huner, G. Öquist, V. M. Hurry, M. Krol, S. Folk and M. Griffith, "Photosynthesis, photoinhibition and low temperature acclimation in cold tolerant plants", *Photosyn. Res.*, **37**, 19–39 (1993).